Journal of Chromatography A, 1497 (2017) 127–134

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Development of a short path thermal desorption–gas chromatography/mass spectrometry method for the determination of polycyclic aromatic hydrocarbons in indoor air

Yingjie Li[a,b,c,*], Qiming Xian[d], Li Li[a,b]

[a] Shanghai Academy of Environmental Sciences, Shanghai, China
[b] State Environmental Protection Key Laboratory of the Cause and Prevention of Urban Air Pollution Complex, Shanghai, China
[c] College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai, China
[d] State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing, China

ARTICLE INFO

Article history:
Received 24 January 2017
Received in revised form 18 March 2017
Accepted 20 March 2017
Available online 27 March 2017

Keywords:
Semi-volatile organic compounds
Polycyclic aromatic hydrocarbons
Short path thermal desorption
Gas chromatography/mass spectrometry

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are present in petroleum based products and are combustion by-products of organic matters. Determination of levels of PAHs in the indoor environment is important for assessing human exposure to these chemicals. A new short path thermal desorption (SPTD) gas chromatography/mass spectrometry (GC/MS) method for determining levels of PAHs in indoor air was developed. Thermal desorption (TD) tubes packed with glass beads, Carbopack C, and Carbopack B in sequence, were used for sample collection. Indoor air was sampled using a small portable pump over 7 days at 100 ml/min. Target PAHs were thermally released and introduced into the GC/MS for analysis through the SPTD unit. During tube desorption, PAHs were cold trapped (−20 °C) at the front end of the GC column. Thermal desorption efficiencies were 100% for PAHs with 2 and 3 rings, and 99–97% for PAHs with 4–6 rings. Relative standard deviation (RSD) values among replicate samples spiked at three different levels were around 10–20%. The detection limit of this method was at or below 0.1 μg/m^3 except for naphthalene (0.61 μg/m^3), fluorene (0.28 μg/m^3) and phenanthrene (0.35 μg/m^3). This method was applied to measure PAHs in indoor air in nine residential homes. The levels of PAHs in indoor air found in these nine homes are similar to indoor air values reported by others.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are present in petroleum based products. They are also formed during incomplete combustion of organic materials. PAHs are emitted during certain industrial processes and consumers' daily activities, such as power generation, automobile, cigarette smoking, and indoor domestic heating systems such as furnaces and wood stoves. Thus they are ubiquitously present in the environment. Some PAHs are carcinogenic and mutagenic. There are environmental and human health concerns about exposure to PAHs at environmental levels. Many of them, especially benzo(a)pyrene, are designated as priority air pollutants by the United States Environmental Protection Agency [1].

Gas chromatography/mass spectrometry (GC/MS) is the most common analytical method for measuring levels of airborne PAHs. PAHs can partition between vapour and particulate phases. Active sampling methods for airborne PAHs include the use of a combination of filter paper to collect particulate-bound PAHs and an adsorbent to collect vapor-phase PAHs [2–6]. Passive sampling of airborne PAHs is mostly carried out by using polyurethane foam (PUF) disks [7,8] or diffusion denuders [9]. Air samples collected by these methods were extracted with different organic solvents. Solvent extraction and clean up procedure however, is time consuming and labor intensive. The procedure is also susceptible to potential contamination and error [7,10].

Thermal desorption (TD) is a relatively new sample introduction technique [11] and has been proven to be an efficient sample introduction method for GC/MS analysis of volatile organic compounds (VOCs) [12–16]. However, only a few studies so far have reported the use of TD for the analysis of semi-volatile organic compounds (SVOCs) such as PAHs. Martins et al. [17] developed a TD/GC/MS method to determine airborne 2- and 3-ring PAHs using

* Corresponding author at: Shanghai Academy of Environmental Sciences, Shanghai, China.
E-mail address: Liyj@saes.sh.cn (Y. Li).

http://dx.doi.org/10.1016/j.chroma.2017.03.050
0021-9673/

Tenax TA as the adsorbent. For particle-bound PAHs (4- to 6-ring PAHs), Bates et al. [18] used a direct thermal desorption approach by thermally desorbing PAHs from exposed quartz wool into the GC/MS. Other studies have used multi-sorbent (polydimethylsiloxane (PDMS)/Tenax TA) tubes for collecting and analysing 2- to 6-ring PAHs in air [19,20]. A stir bar was also used as a collection medium for airborne PAHs followed by TD/GC/MS analysis [21]. TD units used in the above mentioned studies for PAHs are connected to a GC column through a heated and insulated transfer line.

Carry-over of some heavy PAHs with low volatility in the sample introduction system was reported to be a challenge in these studies [17,20,21]. For example, Lazarov et al., reported a 20–25% carry-over for PAHs with a molecular weight of 276 or 278 Da [20], independent from spiked amount between 0.25 ng/tube and 8 ng/tube.

The short path thermal desorption (SPTD) device used in this study has a TD heating block located directly above the GC injection port. Thermally desorbed analytes (such as PAHs) therefore can be directly introduced into the GC injection port without the need for a transfer line. The objective of this study was to develop an SPTD–GC/MS method for measuring airborne PAHs and to demonstrate the usefulness of this method for determining airborne PAHs in residential indoor air. Multi-sorbent tubes (Glass beads, Carbopack C, and Carbopack B) were used to expand the analytical window to cover PAHs from 2-ring to 6-ring.

2. Materials and methods

2.1. Chemicals and materials

A standard calibration mixture of PAHs (2000 μg/ml in methylene chloride, catalog number 47930-U), naphthlene-d_8 (200 μg/ml in dichloromethane (DCM), isotope purity of 99%), and chrysene-d_{12} (2000 μg/ml in DCM, isotope purity of 99%) were purchased from Supelco (Bellefonte, PA, USA). $^{13}C_{12}$-benzo(g,h,i)perylene (100 μg/ml in nonane, isotope purity of 99%) was purchased from Cambridge Isotope Laboratories, Inc. (CIL, Tewksbury, MA, USA). All standard solutions were prepared by series dilutions in DCM (>99.99%) that was bought from Supelco (Oakville, ON, Canada). Glass beads (250 μm, acid washed), Carbopack C (60/80 mesh), and Carbopack B (60/80 mesh) were obtained from Supelco (Bellefonte, PA, USA). Glass wool was purchased from Valley Specialty Chemical (Marietta, OH, USA). Nitrogen gas (99.999% purity) was used for dispersal of chemicals in the spiked tubes and for conditioning thermal desorption sorbent tubes. Pure air (99.999% purity) was used for the SPTD switching valves. Helium gas (99.999% purity) was used for dry purging, thermal desorption, and GC/MS analysis.

