



Determination of polycyclic aromatic hydrocarbons from ambient air particulate matter using a cold fiber solid phase microextraction gas chromatography–mass spectrometry method

Helvécio Costa Menezes, Zenilda de Lourdes Cardeal*

Departamento de Química, Universidade Federal de Minas Gerais, Avenida Antonio Carlos, 6627, Pampulha – Belo Horizonte/MG 31270901, Brazil

ARTICLE INFO

Article history:

Available online 3 November 2010

Keywords:

PAH
SRM1649b urban dust
Cold fiber
SPME-GC/MS

ABSTRACT

Polycyclic aromatic hydrocarbons (PAH) from ambient air particulate matter (PM) were analyzed by a new method that utilized direct immersion (DI) and cold fiber (CF) SPME-GC/MS. Experimental design was used to optimize the conditions of extraction by DI-CF-SPME with a 100 μm polydimethylsiloxane (PDMS) fiber. The optimal conditions included a 5 min equilibration at 70 °C time in an ultrasonic bath with an extraction time of 60 min. The optimized method was validated by the analysis of a NIST standard reference material (SRM), 1649b urban dust. The results obtained were in good agreement with certified values. PAH recoveries for reference materials were between 88 and 98%, with a relative standard deviation ranging from 5 to 17%. Detection limits (LOD) varied from 0.02 to 1.16 ng and the quantification limits (LOQ) varied from 0.05 to 3.86 ng. The optimized and validated method was applied to the determination of PAH from real particulate matter (PM10) and total suspended particulate (TPS) samples collected on quartz fiber filters with high volume samplers.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are compounds that have proven to be carcinogenic and mutagenic [1]. Their ubiquitous nature is evident in the fact that 16 PAH are considered priority pollutants by the U.S. Environmental Protection Agency (EPA) [2]. Among these priority PAH, benzo[a]pyrene (BaP) is used as a marker for carcinogenic risk in Environmental Studies. Recently, the European Union, seeking to avoid adverse effects of PAH to health and the environment, set the target value of 1 ng/m³ for BaP in air [3]. The main anthropogenic sources of PAH are the incomplete combustion of petrol and diesel in vehicles, incineration of organic waste, burning of wood and coal for household heating, and industrial processes involving coal tars and crude oil products such as creosote and asphalt. PAH can occur as gases, adsorbed/absorbed on particulate matter (PM), or distributed between the gas-particle phases as is the case of semi-volatile materials. The gas-particle partitioning depends mainly on the molar mass of PAH. Those PAH made up of two or three chains are concentrated mainly in the gas phase, whereas those containing up to four chains are adsorbed on the particulate phase [4]. This

association facilitates the transport of PAH of larger mass over long distances and contributes significantly to the increase in the carcinogenic potential of the particulate phase [5].

Glass fiber filters (GFF) or quartz-fiber filters (FFQ) in active samplers are mainly used for sampling of PAH in PM. After collecting, the PAH are traditionally extracted from these filters by the Soxhlet method [6] with the use of large amounts of toxic solvents during long periods of time. Generally, the method requires a clean-up step with alumina or silica gel after extraction to reduce contamination and the evaporation of excess solvent in a pre-concentration step [7]. Methods such as sonication [8], microwave-assisted extraction (MAE) [9], supercritical fluid extraction (SFE) [10], and pressurized liquid extraction (PLE) [11] have been proposed to improve the performance of the PAH extraction and to minimize the use of solvents. Also, some of these methods require the pre-concentration of the extracted solutions before the analysis. This step increases the run time and can cause a decrease in analytical reproducibility. Therefore, alternative procedures reduce the number of steps by eliminating the use of solvents to avoid exposure and environmental contamination. The solid phase microextraction (SPME) is a simple method that meets these requirements since it combines sampling and pre-concentration in one step, does not require the use of solvents, and permits desorption directly into the injector of the chromatographic system [12]. This method has been used successfully in the analysis of PHA in complex environmental matrices [13].

* Corresponding author. Tel.: +55 3134095725; fax: +55 3134095700.
E-mail address: zenilda@ufmg.br (Z. de Lourdes Cardeal).

The objective of the present work was to demonstrate that a new simple and low cost device for direct immersion (DI) and cold fiber (CF) SPME-GC/MS can be used for the determination of PHA in particulate material.

