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Screening direct analysis of PAHS in atmospheric particulate matter with SPME

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Abstract

A direct headspace SPME method with PDMS fiber was developed for the determination of polynuclear aromatic hydrocarbons (PAHs) in atmospheric particulate matter collected in HiVol filter. The recovery obtained for PAHs lower than four congeners with the proposed method falls in the range 50–125% and DL was around 5–20 pg. The results obtained with standard reference materials (SRM 1649 and SRM 1650) for determination of PAHs showed acceptable agreement with the declared or certificated values.

Keywords: PAH; SPME; GC/MS; PM_{10}

1. Introduction

Polynuclear aromatic hydrocarbons (PAHs) are by-products of the combustion of organic matter. Sources of atmospheric PAHs are mostly anthropogenic (e.g. motor vehicles, industrial processes, domestic heating, waste incineration, and tobacco smoke) and natural processes (e.g. forest fires and volcanic eruptions) [1,2]. To help identify the major emission sources responsible for adverse health effects, a comprehensive survey of atmospheric contaminants from a variety of sources have been performed worldwide. Urban measurements of the atmospheric PAHs in several cities have been reported and several analytical methodologies have been employed to evaluate the PAHs contents in the atmosphere [1,3–7].

The low concentration of organic pollutants in airborne particulate matter is a great challenge to analytical chemists [8]. Besides the need of an accurate, precise, sensitive and, if possible, selective analytical technique, the separation of the interesting compounds from extraneous materials and their enrichment during the extraction and clean-up steps is crucial for obtaining reliable results. Normally, the analysis of airborne particulate matter prior to chromatographic separation and detection requires some form of extraction with an organic solvent (or solvent mixture). This has been traditionally done by either heating or

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agitation of the organic solvent–solid mixture. The techniques more utilized have been Soxhlet extraction, sonication, or shake-flask extraction. More recently, other instrumental extraction techniques have been applied and these include supercritical fluid extraction, microwave-assisted extraction, and accelerated solvent extraction [9,10]. All these approaches are costly in terms of organic solvent usage (and disposal) or equipment costs. A particularly promising extraction technique is solid-phase microextraction (SPME) due to its several apparent advantages over other extraction techniques [11–13]. It is a sample preparation technique that requires no solvents and permits sample transfer and analysis with little or no modifications to existing chromatographic equipment. Methods employing SPME can be easily adaptable to extraction PAHs of airborne particulate matter especially those compounds lower than four congeners [14]. However, only a few researchers indicated that SPME might be applied to air sampling for PAHs in airborne particulate matter [15,16]. In this work, an analytical procedure based on headspace-solid-phase microextraction (HS-SPME) [17] coupled to gas chromatography/mass spectrometry (GC/MS) for characterization of PAHs in atmospheric particulate matter (PM_{10}) is proposed and applied to real and certificated samples.

2. Experimental

2.1. Chemicals and materials

PAHs standards were purchased from Supelco, sodium sulfate (purity grade $>99\%$) from Merck, and deionized water was obtained from a Nanopure water purification system (Bransted). Stock solutions at a concentration of 500 μg ml^{-1} in acetonitrile (grade HPLC, Merck) of the following individual standards, naphthalene (Nap), acenaphtylene (Acy), acenaphtene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[*a*]anthracene (BaA), crysene (Cry), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), indeno[1,2,3-*cd*]pyrene (Ind), benzo[*a*]pyrene (BaP), dibenzo[*a*,*h*]anthracene (DaA), and benzo[*g*,*h*,*i*]perylene (BghiP), were prepared and stored in freezer at 4 °C. Mixtures containing appropriate amounts of each PAH standard were prepared by dilution of the stock solutions with acetonitrile.

