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Multi-walled carbon nanotube-impregnated agarose film microextraction of polycyclic aromatic hydrocarbons in green tea beverage

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ABSTRACT

A new microextraction procedure termed multi-walled carbon nanotube-impregnated agarose film microextraction (MWCNT–AFME) has been developed. The method utilized multi-walled carbon nanotubes (MWCNTs) immobilized in agarose film to serve as adsorbent in solid phase microextraction (SPME). The film was prepared by mixing the MWCNTs in agarose solution and drying the mixture in oven. Extraction of selected polycyclic aromatic hydrocarbons was performed by inserting a needle through circular MWCNT-impregnated agarose films (5 mm diameter) and the assembly was dipped into an agitated sample solution prior to micro high performance liquid chromatography–ultraviolet analysis. Back extraction was then performed using ultrasonication of the films in 100 μL of solvent. The film was discarded after single use, thus avoiding any analyte carry-over effect. Due to the mesoporous nature of the agarose film, the MWCNTs were immobilized easily within the film and thus allowing for close contact between adsorbent and analytes. Under the optimized extraction conditions, the technique achieved trace LODs in the range of 0.1 to 50 ng L^{-1} for the targeted analytes, namely fluoranthene, phenanthrene and benzo[a]pyrene. The method was successfully applied to the analysis of spiked green tea beverage samples with good relative recoveries in the range of 91.1 to 107.2%. The results supported the feasibility of agarose to serve as adsorbent holder in SPME which then minimizes the consumption of chemicals and disposal cost of organic wastes.

1. Introduction

Miniaturization has become an important trend in the development of sample preparation techniques due to the concern of environment pollution. Aware of the pollution issue, environmental friendly practices and green analytical chemistry have been incorporated into research with the aim to reduce the use of hazardous chemicals.

Solid phase microextraction (SPME) is a solventless technique developed by Arthur and Pawliszyn [1]. The advantages and drawbacks of SPME essentially originated from the same source, where the SPME extract can be injected directly into chromatography but excessive device must be attached or modified at the inlet of the instruments. Aware of the insufficient instrument and excessive device required for the SPME analysis, the use of stir bar sorptive extraction (SBSE) [2,3], microextraction in packed syringe (MEPS) [4], solid phase membrane tip extraction (SPMTE) [5], membrane protected adsorbent SPME [6] and adsorbent film SPME [7–9] have been reported to simplify the lab procedure, where the back extraction was carried out in solvent with the aid of either temperature, ultrasonication or electric force. The modified or enhanced SPME techniques are not solventless but have greatly reduced the organic solvents and waste.

Polycyclic aromatic hydrocarbons (PAHs) are environmental pollutants identified as mutagen or carcinogen since 1976 [10]. Green tea is one of the popular beverages widely consumed by the world's population. Green tea with its well known antioxidant properties has led to the realization of its importance in anti-mutagenic and anticlastogenic treatments [11]. However, the contamination of PAHs in vegetation [12–14] from gaseous and particle-bound PAHs was frequently reported and this included tea leaves [15,16]. It was reported that factors such as tea variety, tea/water ratio, brewing time, washed tea or unwashed tea, and covered-up or uncovered-cup tea during tea manufacturing process significantly affect the transfer of PAHs to end product [17]. Therefore, determination of PAHs residues in green tea is important in order to prevent adverse effect to drinking green tea and to assist in the establishment of the maximum residue limits. Solid phase extraction (SPE) [18] and liquid–liquid extraction

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(LLE) followed by column chromatography clean-up [15,19] have been extensively applied to extract PAHs in tea. However, both techniques consume large amounts of organic solvents and chemicals and thus they are less supportive towards green chemistry. Lately, micro-scale sample preparation techniques have emerged to address this shortcoming. SBSE [20] offered trace detection limit with longer extraction time that exceeded one hour. First generation headspace SPME [21] required excessive injection port at instrument which might not be convenient for routine analysis although the technique gave detection limits as low as SBSE with shorter extraction time. In short, the application of micro-scale sample preparation techniques to extract PAHs from tea is still limited.