2. Experimental

2.1. Reagents and supplies

A US Environmental Protection Agency (EPA) PAH Mix, containing naphthalene, acenaphthene, acenaphthylene, anthracene, benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[ghi]perylene, chrysene, dibenz[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-d]pyrene, naphthalene, phenanthrene, and pyrene at 2000 µg/mL in methanol:methylene chloride (1:1) was purchased from Supelco (Bellefonte, PA, USA). Standard solutions of 1000 µg/L were prepared by appropriate dilution in HPLC-grade methanol Sigma–Aldrich (St. Louis, MO, USA). Standard reference material, SRM1649b urban dust, was obtained from the National Institute of Standards & Technology NIST (Gaithersburg, MD, USA). HPLC-grade methylene chloride and acetone from Sigma–Aldrich (St. Louis, MO, USA) were used to prepare standard solutions of PAH; ultra-pure Milli-Q water Millipore (Molsheim, France) was used.

2.2. Particulate matter samples

Quartz filters (20.3 cm × 25.4 cm and 47 mm thickness from Whatman International (Maidstone, Kent, England)) were used to collect aerosol samples in the outdoor environments. These filters were pre-heated at 500 °C for 24 h prior to use to reduce their water and organic matter blank values. After cooling, the filters were weighed and stored at 4 °C in aluminum foil until the time for analysis. Real samples of PM10 (particulate matter with aerodynamic diameter < 10 µm) were collected using a high-volume Model VFC-PM10 sampler from Thermo Scientific Inc. (Franklin, MA, USA) which utilizes a volumetric flow controlled system (a dimensional venturi device) for sampling large volumes of air. Samples of Total Suspended Particles (TSP) were collected using a high-volume Model VFC-TSP sampler from Thermo Scientific Inc. (Franklin, MA, USA). The particulate phase samples were collected in November 2009, at Divinópolis, Minas Gerais, Brazil (20°9'S; 44°53'W) in two different environmental locations. The average ambient temperature was of 23 ± 3 °C with a mild breeze and 70% relative humidity. The sampling of PM10 was near a steel industry that uses coke and coal in its production process. The flow was 62 m³/h with a final collected volume of 1488 m³ of air. Sampling of TSP was near a steel industry that only uses coal in its production process. The sampling flow was 90 m³/h with a final volume of 2170 m³. Particles were collected for 24 h on quartz filters. After sampling, the filters were stored in the dark in aluminum foil at –20 °C and transported to the laboratory.

2.3. Instruments

A Finnigan Trace DSQ GC/MS equipped with an ion trap spectrometer from Thermo Scientific Inc. (West Palm Beach, FL, USA) and a capillary column (30 m length × 0.25 mm I.D. × 0.25 µm film thickness) containing 5% diphenyl, 95% dimethylpolysiloxane HP-5MS Agilent Technology Inc. (Santa Clara, CA, USA) was used. The oven temperature program began at 35 °C, was held for 2 min, raised to 270 °C at 8 °C/min, and held for 20 min. The carrier gas was helium at a flow rate of 4.5 mL/min. The injector was operated at 270 °C in splitless mode for 1 min, followed by a 1:20 split ratio (RD). The mass spectrometer was operated in electron impact mode (EI) with an energy of 70 eV. The ion source temperature was 200 °C,

Table 1
Experimental variables 2³ two-levels full factorial design for PAH extraction.

Variable	Level		
	Low	Centre	High
Extraction temperature (°C)	30	50	70
Time of equilibrium in ultrasonic bath (min)	0	5	10
extraction time (min)	20	40	60

and the GC/MS interface temperature was 290 °C. The analysis was performed in full scan mode (range 50–300 *m/z*), scan time of 3 scan/s. The quantification was achieved in selected ion monitoring (SIM) mode using the ion fragments presented in Table 3. Signal acquisition and data processing were performed using the Xcalibur software Thermo Finnigan Inc. (West Palm Beach, FL, USA). A USC 1600 ultrasonic bath from Unique (Indaiatuba, SP, Brazil) with a 40-kHz frequency and 135-W power was used to facilitate the dispersion of PAH that are less soluble in aqueous media.