A sample of PM_{10}, collected in an urban site of São Paulo City, Brazil, was used in this study [3]. PM_{10} was collected near downtown São Paulo using a high-volume air sampler with a size-selective inlet and a Teflon-coated glass fiber filter. Approximately 1300 m^3 of air was passed through the filter over 24 h. The filter was weighed prior to use and again afterwards to determine the amount of particulate matter collected ($\sim$150 mg). For SPME analysis, the filter was cut in disks (1.31 cm of diameter) and the particulate matter mass in each disk was estimated by using the relationship between disk area and total area of the filter ($\sim$ 490 μg). Certificated samples (standard reference materials: SRM 1649—Urban Dust/Organics and SRM 1650—Diesel Particulate Matter) and spiked samples were used to determine the efficiency of the extraction and analysis. The recovery studied was made by adding the appropriated amount of PAHs stock solutions in a clean disk filter. The disks were carefully dried in and then extracted by SPME method.

2.2. Sample preparation and SPME procedures

HS-SPME extractions were performed in 0.6 ml of 20% sodium sulfate in deionized water into 2.0 ml amber vials with magnetic stirring and capped with PTFE-coated septa. The extraction procedure was conducted in two steps. Initially, the equilibrium of the sample and liquid phase was conducted with continuous stirring for 2 h at room temperature. SPME procedure in the headspace was made for 120 min at 50 °C with a polydimethylsiloxane (PDMS) fiber, from Supelco, with film thickness of 100 μm. After extraction, the fiber was thermally desorbed for 4.5 min into the glass liner of the gas chromatograph injector at 260 °C in split-less mode.

The fiber was conditioned before use by heating, then in a gas chromatograph injection port at 280 °C for 2 h.

2.3. Gas chromatography/mass spectrometry analysis

A gas chromatograph (Model GC-17A, Shimadzu) coupled with a mass spectrometry detector (Model QP5000, Shimadzu) was used for the experiments to determine the optimized SPME conditions. A 30 m × 0.25 mm HP-5 MS column (0.25 μm film thickness) was used for separating PAHs. The column was held at 45 °C for 1 min, increased to 190 °C at a rate of 30 °C min^{-1}, and again ramped at 5 °C min^{-1} to 310 °C held for 10 min. Helium at 114 kPa was used as the carrier gas. The single ion-monitoring (SIM) detection mode was acquired in the electron impact (EI) mode. The interface temperature was maintained at 240 °C and the detector tension was of 2.75 kV. For each PAH, two ions (M and M+1) were selected and integrated. Calibration curves for all the target analytes were obtained by using HS-SPME procedure by extracting five aqueous standards with increased concentration over a range between 7.5 pg and 9.6 ng in order to evaluate the linearity of mass detector response.

3. Results and discussion

PAHs studied present physical–chemical properties that cover a wide range of water solubility (10^{-10}–10^{-3} mol l^{-1}), log K_{ow} (octanol–water partition coefficient) values in the range 3–7, vapor pressure (10^{-9}–10^{-2} mmHg), and Henry's constant (1–500 ml atm mol^{-1}). PAHs can be classified as non-polar compounds and would be expected that their partition could occur easily in a non-polar fiber such as PDMS. The low range of vapor pressure for these compounds suggests the use of 100 μm film thickness for headspace extraction [18].

In the procedure, the extraction of PAHs was performed in three steps: aqueous equilibrium, gas-phase partition, and headspace extraction. In the equilibrium step, PM_{10} was partitioned from the sample matrix to saline phase and PAHs were transferred to solution. In the gas-phase partition, PAHs were transferred from saline phase to the above-mentioned gas-phase solution (headspace). In the extraction step, the fiber was exposed to headspace of aqueous saline solution containing PM_{10} and PAHs were partitioned from the gas phase (headspace) to the polymeric film of PDMS in the fiber and then desorbed onto the injector of GC/MS.

3.1. Linearity, detection limits, and recovery

The reconstructed SIM chromatogram for standard of PAHs obtained by HS-SPME method proposed was presented in Fig. 1. From Table 1, it