Agarose, a polysaccharide extracted from seaweed [22], is quoted as green polymer due to its biodegradable nature. Due to its hydrophilic, gelling and inert properties, agarose has been extensively studied and applied as a medium in gel electrophoresis, template to control the structural properties, drug delivery agent and optical sensor supporting material [22–25]. Lately, agar–agar powder has been modified and employed as sorbent in SPE for the extraction of mercury in water and fish samples [26]. A simple approach termed agarose film liquid phase microextraction has been demonstrated for the extraction and pre-concentration of PAHs from environmental water samples [27]. In this report, agarose film was utilized as a barrier between organic extractant and sample solution. This approach has a double “green chemistry” nature due to its microextraction format and the biodegradability of the agarose film.

Carbon nanotubes (CNTs) with tubular structure of carbon atom sheets were discovered by Iijima [28]. Since then, CNTs have become multidisciplinary research focus due to its unique mechanical, electrical, chemical and thermal properties [29]. Recently, the application of CNTs as sorbents in separation science has gained considerable interest, especially for the extraction and pre-concentration of targeted analytes. The application of multi-walled carbon nanotubes (MWCNTs) as adsorbent in SPE has resulted in superior enrichment of PAHs [30] and triazines [31] from water samples. Basheer and co-workers demonstrated porous membrane protected MWCNT micro-SPE for the extraction of organophosphorus pesticides from sewage sludge samples. The technique provided cost effective and selective extraction which eliminated the filtration step [6]. Recently, Pardasani et al. [32] reported the application of magnetic MWCNTs assisted dispersive SPE that was simple, rapid and offered higher recoveries of nerve agents and their markers from muddy water as compared to SPE that utilized C_{18} as sorbent. The high surface area of MWCNTs has been beneficial to the effective mass transfer of analytes [32].

In this work, multi-walled carbon nanotube-impregnated agarose film microextraction (MWCNT-AFME) system is proposed for the first time and applied to the analysis of PAHs in green tea beverage. Mesoporous agarose film was employed as adsorbent holder and MWCNTs were utilized as adsorbent and immobilized within the agarose film. Circular-shaped MWCNT-impregnated agarose film was pierced by a needle and dipped into the sample solution for extraction. This innovation utilizes biodegradable agarose to serve as adsorbent holder in SPME and contributes to minimize the use of chemicals and organic disposal.

2. Experimental

2.1. Chemicals and materials

Phenanthrene (PHE), fluoranthene (FLA) and benzo[a]pyrene (BaP) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Stock solutions (200 mg L^{-1} of each analyte) were prepared by dissolving in acetonitrile (PHE and BaP) and methanol (FLA). Working standard solutions were prepared weekly using methanol from stock standard solutions. All standard solutions were stored in dark at 4 °C when not in use. Tetrahydrofuran (THF), isopropyl alcohol (IPA), methanol (MeOH) and acetonitrile (ACN) were HPLC grade purchased from Merck (Darmstadt, Germany). Agarose (molecular grade) was obtained from Promega (Madison, USA). MWCNTs (specific surface area >233 m^2 g^{-1}, purity $>95\%$, 8–15 nm outer diameter × 50 μm in length) were purchased from Sun Nanotech (Jiangxi, China). A hot plate stirrer (Corning, USA) and a stirring bar (12 × 4 mm) were used to agitate the samples during extraction.

2.2. Chromatographic conditions

All analyses were performed using a micro high performance liquid chromatography (μ–HPLC) (Agilent Technologies, Milan, Italy) coupled with a ultraviolet detection (Agilent Technologies). The chromatographic separation of PAHs was carried out on a ZORBAX Eclipse Plus C_{18} column (2.1 × 100 mm, 3.5 μm) from Agilent. The separation was performed using isocratic mobile phase ACN-water (80:20) (v/v) at column temperature of 25 °C. The flowrate, injection volume and detection wavelength were fixed at 0.2 mL min^{-1}, 2 μL and 254 nm, respectively. Chromatographic data were processed using Agilent Chemstation software.