2.4. Cold-fiber SPME device

The device scheme for the CF-DI-SPME is presented in Fig. 1. A copper tube with a length of 70 cm, O.D. of 2.4 mm, and I.D. of 1.6 mm was used to transfer liquid nitrogen from a Dewar flask to the SPME device. One extremity of the tube was inserted into the Dewar flask through a rubber stopper, and the other end, composed of a 3-cm-long spiral with 2 mm I.D., 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). The rubber stopper (4 mm top diameter and 3 mm bottom diameter) was used to cap the Dewar flask containing 0.5 L of liquid nitrogen. Another copper tube (10 cm length, 6.4 mm O.D. and 4.7 mm I.D.) was used as a valve controlling the nitrogen pressure in the Dewar flask; 0.5 L of liquid nitrogen permitted a 3 h cooling period. 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, hence, the fiber. When the valve was open, the nitrogen was purged from the Dewar flask and no longer passed through the spiral. Thus, the cooling process in the spiral was terminated. For the extraction, the cooled fiber was immersed in 20 mL Pyrex vials sealed with silicone/PTFE septa and aluminum caps containing an aqueous solution of PAH. The vial was placed in an aluminum block with controlled temperature and constant stirring.

2.5. Experimental design

To optimize the SPME method, all experiments were performed with quartz filter disks (diameter of 0.5 cm) pre-heated at 500 °C for 24 h and spiked with 10.0 µg/L of PAH solution in 50% (v/v) methylene chloride and acetone. These spiked filters were stored at –20 °C for 24 h prior to testing. A study was conducted using a 2³ two-level full factorial design (FFD) [14] to investigate the variables: extraction temperature (*T*), time of equilibrium in an ultrasonic bath (*t_{eq}*), and extraction time (*t_{ex}*) with direct immersion of the SPME fiber. The experimental values of these variables are presented in Table 1. The minimum and maximum levels of the parameters were selected based on the properties of the PAH analyzed. Extraction temperatures above 70 °C cause losses of low molecular weight PAH. On the other hand, temperatures below 30 °C make it difficult to extract the PAH. In the same way, 150 µL of a solution of 50% (v/v) methylene chloride and acetone was employed as a modifier during the equilibrium time. Acetone was selected to compose the modifier because it has been reported that solvents improve PAH extraction in environmental samples [15]. Moreover, studies show that the combination of acetone with other solvents tends to faci-

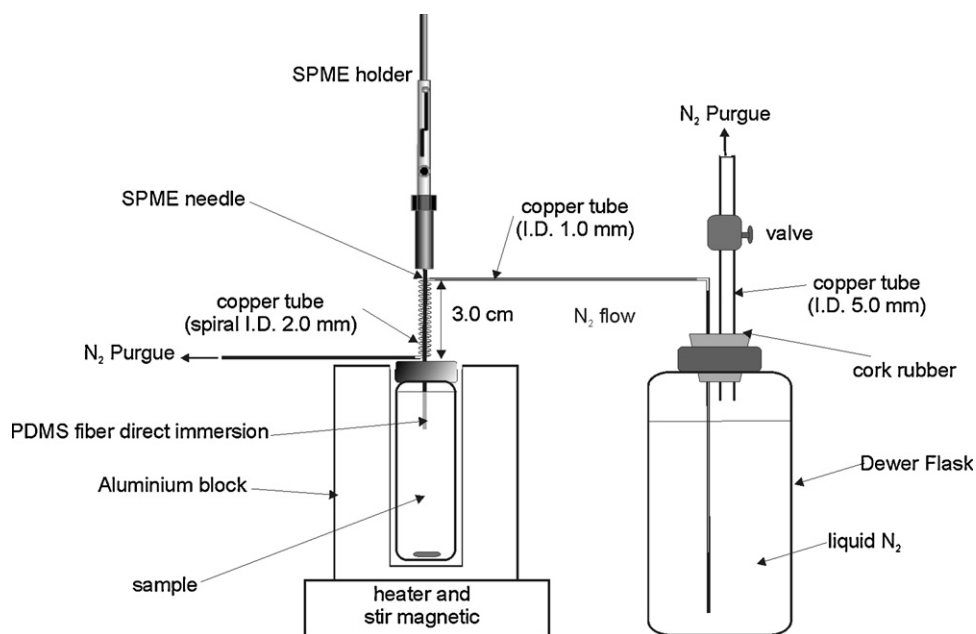


Fig. 1. Schematic of the device for DI-CF-SPME.