2.2. Sampling tubes

Empty stainless steel tubes (3 mm internal diameter (I.D.) × 101 mm length) were purchased from Scientific Instrument Services, Inc. (SIS, Ringoes, NJ, USA). Single adsorbent tubes were prepared by packing about 20 mm of single adsorbent, which corresponds to 220 mg of glass beads, 90 mg of Carbopack C, and 60 mg of Carbopack B, respectively. For multi-sorbent tubes, the tube was packed (from weak adsorbent to strong absorbent) with 200 mg of glass beads, 45 mg of Carbopack C, and 15 mg of Carbopack B in sequence. Glass wool was used to separate the adsorbents and to retain the adsorbents at both ends. Prior to their initial use, packed tubes were conditioned at 350 °C for 16 h under nitrogen, at a flow rate of 100 ml/min, using a tube conditioning system (SIS, Ringoes, NJ, USA). For subsequent uses, tubes were subjected to a clean-up at 350 °C for 1 h at a flow rate of 100 ml/min. Once clean, the tubes were sealed with end caps, wrapped in aluminum foil, and stored in a refrigerator at 4 °C.

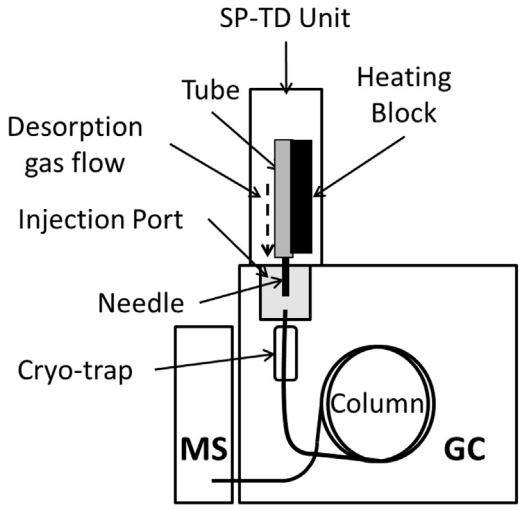

Fig. 1. Scheme of short path TD–GC/MS.

2.3. Spiking of tubes with standard solutions

TD tubes were spiked with 1.0 μl of a standard solution and then purged with N_2 (99.999%) at a flow rate of 100 ml/min for 20 min to remove the solvent and to disperse the standards.

2.4. Sampling of indoor air

Indoor air samples were collected using a pocket air sampling pump (210-1000MH, SKC, Houston, TX, USA) at a nominal flow rate of 100 ml/min for 7 days. The actual flow rate of the pump was calibrated using a digital flow meter (Sensidyne Gilian Gilibrator, Petersburg, FL, USA) before and after sampling. Multi-sorbent tubes were spiked with 1 ng of each of the three internal standards (NAP-d_8, CHR-d_{12}, and $^{13}C_{12}$-B(g,h,i)P) prior to sample collection. After sampling, the tubes were immediately sealed with the end caps and wrapped in aluminum foil. Upon arrival in the laboratory the sample tubes were stored in a refrigerator at 4 °C until analysis. All samples were analyzed within a week after the collection.

2.5. SPTD–GC/MS analysis

TD was carried out on an SIS AutoDesorb® Short Path Thermal Desorption device (Model 2000, Scientific Instrument Services, Inc., Ringoes, NJ, USA) (Fig. 1). Helium was used as the desorption gas to direct the desorbed organic compounds to the GC injection port. SPTD Tubes were screw-mounted with a GC injection needle (35 mm long with flat tip, parts number: 786035, Scientific Instrument Services, Inc., Ringoes, NJ, USA) and placed on a 12-tube carousel for automated analysis. The tube picked from carousel for analysis was first dry-purged with helium for 2 min to remove possible moisture in the tube. Then the tube was connected to GC injection port through the needle. TD started 1.0 min after the needle was inserted through the GC septum into heated GC inlet (350 °C) for pressure stabilization. During desorption, the analytes were trapped on a micro cryo-trap (−20 °C) at the front end of the GC column that was mounted inside the GC oven beneath the injection port. When desorption was completed, the cryo-trap was held at −20 °C for an additional 0.5 min to prevent pressure fluctuations, after which time, the GC/MS program started and the cryo-trap was rapidly heated at about 400 °C/min to 350 °C.

Table 1
Targets with number of rings (R_N), retention time (RT), quantitation (T) and qualifier ion (Q) used for SIM detection of targeted PAHs and internal standards.

Peak	Name	Abbreviation	R_N	RT, min	T	Q
1	Naphthlene-d_8	NAP-d_8	2	8.93	136.1	108.1
2	Naphthalene	NAP	2	8.99	128.0	102.0
3	Acenaphthylene	ACP	3	15.01	152.1	76.30
4	Acenaphthene	ACE	3	15.73	153.0	76.1
5	Fluorene	FLU	3	17.83	166.1	82.3
6	Phenanthrene	PHE	3	21.64	178.1	89.0
7	Anthracene	ANT	3	21.85	178.1	89.0
8	Fluoranthene	FLUO	4	26.38	202.1	101.1
9	Pyrene	PYR	4	27.11	202.1	101.1
10	Benz(a)anthracene	B(a)A	4	30.89	228.1	114.0
11	Chrysene-d_{12}	CHR-d_{12}	4	30.91	240.2	236.2
12	Chrysene	CHR	4	30.95	228.1	114.0
13	Benzo(b)fluoranthene	B(b)F	5	33.62	252.1	126.0
14	Benzo(a)pyrene	B(a)P	5	34.21	252.1	126.0
15	Indeno(1,2,3-cd)pyrene	IND	6	36.57	276.2	138.0
16	Dibenz(a,h)antheracene	DBA	5	36.65	278.2	139.0
17	$^{13}C_{12}$-Benzo(g,h,i)perylene	$^{13}C_{12}$-B(g,h,i)P	6	37.01	288.2	144.0
18	Benzo(g,h,i)Perylene	B(g,h,i)P	6	37.01	276.2	138.0

The SPTD device was connected to an Agilent GC 6890 coupled with an Agilent 5973 MS detector (Agilent, Santa Clara, CA, USA). The compounds were separated on a DB-5MS capillary column (30 m length × 0.25 mm I.D. × 0.25 μm film thickness). The GC was operated in constant pressure (23 psi) mode. The MS was operated in the electron impact (EI, 70 eV) ionization mode. The ion source and quadrupole temperatures were set at 230 °C and 150 °C, respectively. Samples were monitored in full scan mode for the optimization of thermal desorption parameters and in single ion monitoring mode (SIM) for evaluating the method performance and for the analysis of samples. The ions selected for each of the targets under SIM are listed in Table 1.