2.3. Preparation of multi-walled carbon nanotube-impregnated agarose film (MWCNT-AF)

Agarose (0.30 g) was added with 30 mL of deionized water (Millipore, France) and mixed. The content was brought to boil to completely dissolve the agarose. MWCNTs (90 mg) were added into the boiled agarose solution and stir to mix well. An aliquot of the warm solution (4.0 mL) was pipetted into a glass Petri dish (50 mm in diameter) and the solution was allowed to cool and gel at room temperature for at least 30 min. The Petri dish was dried in an oven at 40 °C for 24 h. The MWCNT-AF formed was punched into circular pieces with certain size (5 mm diameter) with a puncher.

The film obtained was then sent for subsequent characterization using Hitachi S-4800 field emission scanning electron microscope (FESEM) (Tokyo, Japan) and nitrogen adsorption method. FESEM was used to analyze the morphology of the agarose film whereas Nitrogen adsorption ASAP 2010 Micromeritics surface analyzer (Norcross, GA, USA) was used to obtain Brunauer Emmett Teller (BET) surface area of the film.

2.4. Multi-walled carbon nanotube-impregnated agarose film microextraction (MWCNT-AFME)

Water sample (20 mL) was pipetted into a 25-mL sample vial and a magnetic stirrer was placed into the sample. Hypodermic needle was used to pierce the Parafilm and then pieces (1–4) of the MWCNT-AF, alternately separated by silicone septum. The assembly was then dipped into IPA for 2 min followed by deionized water for 1 min to condition the films before dipping it into the sample solution for extraction. The sample vial was sealed immediately with the Parafilm (Fig. 1). After stirring at a speed of 800 rpm for 40 min, the films were removed and sonicated with 100 μL of THF for 15 min. The THF was filtered through 0.2 μm nylon syringe filter prior to μ–HPLC analysis.

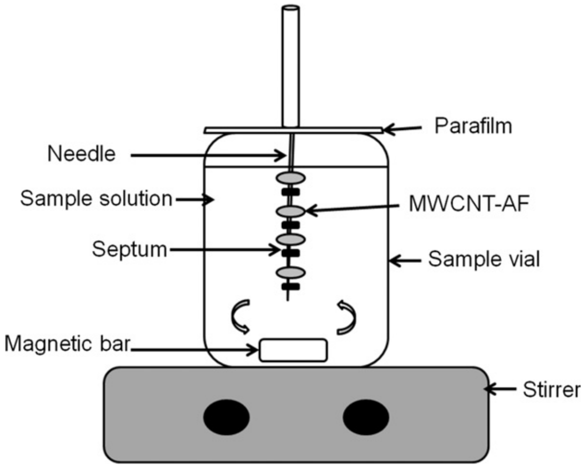

Fig. 1. Schematic drawing of MWCNT-AFME system.

2.5. Validation of analytical method

The extraction method was assessed for linearity, recovery, reproducibility, limit of detection (LOD) and limit of quantification (LOQ) before sample analysis.

2.6. Sample analysis

Green tea beverage samples were obtained from local retail shops. The samples were subjected to extraction without any pretreatment.

3. Results and discussion

3.1. Optimization of MWCNT-AFME

Optimization was carried out using deionized water samples spiked with each PAH to give concentrations of 1 μg L^{-1} for PHE and FLA and 20 μg L^{-1} for BaP. Triplicate extractions were carried out for each parameter optimized in this study.

3.1.1. Conditioning solvent

Organic solvent was required to condition the film to increase its wettability as the MWCNTs were hydrophobic in nature. ACN, MeOH, THF and IPA with water miscibility properties and decreasing polarities were applied as conditioning solvents. It was observed that film conditioned with IPA gave highest extraction efficiencies for all targeted analytes. Non-polar solvent overcame the wettability issue and enhanced the interaction between hydrophobic adsorbent and sample solution.

3.1.2. Sample volume, concentration of MWCNTs and number of films

The sample volume is important to determine the adsorption capacity of the MWCNT-AF. Sample volume in the range of 10–25 mL was studied. Results showed that the lowest sample volume (10 mL) gave the lowest extraction efficiency. Sample volume of 20 mL was applied for subsequent studies as the extraction efficiencies for analytes were at maximum. No significant increase in extraction efficiency was observed with further increase in sample volume. This suggests that the adsorption sites of MWCNTs reached saturation, where increasing concentration of PAHs did not further contribute to the extraction efficiency.