litate the solvation of analytes [16]. The volume of modifier was set at 150 μ L to avoid damaging the fiber used in the extraction. The Doehlert design (Table 2) was applied using the most significant variables with the objective of reaching the optimum region of the investigated area. The Doehlert design can be applied from two variables, requires fewer experiments, and has a higher efficiency (φ) than designs such as Central Composite and Box-Behnken. The efficiency value can be determined by dividing the number of coefficients of the quadratic equation (p) by the number of experiments (N) required for the design [17]. A Doehlert design with two factors ($k=2$) requires seven experiments to be completed. The experimental response (Y) as a function of variables (X_1 and X_2) is given by Eq. (1):

$$Y = b_0 + b_1(X_1) + b_2(X_1)(X_1) + b_3(X_2) + b_4(X_2)(X_2) + b_5(X_1)(X_2) \quad (1)$$

where b_0 is the constant term, b_1 and b_3 are coefficients of the linear terms, b_2 and b_4 are coefficients of the quadratic terms and b_5 is the coefficient of interaction between the two factors. Since p is 6 in this case, the efficiency value is 0.77. On the other hand, for Central Composite designs with the same number of factors, an efficiency value of 0.67 is obtained. The model fits were validated using the analysis of variance (ANOVA). The p -values smaller than 0.05 were considered significant. All the statistical analyses were

performed using the statistical package Statistica 8.0 for Windows Statsoft Inc. (Tulsa, OK, USA).

3. Results and discussion

3.1. Experimental design and optimization procedure

The Pareto chart analysis of the effects showed different behaviors for each of the analytes. The PAH with lower molecular weights presented a non-significant equilibrium time, temperature, and extraction time (for a p -value < 0.05), however, the higher temperatures and longer extraction times significantly increased the responses of benzo[a]anthracene, benzo[a]pyrene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[ghi]perylene. The main interaction observed for these analytes occurred between the temperature and extraction time. For this reason, these two parameters were used in the Doehlert design with the equilibrium time in the ultrasonic bath set at 5 min to reduce the total time of analysis.

The experimental conditions of the Doehlert design for real and coded values of each factor are shown in Table 2. For simplicity, the responses are not shown in this table. To assess the effect of each variable on the response, they were coded to eliminate the influence of their different magnitudes on such evaluation. The central point was achieved three times to obtain an estimation of the experimental error. An estimation of the coefficients ($b_0 - b_5$) of a second-degree polynomial model indicated by Eq. (1) was performed with the experimental responses. The level of significance for each regression was calculated by ANOVA and showed that the models were well fitted. The fractions of the explained variations (R^2) ranged from 0.971 for the benzo[a]anthracene to 0.989 for benzo[ghi]perylene. This fact indicated that a good capability for prediction existed under the experimental conditions employed. The optimum values for each independent variable were calculated using the adjusted models since they represent the point of the function where the extraction of each PAH is maximized and, therefore, should be used in the experimental procedure for the extraction of the analytes.

Table 2
Experimental planning for PAH extraction according to Doehlert design.

No.	Coded values		Real values	
	X_1	X_2	Extraction temperature ($^{\circ}$ C)	Extraction time (t_{ex} , min)
1	-0.5	-0.87	40	20
2	+0.5	-0.87	60	20
3	+1	0	70	40
4	+0.5	+0.87	60	60
5	-0.5	+0.87	40	60
6	-1	0	30	40
7	0	0	50	50
8	0	0	50	50
9	0	0	50	50