Quantification of the target compounds (T) was performed using an internal standard calibration as following. Calibration tubes were spiked with known amounts of the PAHs shown in Table 1 (0.03, 0.1, 0.3, 1, 3, 10 ng/tube) and internal standards (IS) (1 ng/tube) to generate the calibration curve. The regression of the calibration curve was based on a power law relationship. The amount of PAH in the sample = $a \times x^b$, where x is the peak area ratio of PAH to IS in the sample, and a and b are regression constants determined by the calibration. Detailed description of this internal standard quantification method was provided in part II of the Supplementary Information. NAP-d_8 was used for generating the peak area ratio for NAP; CHR-d_{12} for ACP, ACE, FLU, PHE, ANT, FLUO, PYR, B(a)A, CHR, B(b)F, and B(a)P; and $^{13}C_{12}$-B(g,h,i)P for IND, DBA, and B(g,h,i)P.

3. Results and discussions

3.1. Selection of adsorbents

To select appropriate adsorbents for collecting and analysing airborne PAHs, each of the three individual adsorbents (Glass beads, Carbopack C, and Carbopack B) was first tested under the TD condition of 325 °C for 20 min. GC/MS chromatograms of PAHs (Fig. 2) were compared among the three adsorbents and also to the results of the direct liquid injection (10:1 split). Visual inspection of relative peak abundances among the four chromatograms provided a quick estimation on the sorption strength of different sorbents for the measured PAHs. Relative peak intensities of PAHs from glass beads (Fig. 2B) and Carbopack C (Fig. 2C) tubes were similar. They were also similar to those of the direct injection (Fig. 2A), except for the last three eluting peaks (IND, DBA, and B(g,h,i)P). The reduced relative peak intensity of the last three eluting PAHs in thermal desorption (Fig. 2B and C) compared to direct liquid injection (Fig. 2A)

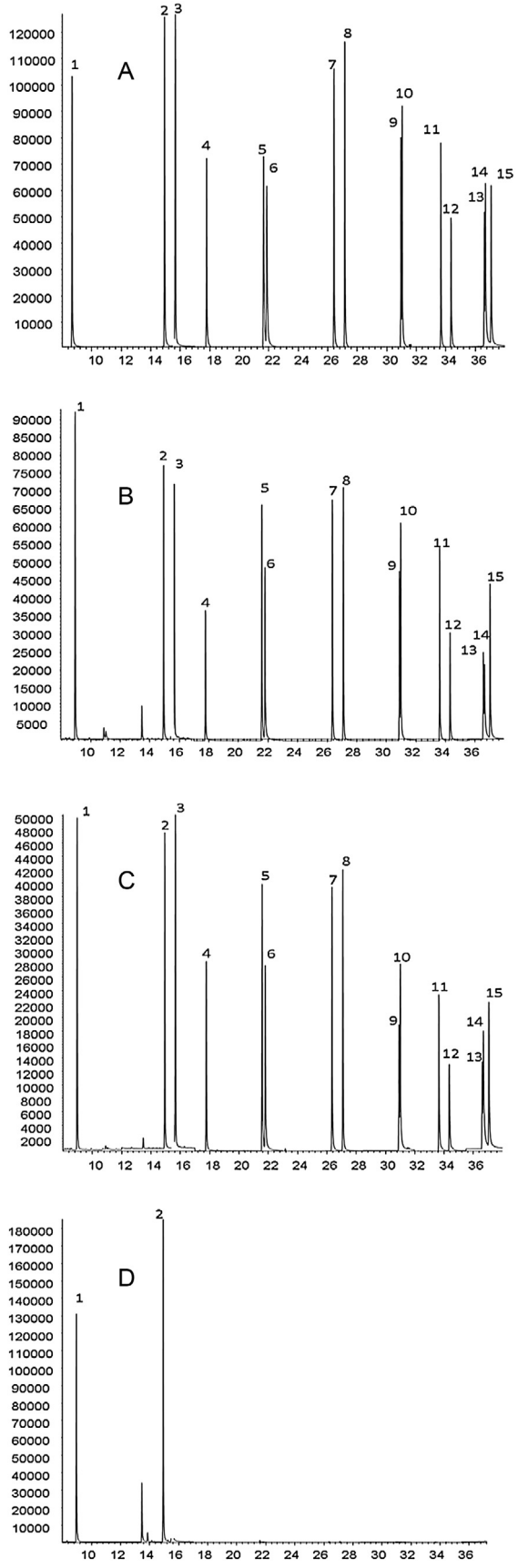

Fig. 2. GC/MS chromatogram of the PAH standard mixture (3 ng of each of the PAHs) generated from A: liquid injection (1 μl, 1:10 split); B: glass beads; C: Carbopack C; and D: Carbopack B. Peaks are 1: NAP, 2: ACP, 3: ACE, 4: FLU, 5: PHE, 6: ANT, 7: FLUO, 8: PYR, 9: B(a)A, 10: CHR, 11: B(b)F, 12: B(a)P, 13: IND, 14: DBA, 15: B(g,h,i)P.

Table 2
Optimized instrumental conditions for SPTD–GC/MS analysis of PAHs.

Parameter	Value
SPTD conditions	
Purge flow rate	60 ml/min
Purge time	2 min
TD temperature and time	280 °C, hold for 0 min, ramp at 10 °C/min to 350 °C, hold for 33 min
Cryogenic trap hold	−20 °C
Trap heating temperature	350 °C
Trap heat duration	30 min
GC/MS conditions	
Pressure of GC head (constant)	23 psi
Column flow at 60 °C	2.8 ml/min
Split ratio	10:1
Oven temperature	60 °C, hold for 2 min, ramp at 6 °C/min to 200 °C, ramp at 10 °C/min to 315 °C, hold for 5 min
GC/MS transfer line temperature	300 °C
Injector temperature	350 °C

indicated some losses of these three heavy PAHs during thermal desorption process due to the fact that they have the lowest vapor pressure among the targeted PAHs. Carbopack B was proven to be too strong for the thermal release of PAHs except for NAP and ACE as shown in Fig. 2D. Carbopack B, however, can be a good adsorbent to trap these low molecular weight PAHs in real-world situations as it prevents their breakthrough when sampling large volumes of air. Based on these results, a multi-sorbent tube consisting of 220 mg of glass beads, 45 mg of Carbopack C, and 15 mg of Carbopack B was assembled for the subsequent experiments.

3.2. Evaluation of thermal desorption processes

Parameters of TD operations that were optimized included desorption temperature (from 305 °C to 350 °C) and desorption time (from 10 min to 33 min), cryo-trap temperature during desorption (from −40 °C to 0 °C) and GC split in GC injection (from 5:1 split to 30:1 split). TD desorption flow (flow rate passing through the sample tube) was determined by the split value of GC injection. Heating temperature of the cryo trap, and GC injector temperature were both operated at 350 °C. Detailed procedures and results of the optimization were provided in part I of the Supplementary Information. Optimal conditions for each parameter were selected for the maximal peak areas on the chromatograms.

