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Optimization and validation of a low temperature microwave-assisted extraction method for analysis of polycyclic aromatic hydrocarbons in airborne particulate matter

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Abstract

A low temperature microwave-assisted extraction method (MAE) is reported for the analysis of polycyclic aromatic hydrocarbons (PAHs) in airborne particulate matter (PM). The main parameters affecting the extraction efficiency (choice of extractants, microwave power, and extraction time) were investigated and optimized. The optimized procedure requires a 20 ml mixture of acetone:*n*-hexane (1:1) for extraction of PAHs in PM at 150 W of microwave energy (20 min extraction time). Clean-up of MAE extracts was not found to be necessary. The optimized method was validated using two different SRM (1648-urban particulate matter and 1649a, urban dust). The results obtained are in good agreement with certified values. PAHs recoveries for both reference materials were between 79 and 122% with relative standard deviation ranging from 3 to 21%. Detection limits were determined based on blank determination using two kinds of quartz filter substrates ($n = 10$), which ranged from 0.001 (0.03) ng m^{-3} (pg/μg) for B(k)Ft to 1.119 (37.3) for Naph in ng m^{-3} (pg/μg), respectively. The repeatability and day-to-day reproducibility obtained in this study were in the range of 4–16 and 3–25% for spiked standards and SRM 1649, respectively. The optimized and validated MAE technique was applied to the extraction of PAHs from a set of real world PM samples collected in Singapore. The sum of particulate-bound PAHs in outdoor PM ranged from 1.05 to 3.45 ng m^{-3} while that in indoor PM (cooking emissions) ranged from 27.6 to 75.7 ng m^{-3}, respectively.

Keywords: Airborne particulate matter (PM); Air pollution; Cooking; Polycyclic aromatic hydrocarbons (PAHs); Microwave-assisted extraction (MAE)

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous atmospheric pollutants that are known to exhibit carcinogenic and mutagenic properties [1]. They are formed and released into the atmosphere through natural and man-made sources. Natural sources include volcanoes and forest fires, while the man-made sources come mainly from high-temperature combustion of fossil fuels in automobile engines, cooking stoves, power plants, refineries, and industrial activities [2,3]. These pollutants have a high persistence in the environment, low biodegradability and high lipophilicity [4]. The association of the toxic four to six-ring PAHs with fine particles in conjunction with their widespread presence in the atmosphere increases the vulnerability of public health upon exposure and inhalation of the aerosols. Consequently, aerosol characterization studies have been carried out in several parts of the world to determine PAHs in airborne particles in order to assess their environmental fate and human exposure [5–11].

To obtain reliable data on the composition and concentrations of PAHs in airborne particulate matter, versatile analytical methods are necessary for efficient sample processing and for subsequent chemical analysis. Traditional methods of sample preparation for the determination of particulate-bound PAHs include Soxhlet extraction and sonication [5,7–11,14]. These methods are both time-consuming and create large amounts of solvent waste, which is not only expensive to dispose of but may itself cause additional environmental problems. To achieve faster

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extraction and reduction of solvent volume, a number of modern extraction techniques such as microwave-assisted extraction MAE, [15–22], supercritical fluid extraction, SFE, [23,24], pressurized liquid extraction PLE, [12,25–28] and subcritical water extraction SWE, [29] have been investigated for extraction of PAHs from various environmental samples. Comparison of different extraction techniques was also studied by several authors [30–33]. As for the analysis step, GC–MS [5–9,11,23–25] and HPLC–fluorescence detection [15,21,31] have been found to be the best for the determination of PAHs in environmental samples. Hyphenated techniques like HPLC–Mass Spectrometry [12,13] and online LC–GC–MS [14] have also been reported to be suitable for the analysis of PAHs and its derviatives.

Among the modern extraction techniques, MAE has attracted particular attention as it allows rapid extraction of solutes from solid matrices, with extraction efficiency comparable to that of the classical extraction techniques [33,34]. This advantage is due to the fact that unlike conventional extraction methods that are subject to the boiling temperature of extraction solvents at atmospheric pressure, the microwave energy heats samples and solvents in a closed pressurized extraction vessel. As a result, the extraction of samples can be completed in minutes as opposed to hours necessary when traditional methods are used. Moreover, the MAE is capable of extracting more than 10 samples simultaneously.