Various concentrations of MWCNTs immobilized within agarose in the range of 0.1–0.6% (w/v) were investigated. The MWCNTs played the adsorbent role in this study. The peak areas of PHE and FLA increased with the concentration of MWCNTs and reached a plateau in the range of 0.3 to 0.6% (w/v) (Fig. 2). However, the adsorption of BaP decreased with the concentration of MWCNTs. From concentration of 0.1 to 0.3%, the increment of extraction efficiency of PHE was 77% but the decrement of BaP was 28% which was less significant. Therefore, 0.3% (w/v) of MWCNTs was prepared and used for the extraction. The film was analyzed by FESEM and the results proved the impregnation of MWCNTs within the agarose film (Fig. 3). The adsorption of PHE was stronger as compared to FLA and BaP suggesting that the highly polarizable PHE appeared to have strong π–π interaction with the MWCNTs' graphene sheets [33]. On the other hand, weaker adsorption may be due to the other form of hydrophobic interactions. The surface area obtained from nitrogen adsorption method provided valuable information on the estimation of aggregation formed when the MWCNTs were immobilized within agarose film. The surface area did not increase proportionally with the concentration of MWCNTs added into agarose film (Fig. 2). This information supported the notion that aggregation of MWCNTs occurred and this lead to the reduction in surface area [34] when higher concentration of MWCNTs was forced to be sandwiched or immobilized within a constant surface area

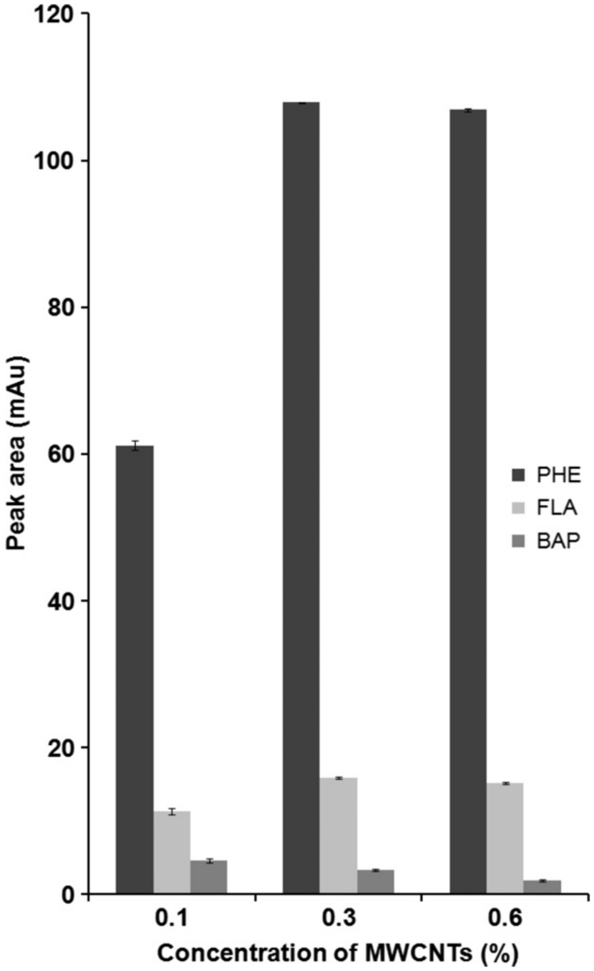

Fig. 2. Effect of concentration of MWCNTs on MWCNT-AFME of PAHs from water sample (n=3 in each case). Error bars represent the standard deviation. The surface area of the 0.1, 0.3 and 0.6% of MWCNTs impregnated within the agarose film were 21.4, 37.6 and 52.0 $m^2\,g^{-1}$, respectively.

or concentration of agarose. When aggregation occurred, PAHs tended to be entrapped in closed interstitial spaces between aggregates [35] and caused incomplete desorption.