Table 1
Linearity and DL for HS-SPME method

PAH	Ions (*m*/*z*)	Slope	Intercept	Linearity	DL (pg)[a]
Acenaphtylene	152; 153	5.57×10^4	3.61×10^5	0.9942	13
Acenaphtene	154; 155	4.09×10^4	2.60×10^5	0.9968	10
Fluorene	166; 167	5.03×10^4	5.40×10^5	0.9903	17
Phenanthrene	178; 179	1.01×10^5	1.15×10^6	0.9889	18
Anthracene	178; 179	4.54×10^4	1.02×10^5	0.9982	8
Fluoranthene	202; 203	3.98×10^4	4.30×10^5	0.9908	16
Pyrene	202; 203	3.57×10^4	3.50×10^5	0.9921	15
Benzo[*a*]anthracene	228; 229	1.10×10^4	2.58×10^4	0.9998	5
Crysene	228; 229	8.97×10^3	6.69×10^4	0.9977	17
Benzo[*b*]fluoranthene	252; 253	4.85×10^3	9.14×10^3	0.9995	33
Benzo[*k*]fluoranthene	252; 253	5.79×10^3	2.16×10^5	0.9980	63
Benzo[*a*]pyrene	252; 253	2.72×10^3	1.27×10^4	0.9998	22
Indeno[*cd*-1,2,3]pyrene	276; 277	4.29×10^2	2.78×10^4	0.9983	570
Benzo[*g*,*h*,*i*]perylene	276; 277	4.44×10^2	1.91×10^4	0.9983	270

[a] Signal-to-noise ratio of 3:1.

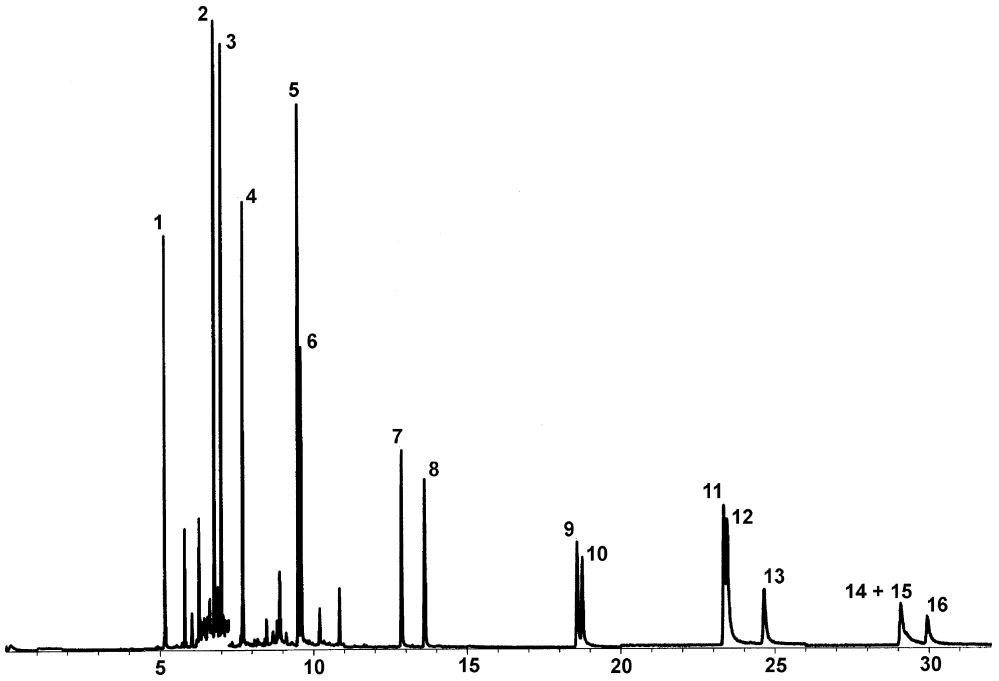

Fig. 1. Reconstructed SIM chromatogram for standard of PAHs obtained by HS-SPME (level 5 for reference curve). (1) Nap (24 pg); (2) Acy (120 pg); (3) Ace (120 pg); (4) Flu (120 pg); (5) Phe (120 pg); (6) Ant (120 pg); (7) Fla (120 pg); (8) Pyr (120 pg); (9) BaA (240 pg); (10) Cry (240 pg); (11) BbF (960 pg); (12) BkF (960 pg); (13) BaP (960 pg); (14, 15) Ind+DaA (9.6 ng each); and (16) BghiP (9.6 ng).