Although the use of MAE methods has been investigated extensively for PAH extraction from environmental solid materials [41], relatively few studies are reported in the literature for the extraction of PAHs in PM [35–39]. Systematic investigations on the use of MAE for the determination of PAHs in PM have not been carried out. Iglesias et al. [36] evaluated the applicability of MAE for extracting PAHs from airborne particles and validated the method using urban (NIST SRM 1648) and diesel exhaust (NIST SRM 1650) particulates. The optimized procedure with acetone–hexane solvent mixture at 400 W (20 min) yielded 70–103% recoveries for urban particulates while diesel exhaust particulates showed low recoveries for higher molecular weight PAHs. Recently, Shu et al. [37] reported a MAE-based procedure for the extraction of PAHs from ambient PM. Their optimized procedure used a mixture of toluene–acetone (95:5) at 150 W for 20 min. The results showed 77–116% recovery of PAHs in NIST SRM 1649a.

In this paper, we report a closed vessel, low-temperature MAE procedure for the determination of the 16 PAHs, listed in the USEPA priority list. The aim of the present work is the optimization of the conditions to carry out a simple, fast, and efficient extraction of PAHs in PM collected from both outdoor and indoor environments. Parameters studied include choice of solvents, microwave power, and extraction time. The optimized procedure was validated using two different SRMs (1648 and 1649a) and spiked filter samples. The application of the proposed MAE technique is demonstrated by extracting and analyzing PAHs in a set of real world airborne particulate samples in Singapore. The results obtained are compared to those reported in the literature.

2. Experimental

2.1. Materials

Solvents used in this study are of HPLC grade: methylene chloride (DCM), *n*-hexane (HEX), acetone (ACE) and cyclohexane (CHEX) (J.T. Baker, USA). The standard mixture USEPA 610 of 16 native PAHs (naphthalene (Naph), acenaphthalene (Aci), acenaphthene, (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene, (Ft), pyrene (Pyr), benz[a]anthracene (B(a)A), chrysene (Chry), benzo[b]fluoranthene (B(b)Ftt), benzo[k]fluoranthene (B(k)Ft), benzo[a]pyrene (B(a)P), indeno[1,2,3-cd]pyrene (IP) dibenz[a,h]anthracene (DB(ah)A), and benzo-[ghi]perylene (B(ghi)P), in methanol:methylene chloride was purchased from Supelco (USA). This solution was used as spiking and calibration solution. SRM 1648 (urban particulate matter) and SRM 1649a (urban dust) were purchased from the National Institute of Standards and Technology (NIST (Gaithersburg, MD, USA). These SRMs were used for recovery studies.

2.2. Aerosol samples

Quartz filters of different dimensions (20.3 cm × 25.4 cm and 47 mm diameter, Whatman, England) were used for collection of aerosols samples in both outdoor and indoor environments. These filters were pre-heated at 400 °C for 24 h prior to use in order to reduce their water and organic matter blank values. After cooling, filters were weighed and stored in solvent-rinsed aluminum foil until use. $PM_{2.5}$ (particulate matter with aerodynamic diameter $< 2.5\ \mu m$) samples were collected using hi-vol sampler (Model: HVP-3800AFC, Hi-Q Environmental Products Co., USA) at the rooftop of the tallest building at the Faculty of Engineering, NUS for 24 h duration over a period of 10 consecutive days while the fine particles were collected using mini-vol portable samplers (Air Metrics, USA) from a commercial kitchen at the NUS canteen for a period of 1 week (5–12 April 2005)

2.3. Spiked standards

The standard samples were prepared by spiking 20 μl methanol:acetone (1:1) mixture containing USEPA 610 PAH mixture (20 times diluted) on pre-baked filter strips (4 cm × 4 cm) followed by 60 min air drying in a clean hood.

2.4. Microwave-assisted extraction

A closed vessel microwave digestion system (MLS-1200 mega, Mileston s.r.l, Italy) was used for the extraction of PAHs from the aerosol samples. It consists of compact terminal touchscreen display with operator selectable 0–800 W output, temperature control up to 300 °C, five-layer PTFE coated microwave cavity, HPR/1000/10S Rotor, and 100 ml Teflon vessels (10 vessels). A portion of filter (1/4 th) or the whole filter (47 mm dia) in the case of minivol sampler was processed in Teflon vessels in 20 ml of the solvent at various solvent composition and microwave energy in the range of 50–300 W was used for 10–60 min duration. After extraction, the vessels were allowed to cool to room temperature before opening. The extracts were then carefully filtered through a PTFE auto vial membrane filter (0.45 μm). The extracts were concentrated to 3 ml using a rotary evaporator and then to near dryness with a gentle stream of nitrogen under low temperature. The residue was re-dissolved in 1 ml of 1:1 aceotone:hexane solvent mixture for subsequent analysis with GC–MS. The low molecular PAH was minimized by carrying out the drying process carefully under low temperature. We used acenaphthene-d10 as a surrogate, and evaluated the recovery efficiency, which was in the range of 90 ± 10%. The residue was re-dissolved in 1 ml of 1:1 aceotone:hexane solvent mixture for subsequent analysis with GC–MS.