Under the optimal conditions (Table 2), thermal desorption performance was evaluated through determination of residual levels of PAHs in the three parts of the analytical system: (1) the mass remained in the sample tube after initial run, (2) the needle connecting the tube, and (3) the GC unit including both the injection port and the GC column [22] in the following order. Residues in the column after the initial sample run were first investigated by running a blank tube connected with a clean needle; the amount of PAH detected in this run was assumed to be the amount left in the GC column and GC injection port from the original sample analysis. Afterwards, about 30 cm of the column at the injection end was cut, and the GC injection port was cleaned and a new septum and a new liner were installed. A blank tube was then analyzed to make sure that the analytical system was free of PAH residues after the maintenance. After GC system was clean, the original sample tube from the initial sample run was connected to a clean needle and was analyzed second time to determine the amount left in the original sample tube. After another blank run to verify the system to be free of PAH residues, a blank tube that was connected to the original needle was analyzed to determine the amount of PAHs left in the original needle from the original sample analysis.

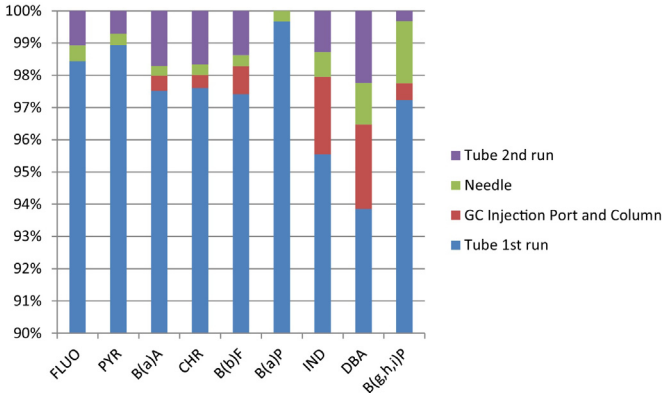

Fig. 3. Stack columns of the amount of the PAHs detected in different parts of the analytical system, based on their peak areas. PAHs with 2- and 3-rings had 100% recovery from the 1st tube run and, therefore, are not included in this figure.

Residual levels were presented in Fig. 3. No residue was found for the 2- and 3-ring PAHs (molecular weight (MW) of 178 Dalton or less) and therefore they were not included in Fig. 3. The amount of a PAH in the original tube was considered to be the sum of the amounts detected in the initial sample analysis, plus the amounts recovered from the above-mentioned three parts. The percentages of the amounts in each part were calculated by the ratio of the peak area of each part to the total peak area of the sum of the four. This approach however did not consider the irreversible loss of PAHs during the thermal desorption and GC/MS analysis.

Among the larger PAHs (4- to 6-ring PAHs), the total residues accounted for about 3% for PAHs with MW of 202, 228, and 252 Dalton, and accounted for 3–6% for the last three eluting PAHs with MW of 276 and 278 Dalton. This range of residual values was significantly lower than the 7 – 25% carry-over reported by Lazarov [20] who used a Unity™ thermal desorption system that was connected to a GC and used multiple sorbent (PSMS/Tenax) tubes for collecting airborne PAHs.

The amount of PAH residues that remained in the GC injection port and column was the largest (up to 2.6%) for the three last eluting PAHs (Fig. 3). A smaller amount of the PAH residues were found to be present in the needle connected to the sample tube. This amount was <0.5% for the 4-ring PAHs, but increased to 1.3% for DBA. Since there was a small unheated space between the heating block for the sample tubes and the GC injection port, a cold spot where the needle was located may exist (Fig. 1), leading to the accumulation of PAH residues in the needle.

For SPTD, PAH residues in the sample tube and in the connecting needle after the initial run will not impact the next sample run as the tube and the needle were thermally conditioned after the initial sample run to remove the residues before the tube and needle were reused for subsequent analysis. PAHs left on the GC injection port and the column could lead to a carry-over to the next run. This carry-over, however, was minimized by running a blank tube between each sample under the same instrumental conditions.

3.3. Performance of the optimized method

Evaluation of the method performance was carried out using spiked standard tubes. Since the standards were dispersed in the tube with 2 L of nitrogen only, the distribution of PAHs in the tube may be quite different from that in real indoor air sample tubes that had 1 m^3 of indoor air passing through it. When interpreting the performance data shown below, one has to keep in mind that a shorter flushing volume of gas to disperse the chemical may

Table 3
Performance of the optimized method which includes: desorption efficiency (DE), coefficient of determination (r^2) for the power law based calibration, repeatability as measured by its relative standard deviation (RSD), and method detection limit (MDL).

PAHs	DE	r^2	RSD (n = 7)			MDL
	%		0.3 ng	1.0 ng	10 ng	μg/m^3
NAP	100	0.9949	12.0%	8.9%	6.1%	0.62[a]
ACP	100	0.9948	16.0%	10.7%	7.7%	0.08[a]
ACE	100	0.9975	8.3%	11.8%	6.0%	0.10[a]
FLU	100	0.9963	19.3%	8.6%	8.1%	0.28[a]
PHE	100	0.9975	6.0%	12.4%	2.3%	0.30[a]
ANT	100	0.9983	13.1%	13.6%	1.5%	0.08[a]
FLUO	98.9	0.9991	6.3%	6.6%	1.1%	0.07[a]
PYR	99.3	0.9994	6.9%	10.8%	1.8%	0.08[a]
B(a)A	98.3	0.9959	6.1%	6.6%	5.3%	0.04[a]
CHR	98.3	0.9982	10.3%	5.4%	1.1%	0.08[a]
B(b)F	98.6	0.9994	13.1%	7.7%	5.6%	0.01[b]
B(a)P	100	0.9939	14.9%	9.1%	10.0%	0.04[b]
IND	98.7	0.9951	10.6%	6.6%	8.4%	0.03[b]
DBA	97.8	0.9999	21.3%	9.8%	10.4%	0.03[b]
B(g,h,i)P	99.5	0.9963	1.5%	1.0%	0.8%	0.05[b]

MDL was based on samples of 1 m^3 air volume.
[a] Residue present in field blanks (n = 7), MDL = 3.14 × s.d. + mean blank.
[b] No residue present in field blank, MDL: instrument detection limit.

lead to a greater thermal desorption efficiency values in the standard tubes. Table 3 lists thermal desorption efficiency (DE) and other method performance indicators for the selected PAHs under the optimized conditions. To determine DE, the same sample was run second and third time. There was no residue detected in the third run. DE in Table 3 therefore was defined as the percentage of amount detected from the first sample run divided by the sum of amount from the first and second sample runs. Since the second desorption of the original sample tubes showed residual levels between 0.5 and 2.2% for the 4- to 6-ring PAHs, DE values for these heavier PAHs were estimated to be between 97.8 and 99.5% (Table 3).