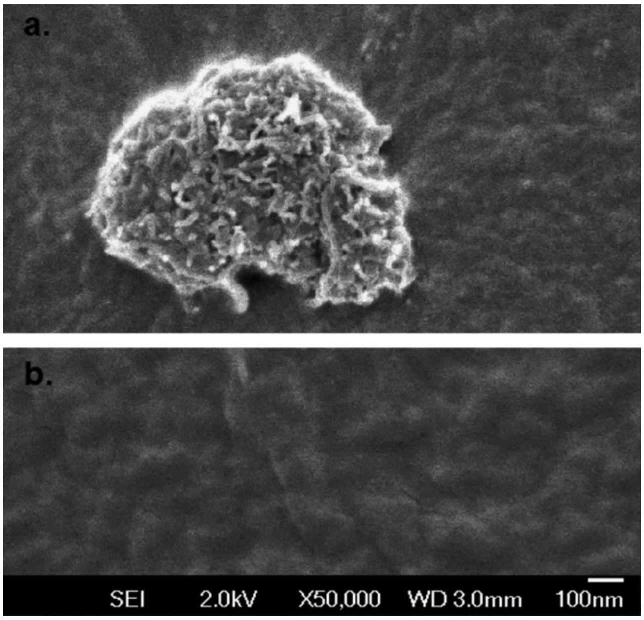

Fig. 3. FESEM image of the (a) 0.3% MWCNT-AF and (b) AF.

A few pieces of the agarose film (1 to 4 pieces) were pierced and held by the needle and tested for extraction efficiency enhancement. It was noted that increasing the number of pieces of film used for the extraction resulted in higher peak areas (Fig. 4). This suggests that extraction efficiencies were increased when more active sites were provided by increasing the number of films. However, due to space limitation, a maximum 4 pieces of films were applied in each of subsequent experiments.

3.1.3. Desorption time and desorption solvent

Ultrasonication method was used to desorb PAHs from the hydrophobic MWCNTs as the technique was suitable to be applied for reversible adsorption. The effect of desorption time in the range of 5–35 min of ultrasonication was investigated. It was found that maximum desorption of the analytes was achieved within 15 min of ultrasonication. No significant increase of peak area was observed beyond 15 min of ultrasonication. Therefore, desorption time of 15 min with ultrasonication was chosen for subsequent experiments.

Desorption of PAHs from film after extraction was conducted using several organic solvents, namely ACN, MeOH, THF and IPA. It was observed that non-polar solvents (THF and IPA) gave better desorption as compared to polar solvents (ACN and MeOH) (Fig. 5). Hydrophobic PAHs were adsorbed strongly on MWCNT-AF, thus only non-polar solvent can disrupt the interaction and desorbed the PAHs.