2.5. Analysis of extracts for PAHs

Sixteen PAHs were analyzed using a Hewlett-Packard 6890 Series GC system with Mass Selective Detector (Agilent Technologies, Wilmington DE). A DB-5MS fused silica capillary column (J&W Scientific, USA) of 0.25 mm i.d. × 30 m with 5% (mole fraction) phenyl substituted methylpolysiloxane phase (0.25 mm film thickness) was used. Injections were done using pulsed split-less, the split opening after 30 s; the injector temperature was 280 °C. The volume of the sample introduced was 2 μl. The oven temperature program was as follows: 50 °C for 2 min; 10 °C min^{-1} to 200 °C; 5 °C min^{-1} to 300 °C, and the hold time was 8 min. The MSD was operated in electron impact mode with electron energies of 70 eV, the ion source temperature being 230 °C. Helium was the carrier gas used at a constant flow condition (0.8 ml min^{-1}). PAHs were monitored using selected ion monitoring mode (SIM). In order to get maximum sensitivity, the 16 ions were divided into groups (seven intervals of retention time), and the detector monitors only the ions programmed for each group. The identification of individual PAHs was based on the comparison of retention times (chromatographic column) and mass spectra (mass detector) of PAHs in aerosol samples with those of PAH standards (full scan mode). A five point external standard calibration was carried out in the range of 40–320 ng ml^{-1} of PAH congeners, and the regression coefficients for all 16 PAHs were between 0.9852 (Aci) and 0.9976 (Ant). The coefficient of variation of the 16 PAHs was calculated to be in the range of 0.7% (BaA) to 5.9% (Ace) at trace level (80–160 ng ml^{-1}) concentrations.

3. Results and discussion

3.1. Optimization of MAE

In this study, the effect of the following parameters on the MAE efficiency were investigated and optimized: solvent combination; microwave power, and extraction time. The pre-baked filter strips, spiked with the EPA 610 PAH mixture, were employed in the optimization studies. After correction for the blank contribution, the recoveries were calculated for evaluating the extraction efficiency.

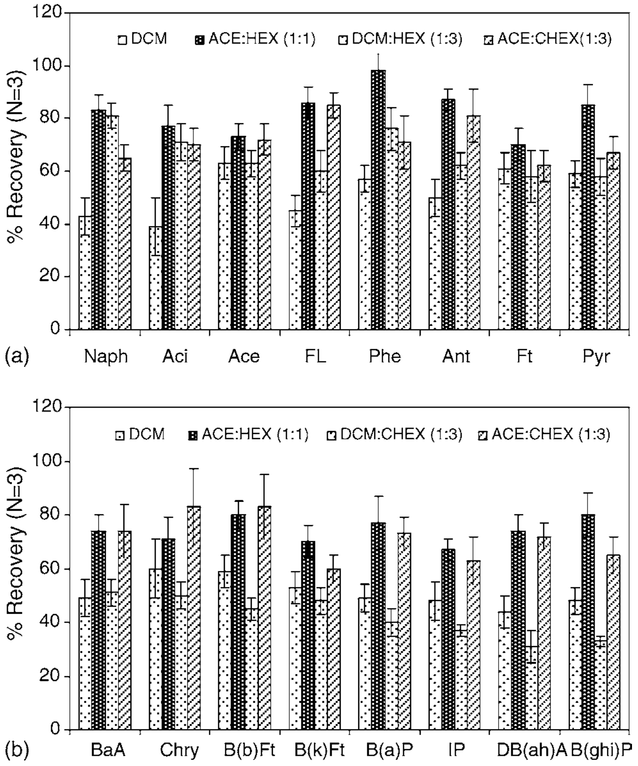

Fig. 1. Effect of solvent on MAE of PAHs: (a) Naph to Pyr and (b) BaA to B(ghi)P.