The calibration curve of PAHs under the optimized SPTD–GC/MS conditions was best described by a power law relationship, instead of a linear regression, with coefficient of determination (r^2) values greater than 0.994. Detailed steps for the calibration and quantification were provided in part II of the Supplementary Information.

Repeatability was evaluated by assessing the relative standard deviation (RSD) of the seven replicate tubes each spiked at 0.3 ng/tube, 1.0 ng/tube and 10 ng/tube, respectively. RSD values at 10 ng/tube level were at or below 10% for all target PAHs, while RSD values at the other two lower spiking levels were slightly larger, up to 14% at 1.0 ng/tube level and up to 21% at 0.3 ng/tube level.

Method detection limit (MDL) was calculated as 3.14 times the standard deviation (SD) of the tubes (n = 7) spiked at low levels (0.03 or 0.3 ng/tube of each PAH, and the MDL was expressed in units of ng/tube. If a compound was detected in the blank tubes, the MDL was calculated as the mean value of the blank tubes plus 3.14 × SD. The MDLs of PAHs were below 0.1 ng/tube, except for NAP (0.62 ng/tube), PHE (0.30 ng/tube) and FLU (0.28 ng/tube) due to their residual levels in the blanks (Table 3). Since the nominal sample volume was 1.0 m^3 for a 7-day sampling period, the detection limit for the PAHs in indoor air in this case was estimated to be less than 0.1 ng/m^3. Though NAP, PHE and FLU had relatively high MDLs compared to other PAHs, their MDLs were well below their typical concentrations (see Section 3.4) in indoor air. Therefore, the relatively high MDLs of these three PAHs do not affect the determination of their levels in field studies.

Another important aspect of the method is the breakthrough volume. Breakthrough volume in this study was investigated for the selected PAHs by analysing two adsorbent tubes connected in series. The first tube in the gas stream was spiked with three internal standards used in the study at 1 ng/tube and PAHs at 3 ng/tube. Then, nitrogen (99.999%) was passed through the two connected tubes at 200 ml/min for a certain period of time, resulting in an air volume equivalent to 0.5 m^3, 1.0 m^3 and 2.0 m^3, respectively. Naphthalene and other PAHs were not detected in the back up tubes, which indicated that no breakthrough occurred for sampling volume up to 2 m^3. In comparison, breakthrough volume for the PDMS material is small for certain light PAHs such as naphthalene and an addition of Tenax TA was required to increase the breakthrough volume for these volatile PAHs [19]. Using the multi-sorbent tube containing PDMS and Tenax TA, Lazarov et al. tested sampling volume up to 732 L and no breakthrough of PAHs was found [20].

3.4. Measurement of airborne PAHs in residential indoor air

To evaluate the effectiveness of this method for measuring airborne PAHs, twelve indoor air samples from nine homes (four houses and five apartments), including one sample taken from an attached garage (Table 4), in the city of Ottawa, Canada, were analyzed in this study. Those were volunteer based samples to illustrate the application of the developed method. Levels of indoor air PAHs presented in the paper therefore were not representative of the city.

Natural gas was used as the primary heating source in all four houses while electric heating devices were the norm in all of the apartments. Natural gas heating systems were in operation in all of the houses when indoor air was collected, except for the S1-L, S2-K and S4-G samples (Table 4). It has been reported that one of the major contributions to the PAHs found in indoor air is incomplete fuel combustion from heating, cooking, or smoking [23]. All of the houses had an attached garage with a connecting door to the living space of the house. Of the five apartments, three (S8-L, S9-L and S10-L) had outdoor parking only, while the other two had both outdoor and underground (indoor) parking facilities.

Before sampling, TD tubes were spiked with 1 ng of each of the three internal standards. The concentrations of the target PAHs in indoor air were calculated by the internal standard calibration method (See Supplementary Information). The levels of airborne PAHs in all nine homes are presented in Table 5. The samples were collected in various living spaces which include: living room (L), kitchen (K) and basement (B) (Table 4). One sample (S4-G) was collected from an attached garage for comparison purposes.

NAP has the highest vapour pressure among all of the selected PAHs. It is present usually in residential indoor air at micro-gram per cubic meter levels [2,24–26], which is several orders of magnitude higher than the other airborne PAHs. NAP is often measured together with volatile organic compounds (VOCs) such as benzene and toluene, and is sometimes excluded from the analytical windows for PAHs [7,27,28]. In order to collect a sufficient amount of other PAHs in the thermal desorption tubes for their detection, a 1 m^3 volume of air was chosen based on the sensitivity of the TD–GC/MS instrument. As a result, the amount of NAP collected in the sample was over-saturated and as a result, the response of the NAP signal on the GC/MS chromatogram was suppressed. This produced underestimated values for NAP in these indoor air samples (Fig. 4). This was evident when the NAP values found in this study were lower than levels reported for indoor air determined by analytical methods developed for VOCs [25,26].

Concentrations of the total PAHs excluding NAP ($\sum$PAH-NAP) in the indoor air of the nine homes ranged from 26 to 344 ng/m^3, with a mean value of 92 ng/m^3. The PAH profile from the indoor air samples was found to be dominated by the 3-ring PAHs (ACP, ACE, FLU, PHE, and ANT), which account for about 95% of $\sum$PAHs-NAP (Fig. 5). Although there was only one garage sample analyzed in this study, the profile of the this sample was quite different from that of the indoor air collected inside the houses and apartments; PHE

Table 4
Description of housing characteristics and heating situation of the sampled homes.

Home	Sample	Description
1	S1-L	Semi-detached house; attached garage connected by a door; heating: natural gas, not in use, except for S3-K
	S2-K	
	S3-K	
	S4-G	
2	S5-L	Single detached house; attached garage connected by a door; heating: natural gas, in use
3	S6-L	Single detached house; attached garage connected by a door; heating: natural gas, in use
4	S7-B	Single detached house; attached garage connected by a door; heating: natural gas, in use
5	S8-L	Apartment-first floor; outdoor parking only; heating: electric, in use
6	S9-L	Apartment-first floor; outdoor parking only; heating: electric, not in use
7	S10-L	Apartment-higher floor; outdoor parking only; heating: electric, not in use
8	S11-L	Apartment-higher floor; outdoor and indoor parking; heating: electric, not in use
9	S12-L	Apartment-higher floor; outdoor and indoor parking; heating: electric, not in use

All homes used electric stoves and are non-smoking. L: living room; K: kitchen; B: basement; G: garage.

Table 5
Concentrations of the PAHs (ng/m^3) in the indoor air samples collected in different homes (see Table 4 for description of air samples).