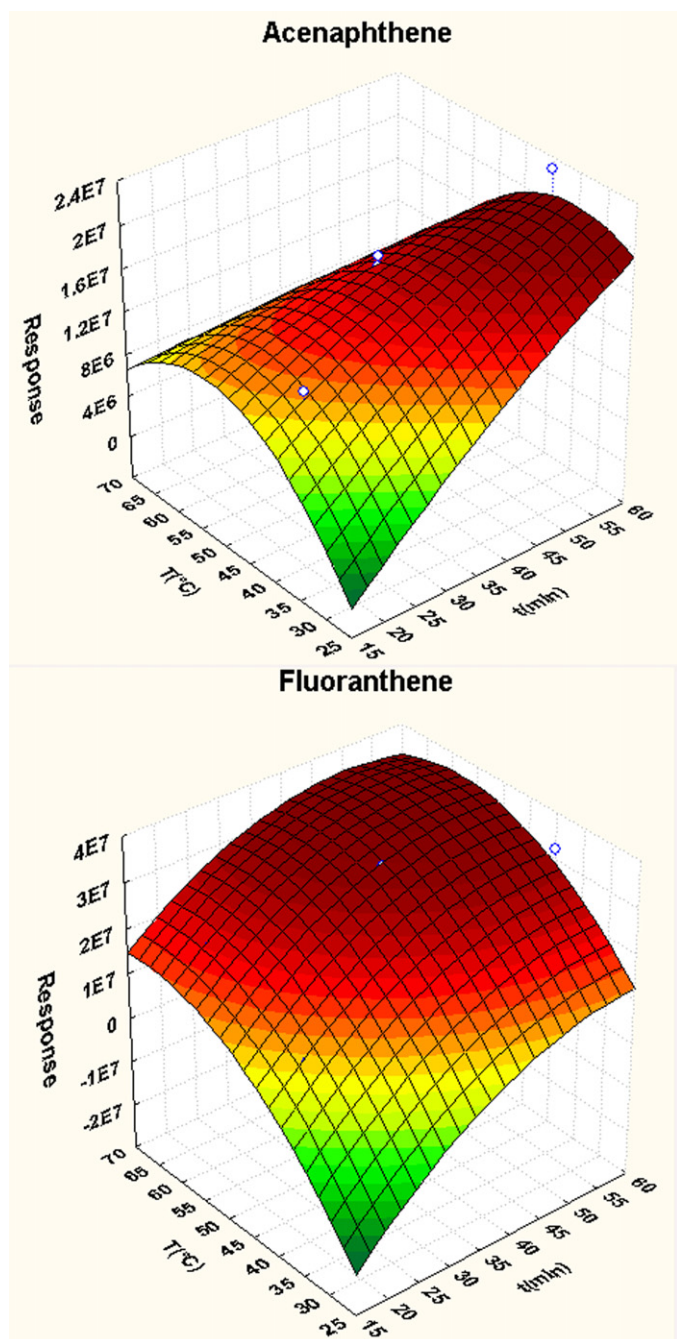


Fig. 2. Response surfaces obtained from the regression models of Doehlert design for acenaphthene and fluoranthene.

The response surfaces obtained from the regression models for acenaphthene, and fluoranthene are presented in Fig. 2. The best responses were presented by the lower molecular weight PAH for the extraction temperature in range of 30–50 °C and an extraction time of 40–60 min. The responses for PAH of higher molecular weights were optimum at temperatures near 70 °C and at all the extraction times. To achieve the optimum conditions for extraction of all the 16 PAH studied within the experimental domain, it was necessary to establish a compromise between the temperature and extraction time at the maximum levels, 70 °C and 60 min, respectively. Fig. 3 displays an overview of the method using optimized extraction conditions. A comparative study was performed with the new CF-DI-SPME device to evaluate the effect of cooling the fiber on the responses. The results of experiments conducted

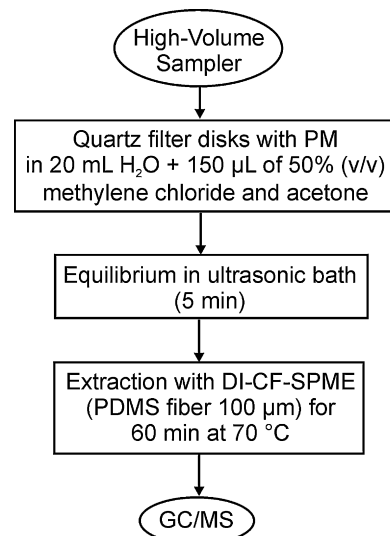


Fig. 3. Overview of the DI-CF-SPME-GC/MS method using optimized extraction conditions.

with three replicates of quartz filter disks employed as a blank matrix spiked with 10 µg/L PAH solution are presented in Fig. 4. The response area for all PAH was larger when the CF-mode DI-SPME was used than with the DI-SPME mode under the same conditions, but without cooling. The sorption process that occurred between the analytes and the fiber was exothermic, so the removal of excess thermal energy to the CF-DI-SPME device favored the mass transfer to the fiber, as was demonstrated by Ghiasvanda and Pawliszyn [18].

3.2. Quality control and quality assurance

The quality control and quality assurance method was performed according to EURACHEM guidelines [19]. Quartz filter disks were used as a blank matrix. Detection limits (LOD) and quantification limits (LOQ) were calculated from the mean and standard deviation of 10 blank measurements with 95% confidence. Linearity was established with quartz filter disks spiked with all the standard