3.1.1. Effect of solvent

It has been reported that acetone is effective for PAH extraction from environmental samples [35]. However, a recent study indicated that a combination of different solvent mixtures tends to improve the solvation of the analytes of interest and thus improve overall efficiency of MAE [29,32]. We have therefore investigated different solvents and their mixtures such as dichloromethane, acetone–hexane, dichloromethane–hexane, acetone–cyclohexane using microwave energy of 100 W for 20 min extraction time. The average recovery results ($n = 3$) and the temperature of the solvent mixtures are given in Fig. 1. The standard deviation values obtained show the reproducibility of the extraction method used. Among the solvents studied, the acetone:hexane mixture gave satisfactory recoveries in the range of 67–98% while that of acetone:cyclohexane (1:3) yielded 60–85% recovery. The other two solvents showed poor recovery. These differences in the recovery of PAHs among the solvents considered in this study may have been the result of PAH solubility in different extraction solvents. The mixture of polar and non-polar solvents appears to assist solvation as well as microwave heating to achieve the recovery in shorter extraction time as compared to the use of semi-polar solvents such as dichloromethane. Based on the results obtained, it was decided to use the acetone–hexane (1:1) solvent mixture in all subsequent studies, which is also reported to be efficient for other environmental matrices [15,17,33,38].

3.1.2. Effect of microwave heating

Fig. 2 shows the effect of microwave energy on the extraction of few selected PAHs from spiked filters. Good recoveries

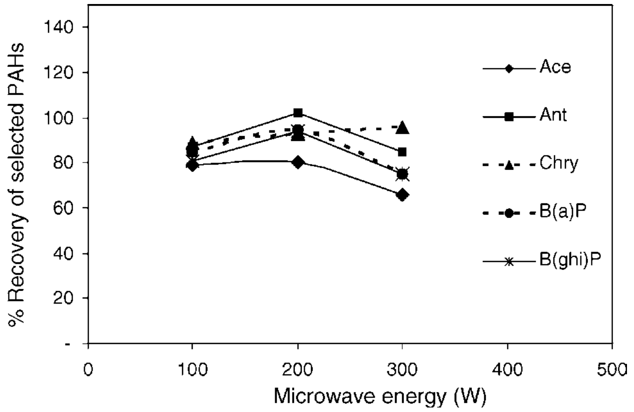

Fig. 2. Effect of microwave energy on extraction of PAHs.

Table 2
Analysis of NIST SRM 1649a (urban dust)

PAH	Measured results[a], mean ± S.D.	Certified value, mean ± S.D.	% Recovery, mean ± S.D.
Phe	4.37 ± 0.34	4.14 ± 0.37	105 ± 8
Ant	0.54 ± 0.01	0.043 ± 0.09	125 ± 3
Ft	5.65 ± 0.41	6.45 ± 0.18	88 ± 6
Pyr	4.95 ± 0.38	5.29 ± 0.25	94 ± 7
B(a)A	2.17 ± 0.16	2.21 ± 0.07	98 ± 7
Chry	3.44 ± 0.29	3.05 ± 0.06	112 ± 13
B(b)Ft	6.43 ± 0.44	6.45 ± 0.64	100 ± 7
B(k)Ft	1.50 ± 0.11	2.21 ± 0.17	79 ± 6
B(a)P	2.21 ± 0.17	2.51 ± 0.09	88 ± 7
IP	3.86 ± 0.76	3.18 ± 0.72	121 ± 26
DBA	0.34 ± 0.10	0.29 ± 0.02	117 ± 16
B(ghi)P	3.42 ± 0.26	4.01 ± 0.91	85 ± 6

[a] Average of triplicates.

were obtained at a microwave power of 100–200 W with a small decrease for selected PAHs at higher microwave energy. The lower extraction efficiency at high microwave energy may have resulted from overheating of the samples and interference due to unwanted matrix extraction along with PAHs. Though higher recoveries of PAH from soil samples were reported at elevated temperature, it must be realized that increased amounts of matrix materials were also extracted at high temperature because of which a vigorous cleaning step is required before the analysis [33]. Based on our results, the microwave energy was fixed at 150 W for subsequent studies at which the temperature of the extract reaches 50–55 °C, close to the boiling point of solvent mixtures employed in this study. Previous studies indicated that the microwave heating temperature close to the boiling point of the extractant mixture can produce better extraction efficiency [33].

3.1.3. Effect of extraction time

In order to determine the optimum extraction time for better recovery, MAE extraction using 150 W in 20 ml of solvent was carried out for 5, 10, 20, 30, 45 and 60 min, respectively. Our results showed increased extraction yield with increasing extraction time for all PAHs except that a lower recovery was obtained for Chry and B(ghi)P, which could be caused by a thermal degradation because of the temperatures reached inside the vessels [40]. However, longer extraction time beyond 20 min did not show any significant improvement in the extraction yield. Therefore it was decided to use 20 min extraction time in all subsequent experiments. In summary, a microwave energy of 150 W and an extraction time of 20 min are suitable for extraction of PAHs from PM.