can be observed that reference curves showed good linear behavior (r^2) and the detection limits (DL) obtained for the relationship signal-to-noise (S/N) of 3. The recovery studies were made in concentrations close to DL and three times DL in a clean disk HiVol filter. The results obtained are presented in Table 2. As expected, the recovery for level 1 was lower than that of level 2, as the lowest concentration for this level was very close to DL, but it can be observed that the recovery falls between 50 and 125% for PAHs with two, three, and four congeners. However, for

Table 2
Recovery of PAHs by using the proposed HS-SPME method (spiked samples in blank filter)

PAH	Level 1		Level 2	
	Spiked (pg)	Recovery (%)[a]	Spiked (pg)	Recovery (%)[a]
Acenaphtylene	15	41±25	60	80±16
Acenaphtene	15	68±18	60	103±12
Fluorene	15	52±26	60	118±20
Phenanthrene	15	50±22	60	125±22
Anthracene	15	60±25	60	102±9
Fluoranthene	15	95±22	60	108±10
Pyrene	15	65±20	60	93±18
Benzo[*a*]anthracene	30	47±24	120	92±12
Crysene	30	68±15	120	108±10

[a] Average±t.s. at 95% confidence for three replicate determinations.

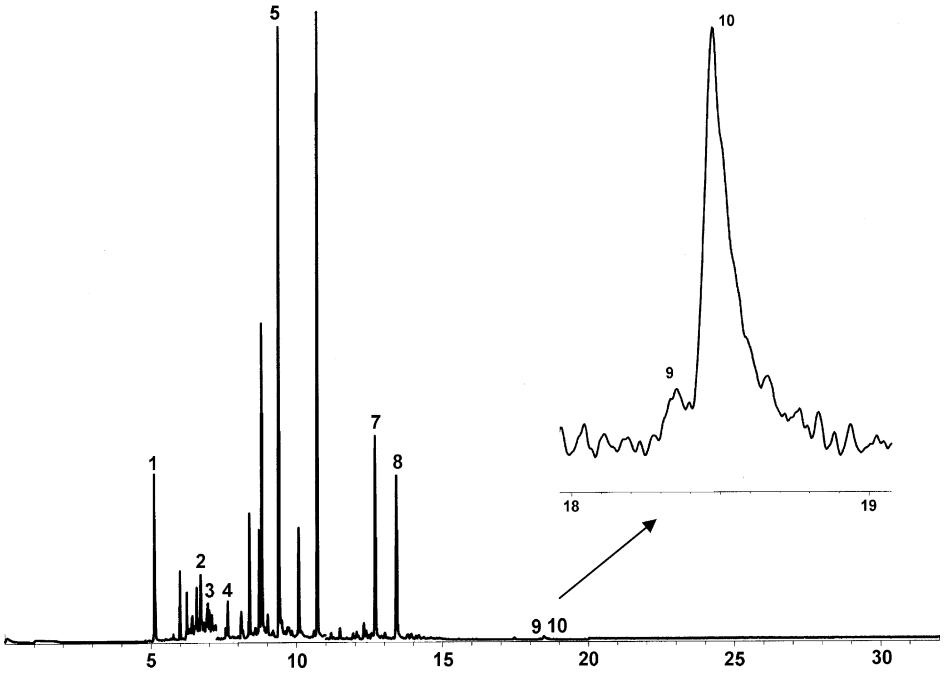

Fig. 2. Reconstructed SIM chromatogram for SRM 1650 obtained by HS-SPME (peak identification number same as in Fig. 1).

PAH with five and six congeners recovery values were not observed possibly due to its low vapor pressure or due to possible adsorption in HiVol filter.

3.2. Determination of PAHs in certified material and PM_{10}

The results and chromatogram obtained for the determination of some PAHs, for the proposed method, in SRM are presented in Table 3 and Fig. 2. The obtained values for PAHs with two, three, and four congeners are in acceptable agreement with the declared or certificated values for these materials. For PAHs with more than five ring members these values were not detected probably due to the high K_{ow} and low vapor pressure. The results and chromatogram obtained for the determination of PAHs in the atmospheric particulate material collected in the city of São Paulo are presented in Table 4 and Fig. 3. The obtained values are in agreement with that obtained by the conventional methodology that uses extraction with solvents [3]. The presence of several PAHs