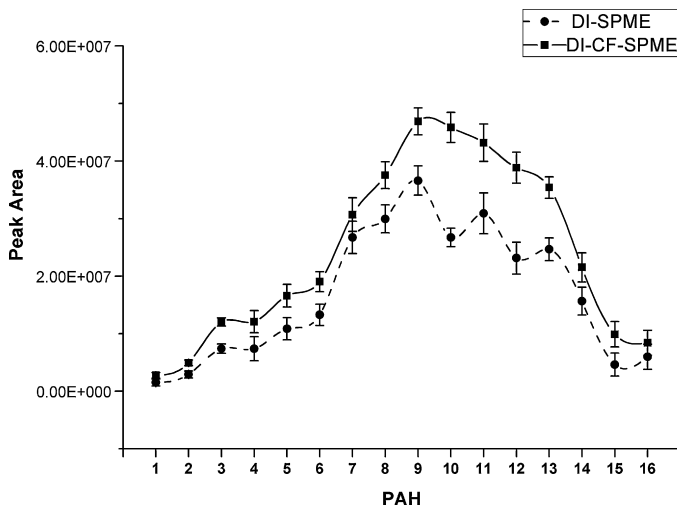


Fig. 4. Effect of the extraction mode using DI-SPME and DI-CF-SPME for 1, naphthalene; 2, acenaphthylene; 3, acenaphthene; 4, fluorene; 5, phenanthrene; 6, anthracene; 7, fluoranthene; 8, pyrene; 9, benzo[a]anthracene; 10, chrysene; 11, benzo[b]fluoranthene; 12, benzo[k]fluoranthene; 13, benzo[a]pyrene; 14, indeno[1,2,3-cd]pyrene; 15, dibenzo[a,h]anthracene; 16, benzo[ghi]perylene.

solutions (0.01–120 ng). Seven concentration levels were analyzed with three measurements at each concentration level. Because of the heteroscedasticity of the instrumental responses, the linear models for the calibration curves were constructed by the least squares method weighted by the experimental variance. The accuracy of the method was tested with samples of standard reference material, the SRM 1649b urban dust. The accuracy of the analytical method is acceptable if:

$$|X_m - X_{CRM}| \leq U$$

where X_{CRM} is the certified value, X_m is the mean experimental value of the replicates, U is the expanded uncertainty of the difference between mean experimental and certified values, corresponding to a confidence interval of approximately 95% [20]. The statistics tests were performed using the Origin 8.0 software from Origin Lab Co. (Northampton, MA, USA).

3.3. Method validation

Using the optimized conditions, some analytical performance was studied to validate the method. The results for linearity, detection limits, and quantification limits are presented in Table 3. A linear relationship was observed between the peak area and analyte concentration over the full range of the calibration curve, with determination coefficients above 0.990 (p value < 0.05).

All the analytes presented a LOD for the PAH between 0.02 and 1.16 ng, the range of LOQ was 0.05–3.86 ng. To assess the true-

Table 3
Linearity and limits of detection (LOD) and quantification (LOQ) of the DI-CF-SPME-GC/MS method.

PAH ^a	Quantitation ions	Linearity (r^2)	LOD (ng)	LOQ (ng)
Naphthalene	128	0.993	0.02	0.05
Acenaphthylene	152	0.991	0.31	1.02
Acenaphthene	153	0.992	0.35	1.18
Fluorene	166	0.990	0.40	1.34
Phenanthrene	178	0.993	0.92	3.06
Anthracene	178	0.992	0.62	2.05
Fluoranthene	202	0.995	0.37	1.24
Pyrene	202	0.991	0.33	1.09
Benzo[a]anthracene	228	0.994	0.30	1.01
Chrysene	228	0.994	0.57	1.89
Benzo[b]fluoranthene	252	0.992	0.43	1.44
Benzo[k]fluoranthene	252	0.993	1.16	3.86
Benzo[a]pyrene	252	0.995	0.75	3.46
Indeno[1,2,3- <i>cd</i>]pyrene	276	0.997	1.02	3.40
Dibenzo[a,h]anthracene	278	0.992	0.38	1.28
Benzo[ghi]perylene	276	0.994	1.13	3.77

^a Compounds are listed in sequence of elution.

Table 4
Quantification of PAH in NIST SRM1649b urban dust.