3.2. Validation using NISTSRM (1648 and 1649a)

To confirm that the MAE method is suitable for its intended use, a validation process was carried out by applying the optimized extraction procedure to the NIST certified reference material SRM 1648 (urban particulate matter) and SRM 1649a (urban dust). The SRM 1649 has been certified for 12 of the 16 PAHs listed in the USEPA priority list while SRM 1648 has reference values for 11 of the 16 PAHs. An accurately weighed 50 mg portion of the material was extracted in triplicates for PAHs using MAE and analyzed by GC–MS. The results obtained are shown in Tables 1 and 2. As can be seen from Table 1 (SRM 1648), the results are in good agreement with the reference values as well as the results reported by Iglesias et al. [36]. The recoveries were in the range of 85–108%, which is with in the range of AOAC (Association of Analytical Communities) interval (80–115%) [38]. The results obtained from SRM 1649a are shown against the certified values in Table 2. In general, the experimental values are in good agreement with the certified values and recoveries

Table 1
Analysis of NIST SRM 1648 (urban particulate matter)

PAH	Reference value, mean ± S.D.	Iglesias et al.[37], mean ± S.D.	Measured. values[a], mean ± S.D.	% Recovery, mean ± S.D.
Phe	4.6 ± 0.3	4.6 ± 0.2	5.0 ± 0.2	109 ± 4
Ant	0.36 ± 0.10	0.39 ± 0.1	0.46 ± 0.05	128 ± 11
Ft	8.7 ± 0.4	7.9 ± 0.1	9.2 ± 0.3	106 ± 3
Pyr	7.3 ± 0.3	7.3 ± 0.2	7.8 ± 0.3	107 ± 4
B(a)A	3.2 ± 0.1	3.3 ± 0.1	2.7 ± 0.5	84 ± 3
Chry	6.6 ± 0.2	6.0 ± 0.1	6.2 ± 0.4	94 ± 7
B(b)Ft	8.0 ± 0.5	8.0 ± 0.1	8.6 ± 0.4	108 ± 2
B(k)Ft	3.4 ± 0.5	3.6 ± 0.1	2.9 ± 0.3	85 ± 10
B(a)P	3.4 ± 0.5	3.5 ± 0.1	3.2 ± 0.3	94 ± 9.4
IP	4.7 ± 0.2	4.7 ± 0.24	4.9 ± 0.2	104 ± 4
B(ghi)P	4.7 ± 0.1	4.5 ± 0.2	4.9 ± 0.3	104 ± 6

[a] Average of triplicates.

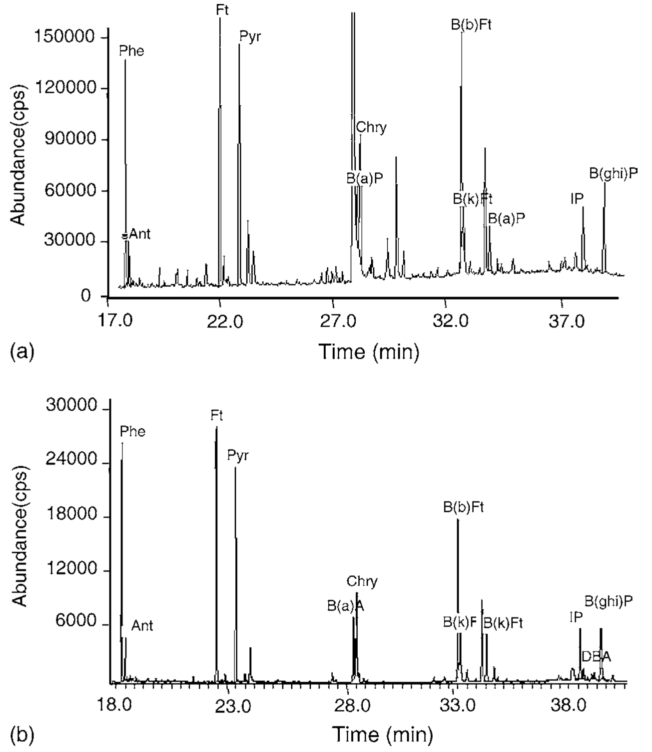

Fig. 3. GC–MS chromatogram of NIST SRMs extracts (a) SRM 1648 (urban particulate matter); (b) SRM 1649a (urban dust).

ranged from 79% (BkF) to 122% (DB[ah]A). The recoveries of DB[ah]A and IP were higher than those included in the AOAC interval.