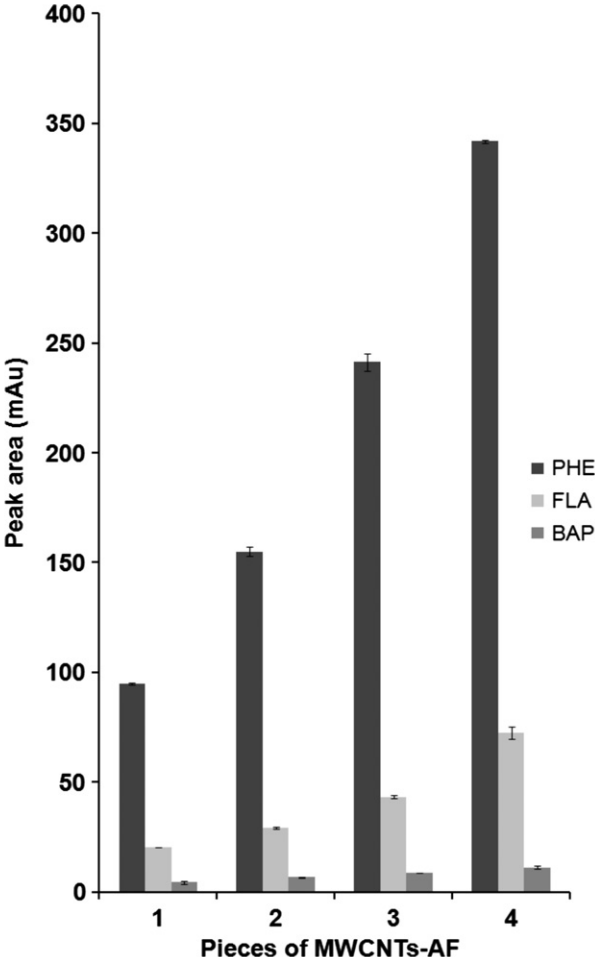

Fig. 4. Effect of pieces of MWCNT-AF on MWCNT-AFME of PAHs from water sample ($n=3$ in each case). Error bars represent the standard deviation.

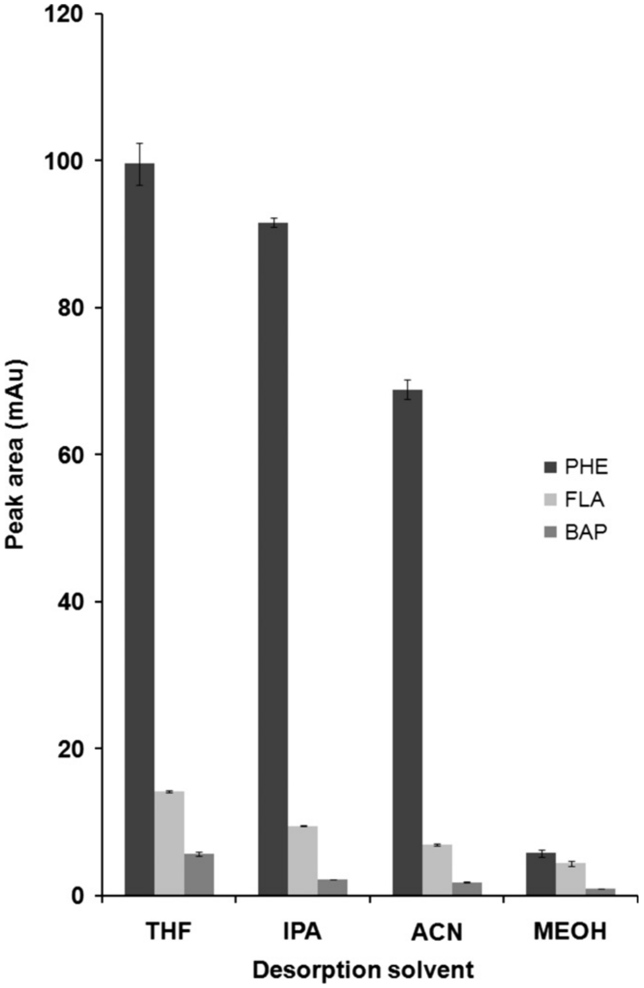

Fig. 5. Effect of desorption solvent on MWCNT-AFME of PAHs from water sample ($n=3$ in each case). Error bars represent the standard deviation.

3.1.4. Stirring speed and extraction time

Effect of stirring speed on extraction efficiency was investigated in the range of 200–1000 rpm. Results indicated that the extraction efficiencies increased with the stirring speed and reached a maximum at 800 rpm (Fig. 6). This was because higher stirring speed enhanced the kinetic of targeted analytes and thus resulting in higher diffusion rate and improved interaction between analytes and film. However, the vortex flow created at 1000 rpm reduced the contact between analytes and MWCNT-AF and disrupted the adsorption of analytes onto MWCNTs [36], thus causing low peak areas. Therefore, 800 rpm was chosen and used in subsequent experiments.

The MWCNT-AFME is not an exhaustive extraction but it depends on equilibrium time. Extraction times in the range of 10 to 50 min were investigated to determine the equilibrium time required for analytes to be adsorbed on adsorbent film. It was found that equilibrium was reached in 40 min. No significant increase was observed in the extraction efficiencies for all targeted analytes at extraction time of 50 min. Therefore, extraction time of 40 min was adopted in the subsequent experiments.