PAH	Mean (ng) ^a	Certified (ng) ^a	RSD (%) ^b	Difference (ng) ^c	Recovery (%)
Phenanthrene	21.91 ± 2.92	22.345 ± 0.266	13.31	-0.43 (1.46)	98.05
Anthracene	2.82 ± 0.15	2.886 ± 0.079	5.36	-0.06 (0.08)	97.71
Fluoranthene	34.05 ± 3.60	34.81 ± 0.68	10.56	-0.76 (1.83)	97.82
Pyrene	26.31 ± 2.82	27.125 ± 0.164	10.71	-0.82(1.41)	96.99
Benzo[a]anthracene	11.54 ± 0.62	11.862 ± 0.272	5.40	-0.32 (0.34)	95.43
Chrysene	16.54 ± 1.64	17.055 ± 0.249	9.93	-0.51(0.83)	96.98
Benzo[b]fluoranthene	33.05 ± 5.01	33.96 ± 1.13	15.16	-0.91(2.57)	97.32
Benzo[k]fluoranthene	9.74 ± 1.56	9.91 ± 0.471	16.05	-1.71(0.81)	98.28
Benzo[a]pyrene	12.44 ± 2.04	14.00 ± 0.96	16.38	-1.56 (1.12)	88.85
Indeno[1,2,3- <i>cd</i>]pyrene	14.82 ± 2.24	16.78 ± 0.96	15.12	-1.96 (1.22)	88.31
Dibenzo[a,h]anthracene	1.60 ± 0.25	1.62 ± 0.02	15.87	-0.04 (0.13)	97.76
Benzo[ghi]perylene	19.68 ± 3.39	22.323 ± 0.295	17.23	-2.65 (1.70)	88.16

^a Expanded uncertainty at the 95% of confidence.

^b Four 5 mg samples of SRM1649b.

^c Difference = (experimental value – certified value). The expanded uncertainty at the 95% of confidence of difference for each PAH is given within parentheses.

Table 5

PAH concentrations (ng/m³) of samples of particulate material collected in the Divinópolis, MG, Brazil, urban site ($n = 3$).

PAH	PM 10Mean (RSD, %)	TSPMean (RSD, %)
Phenanthrene	0.62(9)	0.51(18)
Anthracene	0.37(27)	0.45(19)
Fluoranthene	0.67(12)	0.56(8)
Pyrene	1.30(7)	1.14(11)
Benzo[a]anthracene	0.81(5)	0.90(4)
Chrysene	0.89(8)	0.80(12)
Benzo[b]fluoranthene	1.38(10)	1.04(14)
Benzo[k]fluoranthene	nd ^a	nd ^a
Benzo[a]pyrene	1.29(13)	1.01(11)
Indeno[1,2,3- <i>cd</i>]pyrene	1.18(9)	1.32(12)
Dibenzo[a,h]anthracene	nd ^a	nd ^a
Benzo[ghi]perylene	1.50(12)	1.26(14)

^a nd (not detected) is assigned for PAH having concentrations lower than the limit of quantification.

ness, four aliquots of 5.00 ± 0.01 mg of SRM 1649b urban dust were extracted and analyzed under the same conditions (Table 4). The accuracy was expressed by the difference between the experimental mean and the certified value, and the precision was represented by the relative standard deviation (RSD). The method presented a good precision. The RSD for all of the PAH was 17.2 or less. Values of 8.3–25.4% RSD were observed in a study of the between-days reproducibility with three aliquots of 5.00 ± 0.01 mg of SRM 1649b urban dust analyzed on three consecutive days.

The accuracy measured was in agreement with SRM1649b certified values, except for benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-*cd*]pyrene, and benzo[ghi]perylene, which presented absolute differences higher than the expanded uncertainty for these compounds. Recovery efficiencies for all the PAH were higher than 88%.

3.4. Application of the method to real samples of PM10 and TSP

The application of the validated DI-CF-SPME-GC/MS method for the determination of PAH to real samples was achieved through the analysis of samples from environmental air ($n = 3$) from two different locations in Divinópolis, MG, Brazil. This study is part of a Brazilian project to assess environmental exposure to carcinogenic chemicals in a city with many steel industries. The results, reported in Table 5, indicate that this method achieved good reproducibility when applied to real samples of PM10 and TSP. Phenanthrene and anthracene were the compounds that exhibited high RSD values in the PM10 and TSP samples because their concentrations were very close to the LOQ. These compounds have high vapor pressures so their concentrations are relatively low in the particulate phase [21]. In general the results for PAH in PM10 and TSP were similar to

average values for other urban areas [22–24]. Using benzo[a]pyrene as an indicator representing the PAH family, the concentrations of 1.29 ng/m³ determined for PM10 and 1.01 ng/m³ for TSP were above the current target set by the European Union.

4. Conclusions

A simple and inexpensive device has been proposed for CF-DI-SPME extraction of PAH at trace levels in particulate matter. The use of an experimental design enabled the optimization of extraction conditions. The DI-CF-SPME-GC/MS method, validated and tested on NIST SRM1649b urban dust, demonstrated the high accuracy and reproducibility and low LOD and LOQ for quantification of PAH in atmospheric aerosol samples collected on quartz fiber filters with high volume samplers. Future modifications of this method for in situ sampling are possible because of the portability of the device. The determination of volatile organic compounds in the environment, plants, drugs, and foods may represent additional applications of the method.