PAHs	S1-L	S2-K	S3-K	S4-G	S5-L	S6-L	S7-B	S8-L	S9-L	S10-L	S11-L	S12-L
NAP[a]	42	50	257	69	305	354	351	215	235	57	45	43
ACP	0.97	1.2	2.9	13	1.4	0.87	14	2.3	10	1.7	1.4	0.59
ACE	5.6	5.4	11	4.6	11	4.9	77	16	52	10	6.5	2.6
FLU	12	14	21	2.9	29	13	163	41	102	26	22	9.7
PHE	6.2	6.2	7.8	97	18	9	77	25	66	14	17	10
ANT	0.27	0.39	0.36	131	0.82	0.46	7.3	3.4	6.7	0.77	0.89	0.32
FLUO	0.31	0.42	0.54	5.8	0.48	0.42	3.4	2.2	4.4	0.71	1.9	1.0
PYR	0.51	0.42	0.6	5.7	0.51	0.42	2.1	1.4	2.6	0.76	1.5	0.74
B(a)A	<MDL	0.89	<MDL	0.13	0.19	0.08	0.09	0.12	0.12	0.26	0.17	0.09
CHR	<MDL	1.7	<MDL	0.18	0.39	0.15	0.09	0.22	0.17	0.43	0.29	0.11
B(b)F	0.04	0.38	0.14	0.12	0.09	0.05	0.06	0.14	0.09	0.14	0.13	0.08
B[a]P	<MDL	0.08	0.15	0.06	0.12	0.06	0.06	0.11	0.07	0.1	0.06	0.06
IND	0.03	0.04	0.08	0.13	0.08	<MDL	<MDL	0.1	0.04	0.07	0.11	0.06
DBA	<MDL	0.11	0.04	0.03	<MDL	<MDL	<MDL	0.06	<MDL	0.03	0.04	0.03
B(g,h,i)P	0.05	0.06	0.13	0.13	<MDL	<MDL	<MDL	0.09	<MDL	0.07	0.13	0.07
∑PAH-NAP	27	31	46	261	62	29	344	93	244	56	51	26

[a] The NAP value might not be reliable due to over-saturation of NAP in samples of 1 m^3 of air volume. Values <MDL (see Table 3) was treated as zero in the statistical analysis.

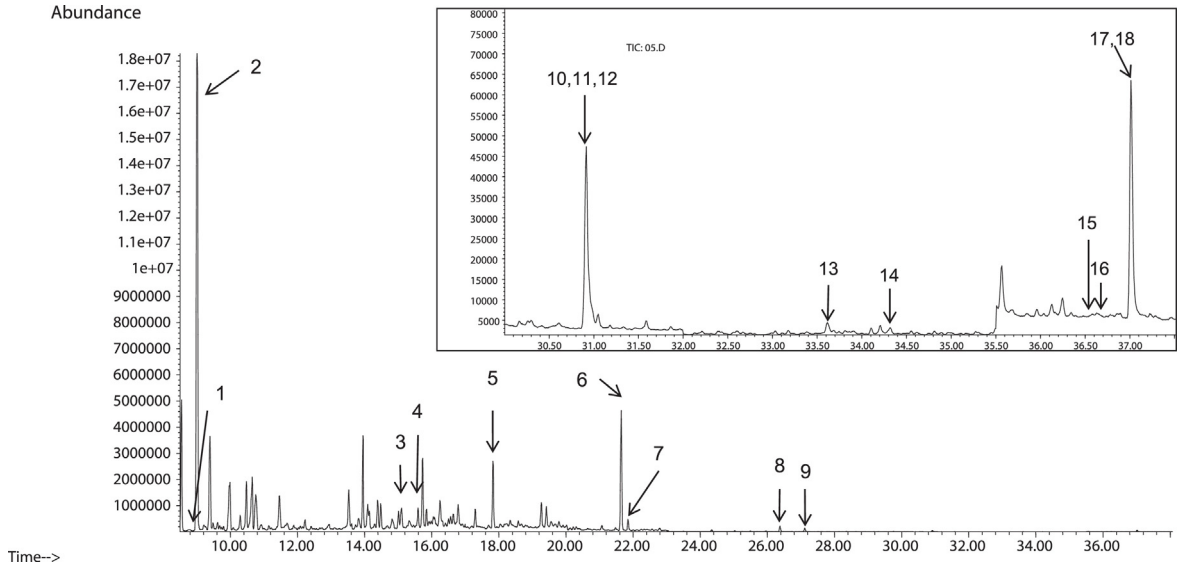

Fig. 4. A typical TD–GC/MS chromatogram of the indoor air samples. The peak numbers correspond to those in Table 1: 1: NAP-d_8, 2: NAP, 3: ACP, 4: ACE, 5: FLU, 6: PHE, 7: ANT, 8: FLUO, 9: PYR, 10: B(a)A, 11: CHR-d_{12}, 12: CHR, 13: B(b)F, 14: B(a)P, 15: IND, 16: DBA, 17: $^{13}C_{12}$-B(g,h,i)P, 18: B(g,h,i)P. A noteworthy feature is the large difference between the level of NAP and the other target PAHs.

and ANT were the dominant PAHs in the garage, while ACE, FLU, and PHE were dominant ones in the indoor air samples (Fig. 5).

Three indoor air samples (S1-L, S2-K, and S3-K) were collected in the same house, but at different times. Higher levels of PAHs in S3-K samples as compared to S1-L and S2-K may be attributed to the operation of the natural gas furnace during the collection period for this sample as gas furnace was not in operation during the sampling of S1-L and S2-K. Gas furnace was identified as one of the indoor sources of PAHs by others too [3,27,29].

Table 6
Comparison between the ranges of PAH concentrations in indoor air from homes reported by others and those determined in this study (ng/m^3).

PAH	Ottawa, Canada 2014 (n = 11) This study	Detroit, USA 2006 (n = 29) Ref. [24]	Hangzhou, China 1999 (n = 8) Ref. [3]	Kuwait 2004 (n = 24) Ref. [7]	Birmingham, England 2010 (n = 81) Ref. [27]	Porto, Portugal 2011 (n = 6) Ref. [17]
ACP	0.59–14	<0.1–86.4	–	0.005–0.613	N.D. – 7.63	–
ACE	2.6–77	<0.1–378.9	45.3–613	0.029–0.746	N.D. – 12.4	–
FLU	10–163	<0.1–77.1	56.3–684	0.087–2.185	N.D. – 3.73	–
PHE	6.2–77	<0.1–363.6	78–851	0.363–11.705	N.D. – 6.42	<LOQ – 89.0
ANT	0.27–7.3	<0.1–382.5	0.621–53.9	0.011–0.564	N.D. – 0.58	–
FLUO	0.31–4.4	<0.1–21.8	6.75–29.9	<MDL – 1.398	N.D. – 6.64	–
PYR	0.42–2.6	<0.1–7.9	10.9–46.4	<MDL – 1.269	N.D. – 24.0	–
B(a)A	<0.04–0.89	–	6.36–35.9	<MDL – 0.441	N.D. – 0.22	–
CHR	<0.08–1.7	–	4.12–14.4	<MDL – 0.629	N.D. – 14.5	–
B(b)F	0.04–0.38	–	1.55–10.4	<MDL – 0.487	N.D. – 5.54	–
B(a)P	<0.04–0.15	–	0.432–9.76	<MDL – 0.479	N.D. – 4.91	–
IND	<0.03–0.11	–	1.11–7.37	<MDL – 0.626	N.D. – 2.10	–
DBA	<0.03–0.11	–	0.187–1.72	<MDL – 0.708	N.D. – 1.51	–
B(g,h,i)P	<0.05–0.13		0.828–15.3	<MDL – 0.623	N.D. – 4.17	