Table 3
Results in μg g^{-1} of the determination of PAHs in SRM 1649—Urban Dust/Organics and SRM 1650—Diesel Particulate Matter by HS-SPME

PAH	SRM 1649[a]	SRM 1650[a]
Acenaphtylene	0.24±0.04	2.9±0.5
Acenaphtene	0.24±0.04	2.7±0.4
Fluorene	0.25±0.07	2.0±0.4
Phenanthrene	4.9±0.9	68±9; 71[b]
Anthracene	0.21±0.03	0.70±0.07
Fluoranthene	7.6±0.9 (7.1)	53±9 (51)
Pyrene	6.9±0.9	52±9 (48)
Benzo[*a*]anthracene	0.35±0.02 (2.6)	0.30±0.02 (6.5)
Crysene	3.0±0.3	7.8±0.9; 22[b]
Benzo[*b*]fluoranthene	ND	ND
Benzo[*k*]fluoranthene	ND	ND; 2.1[b]
Benzo[*a*]pyrene	0.34±0.02 (2.9)	ND (1.2)
Indeno[*cd*-1,2,3]pyrene	ND (3.3)	ND; 2.3[b]
Dibenzo[*a*,*h*]anthracene	ND	ND
Benzo[*g*,*h*,*i*]perylene	ND (4.5)	ND (2.4)

Values within parenthesis are certificated values; ND, not detected.

[a] Average±t.s. at 95% confidence for three replicate determinations.

[b] Declared value.

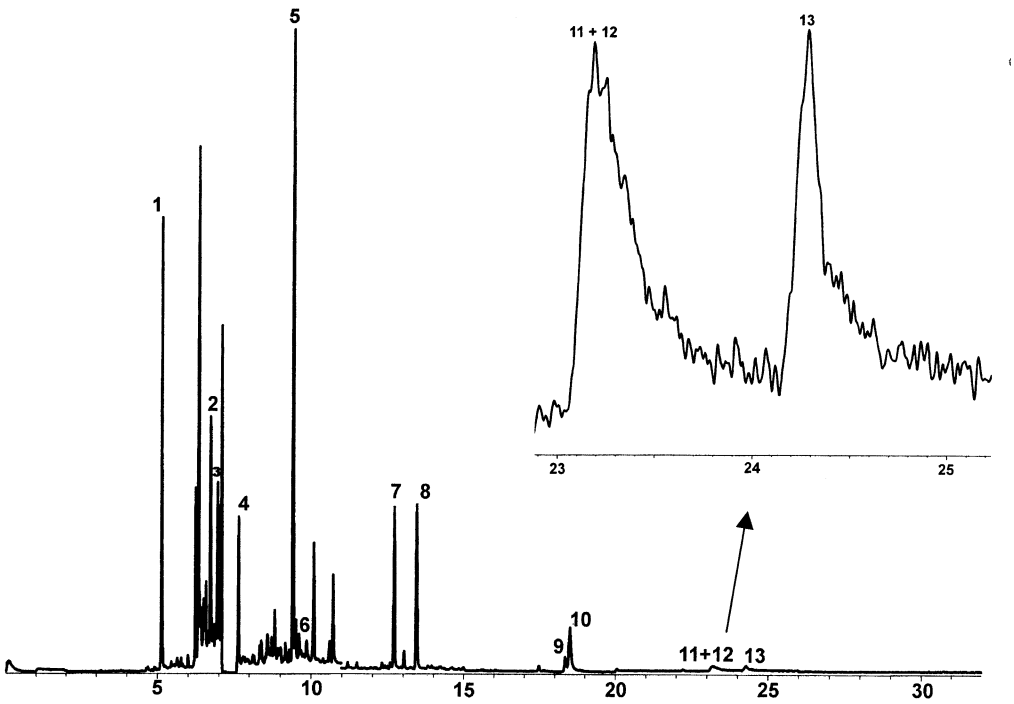

Fig. 3. Reconstructed SIM chromatogram for HiVol filter collected in an urban site of São Paulo (peak identification number same as in Fig. 1).