Acknowledgements

Funding for this study was provided by the Fundação de Amparo a Pesquisa de Minas Gerais (FAPEMIG) and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq). The authors thank the Secretaria Municipal de Meio Ambiente de Divinópolis for supplying the samples of particulate matter.

References

- [1] Polynuclear Aromatic Hydrocarbons. Part I. Chemical Environmental and Experimental Data (IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans (IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, vol. 32), International Agency for Research on Cancer (IARC), Lyon, 1983.
- [2] US EPA, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, 2nd ed., Office of Research and Development, National Risk Management Research Laboratory, Center for Environmental Research Information, 1999, Cincinnati, OH, <<http://www.epa.gov/ttn/amtic/airtox.html>>.
- [3] Directive 2004/107/EC 15-12-2004, Off. J. Eur. Union, L 23 (December 15, 2004) 13.
- [4] M.F. Simcik, T.P. Franz, H. Zhang, S.J. Eisenreich, Environ. Sci. Technol. 32 (1998) 251.
- [5] T. de Kok, H.A.L. Driee, J.G.F. Hogervorst, J.J. Briede, Mutat. Res., Rev. Mutat. Res. 613 (2006) 103.
- [6] R. Westerholm, A. Christensen, M. Tornqvist, L. Ehrenberg, U. Rannug, M. Sjogren, J. Rafter, C. Soontjens, J. Almen, K. Gragg, Environ. Sci. Technol. 35 (2001) 1748.
- [7] A. Albinet, E. Leoz-Garziandia, H. Budzinski, E. Villenave, J. Chromatogr. A 1121 (2006) 106.
- [8] S.G. Riddle, C.A. Jakober, M.A. Robert, T.M. Cahill, M.J. Charles, M.J. Kleeman, Atmos. Environ. 41 (2007) 8658.
- [9] S. Karthikeyan, R. Balasubramanian, S.W. See, Talanta 69 (2006) 79.
- [10] M. Shimmo, H. Adler, T. Hyotylainen, K. Hartonen, M. Kulmala, M.L. Riekkola, Atmos. Environ. 36 (2002) 2985.
- [11] L. Turrio-Baldassarri, C.L. Battistelli, L. Conti, R. Crebelli, B. De Berardis, A.L. Iamiceli, M. Gambino, S. Iannaccone, Sci. Total Environ. 327 (2004) 147.
- [12] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
- [13] B. Tang, U. Isacson, Energy Fuels 22 (2008) 1425.
- [14] Y.Z. Hu, D.L. Massart, J. Chromatogr. 485 (1989) 311.
- [15] I.J. Barnabas, J.R. Dean, I.A. Fowles, S.P. Owen, Analyst 120 (1995) 1897.
- [16] P. Bruno, M. Caselli, G. Gennaro, M. Tutino, Talanta 72 (2007) 1357.
- [17] A.M.G. Campaña, L. Cuadros, A.L. Gonzalez, F.A. Barrero, M.R. Ceba, Anal. Chim. Acta 348 (1997) 237.
- [18] R.H.S. Ghiasvanda, J. Pawliszyn, J. Chromatogr. A 1124 (2006) 35.
- [19] The Fitness for Purpose of Analytical Methods: A Laboratory Guide to Method Validation and Related Topics, EURACHEM Guide, LGC, Teddington, 1st English ed., 1998, <http://www.eurachem.ul.pt/>.
- [20] Application Note 1, Comparison of a Measurement Results with the Certified Value, Joint Research Centre Institute for Reference Materials and Measurements (IRMM), Geel, Belgium, 2005.
- [21] K. Ravindra, E. Wauters, R. Van Grieken, Sci. Total Environ. 396 (2008) 100.
- [22] A.M. Mastral, J.M. Lopez, M.S. Callén, T. Garcia, R. Murillo, M.V. Navarro, Sci. Total Environ. 307 (2003) 111.
- [23] A. Gutierrez-Daban, A.J. Fernandez-Espinosa, M. Ternero-Rodriguez, F. Fernandez-Alvarez, Anal. Bioanal. Chem. 381 (2005) 721.
- [24] M.A. Barrero Mazquiarán, L.C.O. de Pinedo, Atmos. Res. 85 (2007) 288.