The overall results obtained for both SRMs indicate that the proposed MAE technique is suitable for the extraction of particulate-bound PAHs at trace levels. Fig. 3 shows GC–MS chromatogram of the SRM extracts with no clean-up step. As can be seen, there are no chromatographic interferences obscuring the determination of PAHs in the MAE extracts. It is thus evident that a large number of PM samples can be analyzed routinely following the proposed MAE procedure with no clean-up step because of the low temperature extraction, which tends to minimize matrix–analyte interactions.

3.3. Limit of detection (LOD), limit of quantification (LOQ) and precision

The LOD and LOQ were evaluated for the proposed method based on blank determinations ($n = 10$) of both types of quartz filters used in conjunction with hi-vol and mini-vol samplers employed in this study. For this purpose, the pre-baked filters were extracted using the MAE technique and analyzed for PAHs. The LOD were calculated from the following equation [42]:

$$\mathrm{LOD} = \mathrm{blank} + 3\sigma_{\mathrm{blank}}$$

The blank values for each PAH were obtained at their respective retention time. The LOQ were calculated using the same equation, but with a factor of 6. The values for LOD and LOQ are given in Table 3. LODs (ng m^{-3}/pg/μg) for hi-vol and mivol quartz filters ranged from 0.001/0.03 [B(k)Ft] to 0.15/5.0 [Naph] and 0.041 (1.4) [B(a)P] to 1.119/37.3 [Naph], respectively.

The precision of the MAE–GC–MS was examined by six independent measurements of spiked standards (80–160 ng) and coefficients of variations (% CV) were in the range of 4–12% for all 16 PAH compounds. The day-to-day reproducibility was evaluated by conducting the experiments with MAE–GC–MS on 3 days. The coefficients of variation (% CV) were calculated to be in the range of 7–16%, respectively. The precision of the proposed method for real samples was examined using SRM 1649a. The percentage CV ($n = 3$) for serial and day/day was in the range of 3–21 and 7–25%, respectively.

Table 3
Limit of detection and limit of quantification

PAH	Quartz Filter of hi-vol sampler (27 cm × 15 cm)[a]		Quartz filter of mini-vol sampler (47 mm dia)[b]	
	LOD ng m^{-3} (pg/μg)[c]	LOQ ng m^{-3} (pg/μg)[c]	LOD ng m^{-3} (pg/μg)[c]	LOQ ng m^{-3} (pg/μg)[c]
Naph	0.150(5.0)	0.301 (10.0)	1.119(37.3)	2.239 (74.6)
Aci	0.007 (0.2)	0.014(0.5)	0.551(18.4)	1.111(37.0)
Ace	0.016(0.5)	0.032(1.1)	0.890 (29.7)	1.780(59.3)
Fl	0.024 (0.8)	0.048(1.6)	1.224(40.8)	2.448(81.6)
Phe	0.037(1.2)	0.074 (2.4)	0.347(11.6)	0.694(23.1)
Ant	0.009 (0.3)	0.018(0.6)	0.557(18.6)	1.113(37.1)
Ft	0.013 (0.4)	0.025 (0.8)	0.357(11.9)	0.714(23.8)
Pyr	0.015(0.5)	0.031(1.0)	0.760 (25.3)	1.520(50.7)
B(a)A	0.003 (0.1)	0.007 (0.2)	0.231(7.7)	0.461(15.4)
Chry	0.003(0.1)	0.006 (0.2)	0.144(4.8)	0.289(15.4)
B(b)Ft	0.004(0.1)	0.007 (0.2)	0.291 (9.7)	0.581 (19.4)
B(k)Ft	0.001 (0.03)	0.002 (0.2)	0.072 (2.4)	0.144(4.8)
B(a)P	0.003(0.1)	0.005 (0.2)	0.041 (1.4)	0.082 (2.7)
IP	0.002 (0.07)	0.004(0.1)	0.169(5.6)	0.338(11.3)
DB(ah)A	0.009 (0.3)	0.017(0.6)	0.119(4.0)	0.218 (7.9)
B(ghi)P	0.003 (0.1)	0.005 (0.2)	0.345(11.5)	0.690(23.0)

[a] $\mathrm{LOD_{lig}} \times 4/1631$ (based on 24 h sampling at 35.3 $\mathrm{m^3\,min^{-1}}$).
[b] $\mathrm{LOD_{lig}}/7.2$ (based on 24 h sampling at 5 $\mathrm{l\,min^{-1}}$).
[c] Calculated based on an average mass concentration 30 μg m^{-3}.