3.2. Validation of MWCNT-AFME

Calibration was carried out using green tea beverage sample spiked with targeted analytes in the range of 0.0006 to 100 $\mu g\,L^{-1}$ for PHE and FLA and 0.1 to 100 $\mu g\,L^{-1}$ for BaP. Good linearities (Table 1) were obtained in the specified concentration ranges with good correlation coefficients, $r \geq 0.9957$. The validation indicated ultra-trace level LODs in the range of 0.1 to 50 $ng\,L^{-1}$. The LODs obtained revealed that MWCNTs are superior sorbents for both PHE and FLA, where the sorption is supported by combination of hydrophobic and π–π interactions [37].

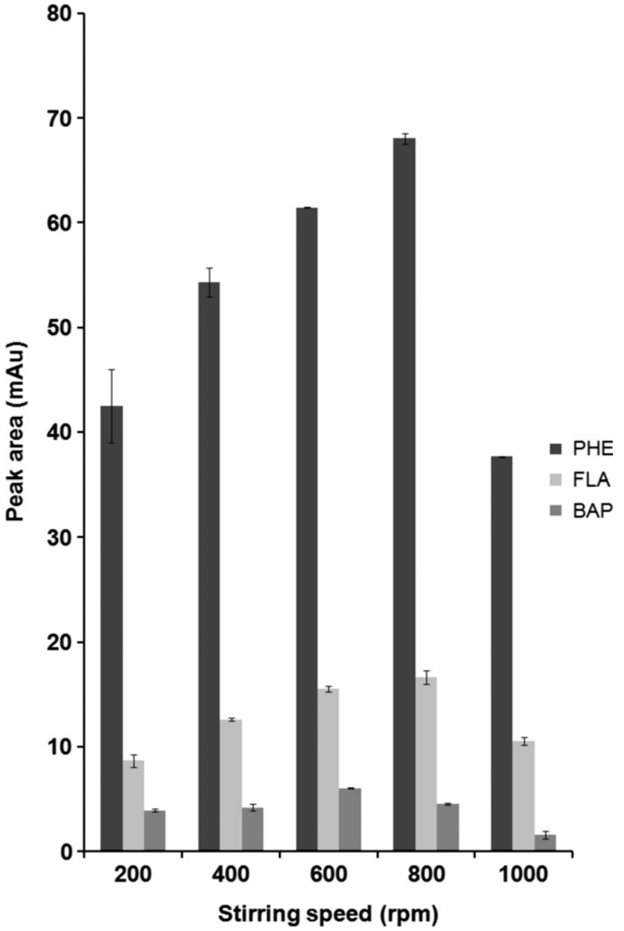

Fig. 6. Effect of stirring speed on MWCNT-AFME of PAHs from water sample ($n=3$ in each case). Error bars represent the standard deviation.

Relative recovery was studied as the MWCNT-AFME system was not an exhaustive extraction. Green tea beverage sample was split into three portions. Blank sample and samples spiked at 0.008 and 50 $\mu g\,L^{-1}$ for both PHE and FLA, and 0.5 and 20 $\mu g\,L^{-1}$ for BaP were extracted with MWCNT-AFME and the results were compared with the calibration curve established using the other brand of green tea beverage sample. The results (Table 2) showed excellent average relative recoveries ranging from 91.1 to 107.2% and good reproducibilities with relative standard deviations (RSDs) of <5%. This revealed that matrix effect was negligible and thus the MWCNT-AFME can be employed in the analysis of green tea beverage samples.

3.3. Application of MWCNT-AFME on green tea beverage samples

The optimized and validated MWCNT-AFME technique was successfully applied to the analysis of eight green tea beverage samples obtained from local retail shops. No BaP residues were detected in all of the samples (Table 3). PHE was detected in a sample at a concentration of 0.02 $\mu g\,L^{-1}$ and FLA was detected

Table 1
Validation data of MWCNT-AFME of PAHs from green tea beverage samples (n=3).

PAH*	Calibration range ($\mu g\,L^{-1}$)	Regression equation (RSD, %)	r	LOD ($ng\,L^{-1}$)
PHE	0.0006–100	$y=67.0x+142.1$(5.5)	0.9957	0.1
FLA	0.0006–100	$y=13.4x+29.9$ (5.8)	0.9958	0.3
BaP	0.1–100	$y=0.5x+0.2$ (4.2)	0.9995	50

* Polycyclic aromatic hydrocarbons: PHE=phenanthrene, FLA=fluoranthene, BaP=benzo[a]pyrene.