N.D.: not detected; LOQ: limit of quantification; MDL: method detection limit.

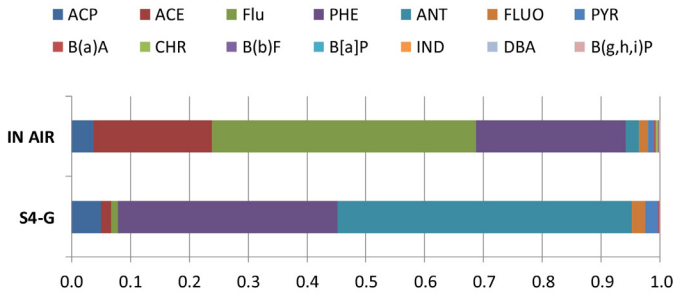

Fig. 5. Composition of PAHs in indoor air (IN AIR) and in an attached garage (S4-G).

As shown in Table 6, indoor air levels of PAHs detected in this study in general agreed with levels reported by others [7,17,24,27] except for the study of Liu et al. [3]. Liu et al. measured PAHs in indoor air and outdoor air of residential homes in Hangzhou, China and found PAH levels in residential indoor air, without counting for NAP, to be in the range of 1.3–6.3 μg/m^3 in the summer and 1.8–5.3 μg/m^3 in autumn. The high PAH values found in Hangzhou, China could be partially due to the typical lifestyle in China, which includes different cooking methods [30], smoking indoors, and use of liquefied petroleum gas as cooking and heating fuels.

B(a)P is the most extensively studied chemical of PAHs due to its known carcinogenicity. Both the World Health Organization (WHO) and the UK Expert Panel on Air Quality Standards (EPAQS) have classified B(a)P as a marker of the carcinogenic potency of PAHs mixtures [27]. In this study, the concentration of B(a)P was found to be between the MDL and 0.15 ng/m^3, which is lower than the value reported by others; this could be attributed to the fact that all of the homes sampled in this study were non-smoking homes.

4. Conclusions

An SPTD–GC/MS method was developed to analyze airborne PAHs. This method used a multi-sorbent tube (Glass beads, Carbopack C, and Carbopack B) for collecting the airborne PAHs. The short path for the transfer of thermally desorbed PAHs from tube to the GC through the GC injection port resulted in the good performance for analyzing PAHs. The residual level in the analytical system was low, even for the three PAHs that have a molecular weight of 276 and 278 Dalton. Use of multi-sorbent tubes allows for the capture of PAHs with a wide range of vapour pressures, namely from NAP to 6-ring PAHs. Therefore, this method can be adapted to measure other SVOCs whose vapour pressures are between those of NAP and 6-ring PAHs. With a 1 m^3 sample volume, this method offers sufficient analytical sensitivities to detect PAHs in indoor air; only very few measurements were below the method detection limits. This method used a portable, low flow pump to collect indoor air and is therefore also suitable for sampling other locations where the use of high-flow pumps is problematic, or not permitted due to noise restrictions.

One major limitation of the SPTD method described in this study is its inability to collect parts of the thermally desorbed PAHs, which are vented due to requirement for splitting desorbed gas stream in TD operation (Table 3), for subsequent analysis. This inability limits the range of detectable concentrations among the target chemicals, since dilution of the samples is impossible. As a result, for any desired volume of air that is collected, there will be either too much or not enough quantity of some target chemicals at both ends of the concentration range. This has been shown by the over-saturation of NAP in the 1 m^3 sample volume of indoor air. Multiple samples with different air volumes may be required to cover a wide range of concentrations of target chemicals.

Acknowledgements

This study was partially supported by the Shanghai Municipal Education Commission (No. ZZJD12052), Shanghai University of Engineering Science Program (No. 2012gp15), Science and Technology Commission of Shanghai Municipality (No. 15DZ1205501), Shanghai Environmental Protection Bureau (No. 12, Hu Huan-Ke [2016]) and the National High-Tech R&D Program of China (863 Program, Grant No. 2013AA06A309). Y.L. wishes to thank Canadian Government for the scholarship under the Government Laboratory Visiting Fellowship Program, managed by the Natural Sciences and Engineering Research Council of Canada (NSERC). The authors also thank Dr. Jiping Zhu of Health Canada for his guidance and help.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chroma.2017.03.050.

References

[1] J.M. Delgado Saborit, N. Aquilina, S. Baker, S. Harrad, C. Meddings, R.M. Harrison, Determination of atmospheric particulate-phase polycyclic aromatic hydrocarbons from low volume air samples, Anal. Methods 2 (2010) 231–242.