Table 4
Concentrations of PAHs in $PM_{2.5}$ particles collected in Singapore's outdoor environment

PAH	Mean ± S.D. ($ng\,m^{-3}$)	Min–Max
Naph	0.62 ± 0.28	0.29–1.21
Aci	0.04 ± 0.01	0.02–0.06
Ace	0.05 ± 0.04	0.01–0.12
Fl	0.04 ± 0.03	0.02–0.08
Phe	0.13 ± 0.06	0.09–0.24
Ant	0.04 ± 0.02	0.02–0.09
Ft	0.04 ± 0.01	0.03–0.08
Pyr	0.09 ± 0.03	0.05–0.12
B(a)A	0.01 ± 0.02	0.01–0.03
Chry	0.01 ± 0.03	0.01–0.07
B(b)Ft	0.17 ± 0.10	0.09–0.31
B(k)Ft	0.04 ± 0.02	0.02–0.08
B(a)P	0.14 ± 0.07	0.07–0.22
IP	0.19 ± 0.08	0.06–0.26
DB(ah)A	0.06 ± 0.09	0.02–0.22
B(ghi)P	0.31 ± 0.12	0.10–0.41
$\sum$PAH	1.98 ± 1.01	0.91–3.60
PM_{mass} ($\mu g\,m^{-3}$)	24.6 ± 9.6	19.8.5–35.5

3.4. *Analysis of real PM samples*

The suitability of the proposed MAE technique was demonstrated by analyzing a set of aerosol samples collected from two different sources.

3.4.1. *Ambient aerosol particles ($PM_{2.5}$)*

The $PM_{2.5}$ particles collected in Singapore for a period of 10 days were analyzed for PAHs. The concentrations of PAHs measured in these samples are shown in Table 4. The total concentration of particulate-bound PAHs was in the range of 0.91–3.60 $ng\,m^{-3}$ with an average of 1.98 $ng\,m^{-3}$ during the study period. Benzo(a)pyrene which is considered to be a carcinogenic, ranged from 0.07 $ng\,m^{-3}$ to 0.22 $ng\,m^{-3}$ with an average value of 0.14 $ng\,m^{-3}$. Among the PAHs detected in this study, Naph, IP, and B(ghi)P were the most abundant PAHs in Singapore during the study period. Table 6 compares the concentration of the 16 PAHs measured in Singapore to those reported from other parts of world. The concentrations of PAHs in the Singapore atmosphere are comparable to those in Hong Kong and Germany, and are lower than those reported for other urban areas.

3.4.2. *Indoor aerosol particles ($PM_{2.5}$)*

In recent years, domestic and commercial cooking sources are also recognized as one of the contributors to PAHs in the urban atmosphere [48,49]. Several authors reported higher concentration of PAHs in PM from different cooking sources. In the present study, we have collected $PM_{2.5}$ samples for a period of 1 week in a commercial Indian cooking stall, and analyzed for particulate-bound PAHs. The results obtained are given in Table 5. The total PAH concentrations ranged from 27.6 to 75.7 $ng\,m^{-3}$ with an average of 51.6 $ng\,m^{-3}$. These concentrations are several folds higher than those seen in the fine particles in the outdoor environment in Singapore (1.98 $ng\,m^{-3}$). The B(a)P concentration ranged from 0.41 to 1.76 $ng\,m^{-3}$ with an average of 1.07 $ng\,m^{-3}$. The most abundant PAHs in cooking emission were low molecular weight-PAHs (Naph, Ace, Fl) and medium molecular weight-PAHs (Phe, Ant, Pyr), which together accounted for 75% of the total PAH concentration. Lower molecular weight PAHs are mainly found in the gaseous phase whereas higher molecular weight PAHs are mainly found in the particulate phase [64]. However, the former are also present in larger size particles in the urban samples. PAHs are primarily coemitted with fine particles and redistribute to other fractions by vaporization followed by sorption because of their lower molecular weight and high vapor pressure [51,64]. Further, their concentrations can be different due to a shift in gas/particle portioning induced by ambient temperature variation. [52,53].

PAHs found in the food stall can be formed from the combustion of any organic matter, e.g. fossil fuels and biomass, at high temperature and low oxygen content through pyrolysis and pyrosynthesis. Incomplete combustion of LPG, the fuel used in the food stall, is known to release PAHs, albeit at lower concentrations compared to other biomass fuels [54]. In addition, cooking oil fumes also contain PAHs [55,56]. These PAHs can either be formed from combustive processes of oil, or expelled directly from the PAH-containing oil [57–59]. The same pathways can also be responsible for emission from food, which already has some PAHs content prior to combustion [60–63]. Therefore, different fuels, oils, and food give rise to varied amounts of PAHs during cooking.