Table 2
Relative recovery studies of MWCNT-AFME using spiked green tea beverage samples (n=3).

PAH*	Spiked concentration ($\mu g\,L^{-1}$)	Average relative recoveries, % (RSD, %)
PHE	0.008	93.7 (1.3)
	50	97.5 (3.5)
FLA	0.008	91.1 (0.8)
	50	96.0 (3.9)
BaP	5	96.3 (4.5)
	20	107.2 (1.8)

* Polycyclic aromatic hydrocarbons: PHE=phenanthrene, FLA=fluoranthene, BaP=benzo[a]pyrene.

Table 3
Application of MWCNT-AFME on green tea beverage samples (n=3).

Sample no.	Residue level ($\mu g\,L^{-1}$) (RSD, %)		
	PHE	FLA	BaP
1	0.02	0.08	ND
2	ND	0.19	ND
3	ND	0.09	ND
4	ND	ND	ND
5	ND	ND	ND
6	ND	ND	ND
7	ND	ND	ND
8	ND	ND	ND

ND=not detected or less than detection limit.

Table 4
Comparison of the MWCNT-AFME with other published methods for the extraction and determination of PAHs from tea samples.

Analysis methods*	Dynamic linear range ($\mu g\ L^{-1}$)	LOD ($ng\ L^{-1}$)	References
SPE-HPLC-FD	4–268	16–140	[18]
LLE-column chromatography-HPLC-UV	100–2500	6–1740	[19]
SBSE-HPLC-FD	0.001–1.2	0.1–8.9	[20]
HS-SPME-HPLC-FD	1–20	4–145	[21]
MWCNT-AFME-μ–HPLC-UV	0.0006–100 and 0.1–100	0.1–50	This work

* Abbreviations: MWCNT-AFME=multi-walled carbon nanotube-impregnated agarose film microextraction; SBSE=stir bar sorptive extraction;SPE=solid phase extraction; LLE=liquid–liquid extraction; HS=headspace; SPME=solid phase microextraction; HPLC=high performance liquid chromatography; μ–HPLC=micro high performance liquid chromatography; FD=fluorescence detection; UV=ultraviolet detector.

in three samples with concentrations ranging from 0.08 to 0.19 $\mu g\ L^{-1}$. It was noted that no sample pretreatment was required prior to MWCNT-AFME which simplified the analytical procedures and shorten the analysis time.

3.4. Comparison with other reported methods

The comparisons of the MWCNT-AFME and other methods published previously for extraction and determination of PAHs from tea samples are tabulated (Table 4). The sensitivities of the reported methods [18–21] were comparable with MWCNT-AFME. SPE and LLE involved multi-stage operation which was tedious but achieved exhaustive extraction [18,19]. SBSE, HS-SPME [20,21] and MWCNT-AFME were non-exhaustive systems. Therefore, the extraction was time-dependent. SBSE offered the lowest LODs as compared to others but required two hours of extraction time [20]. HS-SPME offered slightly shorter extraction time but required excessive injection port for desorption [21] which might not be available in most laboratories. MWCNT-AFME utilized minimal amount of MWCNTs that were distributed evenly on the agarose film to serve as sorbents. The approach has greatly increased the contact between analytes and sorbents, thus resulting in shorter extraction time as compared to SBSE and HS-SPME. As each method has advantages and disadvantages; the application of the method will mainly depend on the analyst's skill, results specification, method simplicity and availability of the equipment.

4. Conclusions

The study revealed that MWCNT-AFME is suitable for trace analysis of environmental pollutants. Agarose film holds the MWCNTs firmly within its three dimensional structure and this approach has eliminated classical separation techniques (centrifugation and filtration) where MWCNTs are used as dispersive sorbent. The high enrichment factors and high sensitivity demonstrated in this study proved that the MWCNT-AFME is capable to stand as an alternative green SPME method.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.12.032.

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