Table 4
Results in ng m^{-3} for the determinations of PAHs in PM_{10} collected onto filter (air sampled volume 1300 m^3) in an urban site of São Paulo City, Brazil

Acenaphtylene	0.28±0.03
Acenaphtene	0.20±0.05
Fluorene	0.27±0.04
Phenanthrene	1.2±0.04
Anthracene	0.20±0.03
Fluoranthene	1.5±0.1
Pyrene	1.8±0.06
Benzo[*a*]anthracene	0.38±0.09
Crysene	2.4±0.3
ΣSummation of benzo[*b*]fluoranthene and benzo[*k*]fluoranthene	5.7[a]
Benzo[*a*]pyrene	1.0[a]
Indeno[*cd*-1,2,3]pyrene	ND
Dibenzo[*a*,*h*]anthracene	ND
Benzo[*g*,*h*,*i*]perylene	ND

Values are average±t.s. at 95% confidence for three replicate determinations; ND, not detected.
[a] One determination.

considered mutagenic and the relationship of fluoranthene concentration with pyrene suggest that PAHs are emitted predominantly from diesel motor exhaust gases. In this sense, the relationship of the phenanthrene concentration with anthracene also suggests that the origin of PAH is of pyrolitic sources [19,20].

4. Conclusions

HS-SPME followed by GC/MS in SIM acquisition mode has been developed for direct determination of some PAH in PM_{10}. The method was optimized under non-equilibrium conditions and simple sample preparations were presented. The analytical performance of the results showed a potential application as a screening tool for chemical characterization, source discrimination, and evaluation of isomer distribution in environmental samples saving time and costs.

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References

[1] P.A.D. Pereira, J.B. Andrade, A.H. Miguel, J. Environ. Monit. 4 (2002) 558–561.
[2] J.B. Andrade, Quím. Nova 19 (1996) 497–516.
[3] B.S. De Martinis, R.A. Okamoto, N.Y. Kado, L.A. Gundel, L.R.F. Carvalho, Atmos. Environ. 36 (2002) 307–314.
[4] A.D.P. Netto, R.P. Barreto, J.C. Moreira, G. Arbilla, Bull. Environ. Contam. Toxicol. 69 (2002) 173–180.
[5] S.S. Park, Y.J. Kim, C.H. Kang, Atmos. Environ. 36 (2002) 2917–2924.
[6] X. Xu, S. Chu, N. Song, J. Chromatogr. A 710 (1995) 21–37.
[7] P.T.J. Scheepers, D.D. Velders, M.H.J. Martens, J. Noordhoeck, R.P. Bos, J. Chromatogr. A 677 (1994) 107–121.
[8] V. Camel, M. Caude, J. Chromatogr. A 710 (1995) 3–19.
[9] K. Peltonen, T. Kuljukka, J. Chromatogr. A 710 (1995) 93–108.
[10] J.R. Dean, Extraction Methods for Environmental Analysis, Wiley, New York, 1998.
[11] B. Zygmunt, A. Jastrzebska, J. Namiesnik, Crit. Rev. Anal. Chem. 31 (2001) 1–18.
[12] J. Pawliszyn, Solid Phase Microextraction Theory and Practice, Wiley/VCH, New York/Weinheim, 1997.
[13] L. Lassagne, V. Jacob, P. Desuzinges, F. Tripoli, P. Kaluzny, P. Baussand, P. Foster, Fresenius Environ. Bull. 10 (2001) 381–385.
[14] W.J. Havenga, E.R. Rohwer, Int. J. Environ. Anal. Chem. 78 (2000) 205–221.
[15] J.A. Koziel, M. Odziemkowski, J. Pawliszyn, Anal. Chem. 73 (2001) 47–54.
[16] J. Namiesnik, D. Gorlo, L. Wolska, B. Zygmunt, Analusis 26 (1998) 170–174.
[17] Z. Zhang, J. Pawliszyn, Anal. Chem. 65 (1993) 1843–1852.
[18] P.A. Martos, J. Pawliszyn, Anal. Chem. 69 (1997) 206–215.
[19] M.B. Yunker, R.W. Macdonald, R. Vingarzan, R.H. Mitchell, D. Goyette, S. Sylvestre, Org. Geochem. 33 (2002) 489–515.
[20] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller, Anal. Chem. 68 (1996) 144–155.