The results on PAH concentrations obtained in this study are compared to those reported from China and Taiwan on cooking emissions (cf. Table 6). In general, the results from the three studies are comparable. Japanese cooking and Chinese cooking from China showed lower concentrations of PAHs compared to the results obtained from other types of cooking. These differences in the levels of PAHs could be due to the type of cooking oil used, and the type and amount of food material cooked as dis-

Table 5
Concentrations of PAHs in $PM_{2.5}$ particles collected from the canteen in Singapore

PAH	Mean ± S.D. ($ng\,m^{-3}$)	Min–Max
Naph	3.21 ± 0.54	2.51–3.82
Aci	1.84 ± 0.61	1.16–2.76
Ace	3.88 ± 1.10	2.74–5.44
Fl	6.34 ± 1.99	3.79–9.18
Phe	15.30 ± 5.68	9.61–25.43
Ant	4.73 ± 2.21	2.27–8.39
Ft	2.32 ± 0.93	1.20–3.39
Pyr	4.80 ± 1.73	2.75–7.52
B(a)A	1.61 ± 0.65	0.73–2.48
Chry	1.35 ± 0.65	0.42–2.15
B(b)Ft	2.19 ± 1.43	0.72–4.44
B(k)Ft	0.54 ± 0.48	0.15–1.30
B(a)P	1.07 ± 0.61	0.41–1.76
IP	1.78 ± 1.08	0.40–3.29
DB(ah)A	1.52 ± 1.40	0.21–4.14
B(ghi)P	2.35 ± 1.57	0.94–5.06
$\sum$PAH	51.6 ± 27.6	27.6–75.7
PM_{mass} ($\mu g\,m^{-3}$)	186 ± 43	32–248

Table 6
Comparison of total PAHs and BaP concentrations (ng m^{-3})

Country	Sampling site	Survey year	Total PAH	BaP	Reference
Ambient aerosol particles					
Singapore	NUS	2005	1.98 ± 1.01	0.14 ± 0.07	Present work
Hong Kong	Kwun Tong	2001	4.67	0.96	[43]
Spain	Sevilla	2000–2001	8.6	0.56	[44]
Italy	Rome	1994	21.17	1.73	[45]
Germany	Munich	1996–98	3.48	0.45	[46]
UK	London	1991–92	825	10	[47]
USA	Chicago	1995	451.6	1.6	[48]
$PM_{2.5}$ from cooking emissions (indoor)					
Singapore	Commercial kitchen (Indian)	2005	51	1.07	Present work
China	Commercial kitchen (Chinese)	2002	17	0.28	[49]
Taiwan	Commercial kitchen (Chinese)	2002	72	1.22	[50]
	Western		86	1.59	
	Japanese		53	0.28	
	Fast food		61	0.30	

cussed above; it is assumed that the fuel itself does not contribute significantly to the differences as LPG was used in all the studies. As a consequence, the cooking method is thought to play a role in affecting the levels of PAHs emitted as cooking techniques like frying involve PAH-containing oil whereas others such as broiling and steaming uses water. Apart from the difference in the cooking methods, the type of ventilation employed in the kitchen areas can also contribute to the different levels of PAHs in kitchens. Naturally ventilated food stalls like the one considered in this study have a smaller air change per hour leading to a build-up of PAHs. On the other hand, PAHs released in the restaurants in the China and Taiwan studies are more effectively dispersed in air since the mechanical ventilation was provided by the central air conditioning system [49].

4. Conclusions

The toxicity of particulate-bound PAHs present in both outdoor and indoor environments justifies the need to establish their content in urban particulate matter. We have developed an extraction method using MAE for the determination of PAHs in airborne particulate matter. The optimized extraction conditions are: 20 ml of acetone/*n*-hexane (1:1), 20 min, and 150 W microwave irradiation. This solvent mixture is less hazardous than chlorinated solvents, which are commonly used in traditional extraction methods. The proposed MAE method employed low temperature for the extraction of PAHs from PM, compared to previous studies reported in the literature, which has helped in minimizing the extraction of matrix materials along with the analytes, thereby eliminating the clean-up step and improving the overall recovery of PAHs. The optimized MAE method was validated by using two different NIST SRMs (1648 and 1649a). Our results showed good agreement with certified as well as reference values of several PAH compounds. The application of the new extraction method was demonstrated by analyzing a set of real world PM samples, colleted from two different sources. The results obtained were compared to the values reported from other countries. Based on our results, it can be stated that the proposed MAE technique is a simple, fast, and reliable extraction method that can be used in conjunction with GC–MS for the determination of PAHs in a large number of PM samples on a routine basis.

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