[2] H. Lu, L. Zhu, S. Chen, Pollution level, phase distribution and health risk of polycyclic aromatic hydrocarbons in indoor air at public places of Hangzhou, China, Environ. Pollut. 152 (2008) 569–575.
[3] Y. Liu, L. Zhu, X. Shen, Polycyclic aromatic hydrocarbons (PAHs) in indoor and outdoor air of Hangzhou, China, Environ. Sci. Technol. 35 (2001) 840–844.
[4] M. Possanzini, V. Di Palo, P. Gigliucci, M.C.T. Scianò, A. Cecinato, Determination of phase-distributed PAH in Rome ambient air by denuder/GC-MS method, Atmos. Environ. 38 (2004) 1727–1734.
[5] E. Krugly, D. Martuzevicius, R. Sidaraviciute, D. Ciuzas, T. Prasauskas, V. Kauneliene, I. Stasiulaitiene, L. Kliucininkas, Characterization of particulate and vapor phase polycyclic aromatic hydrocarbons in indoor and outdoor air of primary schools, Atmos. Environ. 82 (2014) 298–306.
[6] T. Ohura, T. Amagai, T. Sugiyama, M. Fusaya, H. Matsushita, Characteristics of particle matter and associated polycyclic aromatic hydrocarbons in indoor and outdoor air in two cities in Shizuoka, Japan, Atmos. Environ. 38 (2004) 2045–2054.
[7] B. Gevao, M. Al Bahloul, J. Zafar, K. Al Matrouk, M. Helaleh, Polycyclic aromatic hydrocarbons in indoor air and dust in Kuwait: implications for sources and nondietary human exposure, Arch. Environ. Contam. Toxicol. 53 (2007) 503–512.
[8] F.M. Jaward, N.J. Farrar, T. Harner, A.J. Sweetman, K.C. Jones, Passive air sampling of polycyclic aromatic hydrocarbons and polychlorinated naphthalenes across Europe, Environ. Toxicol. Chem. 23 (2004) 1355–1364.
[9] M. Goriaux, B. Jourdain, B. Temime, J.L. Besombes, N. Marchand, A. Albinet, E. Leoz Garziandia, H. Wortham, Field comparison of particulate PAH measurements using a low-flow denuder device and conventional sampling systems, Environ. Sci. Technol. 40 (2006) 6398–6404.
[10] A. May, P. Ashman, J. Huang, S. Dhaniyala, T.M. Holsen, Evaluation of the polyurethane foam (PUF) disk passive air sampler: computational modeling and experimental measurements, Atmos. Environ. 45 (2011) 4354–4359.
[11] E. Woolfenden, Sorbent-based sampling methods for volatile and semi-volatile organic compounds in air Part 1: sorbent-based air monitoring options, J. Chromatogr. A 1217 (2010) 2674–2684.
[12] M.R. Ras, R.M. Marcé, F. Borrull, Volatile organic compounds in air at urban and industrial areas in the Tarragona region by thermal desorption and gas chromatography-mass spectrometry, Environ. Monit. Assess. 161 (2010) 389–402.
[13] E. Gallego, F.J. Roca, J.F. Perales, G. Sánchez, P. Esplugas, Characterization and determination of the odorous charge in the indoor air of a waste treatment facility through the evaluation of volatile organic compounds (VOCs) using TD–GC/MS, Waste Manag. 32 (2012) 2469–2481.
[14] E. Massold, C. Bähr, T. Salthammer, S.K. Brown, Determination of VOC and TVOC in air using thermal desorption GC–MS – practical implications for test chamber experiments, Chromatographia 62 (2005) 75–85.
[15] H. Kawashima, M. Murakami, Measurement of the stable carbon isotope ratio of atmospheric volatile organic compounds using chromatography, combustion, and isotope ratio mass spectrometry coupled with thermal desorption, Atmos. Environ. 89 (2014) 140–147.
[16] C. Rodríguez Navas, R. Forteza, V. Cerdà, Use of thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS) on identification of odorant emission focus by volatile organic compounds characterisation, Chemosphere 89 (2012) 1426–1436.
[17] G.V. Martins, S. Martins, A.O. Martins, Determination of gaseous polycyclic aromatic hydrocarbons by a simple direct method using thermal desorption–gas chromatography–mass spectrometry, Environ. Monit. Assess. 185 (2013) 6447–6457.
[18] M. Bates, P. Bruno, M. Caputi, M. Caselli, G. De Gennaro, M. Tutino, Analysis of polycyclic aromatic hydrocarbons (PAHs) in airborne particles by direct sample introduction thermal desorption GC/MS, Atmos. Environ. 42 (2008) 6144–6151.
[19] E. Wauters, P. Van Caeter, G. Desmet, F. David, C. Devos, P. Sandra, Improved accuracy in the determination of polycyclic aromatic hydrocarbons in air using 24 h sampling on a mixed bed followed by thermal desorption capillary gas chromatography–mass spectrometry, J. Chromatogr. A 1190 (2008) 286–293.
[20] B. Lazarov, R. Swinnen, M. Spruyt, E. Goelen, M. Stranger, G. Desmet, E. Wauters, Optimisation steps of an innovative air sampling method for semi volatile organic compounds, Atmos. Environ. 79 (2013) 780–786.
[21] X.M. Li, Q.H. Zhang, P. Wang, Y.M. Li, G.B. Jiang, Determination of polycyclic aromatic hydrocarbons in air by stir bar sorptive extraction–thermal desorption–gas chromatography tandem mass spectrometry, Chin. J. Anal. Chem. 39 (2011) 1641–1646.
[22] S.S.H. Ho, J.C. Chow, J.G. Watson, J.G. Watson, L.P.T. Ng, Y. Kwok, K.F. Ho, J.J. Cao, Precautions for in-injection port thermal desorption–gas chromatography/mass spectrometry (TD–GC/MS) as applied to aerosol filter samples, Atmos. Environ. 45 (2011) 1491–1496.
[23] T. Ohura, T. Amagai, M. Fusaya, H. Matsushita, Polycyclic aromatic hydrocarbons in indoor and outdoor environments and factors affecting their concentrations, Environ. Sci. Technol. 38 (2004) 77–83.
[24] M.M. Johnson, R. Williams, Z. Fan, Z.-H. Fan, L. Lin, E. Hudgens, J. Gallagher, A. Vette, L. Neas, H. Özkaynak, Participant-based monitoring of indoor and outdoor nitrogen dioxide, volatile organic compounds, and polycyclic aromatic hydrocarbons among MICA-Air households, Atmos. Environ. 44 (2010) 4927–4936.
[25] J. Zhu, S.L. Wong, S. Cakmak, Nationally representative levels of selected volatile organic compounds in Canadian residential indoor air: population-based survey, Environ. Sci. Technol. 47 (2013) 13276–13283.
[26] J. Zhu, R. Newhook, L. Marro, C.C. Chan, Selected volatile organic compounds in residential air in the city of Ottawa, Canada, Environ. Sci. Technol. 39 (2005) 3964–3971.
[27] J.M. Delgado-Saborit, C. Stark, R.M. Harrison, Carcinogenic potential, levels and sources of polycyclic aromatic hydrocarbon mixtures in indoor and outdoor environments and their implications for air quality standards, Environ. Int. 37 (2011) 383–392.
[28] S. Khedidji, R. Ladji, N. Yassaa, A wintertime study of polycyclic aromatic hydrocarbons (PAHs) in indoor and outdoor air in a big student residence in Algiers, Algeria, Environ. Sci. Pollut. Res. Int. 20 (2013) 4906–4919.
[29] K. Ravindra, R. Sokhi, R. Vangrieken, Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation, Atmos. Environ. 42 (2008) 2895–2921.
[30] C.T. Li, Y.C. Lin, W.J. Lee, P.J. Tsai, Emission of polycyclic aromatic hydrocarbons and their carcinogenic potencies from cooking sources to the urban atmosphere, Environ. Health Perspect. 111 (2002) 483–487.