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APPLICATION OF MICROWAVE-ASSISTED EXTRACTION COUPLED WITH DISPERSIVE LIQUID-LIQUID MICROEXTRACTION FOR THE DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN VEGETABLES

(Applikasi Pengekstrakan Berbantukan Mikrogelombang Gandingan dengan Pengekstrakan Mikro Cecair-Cecair Serakan bagi Penentukan Hidrokarbon Aromatik Polisiklik dalam Sayur-Sayuran)

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Abstract

Microwave-assisted extraction (MAE) coupled with dispersive liquid-liquid microextraction (DLLME) followed by gas-chromatography flame ionization detector (GC-FID) for the determination of 13 PAHs in vegetable samples was developed in this study. The analytical performances of the optimized DLLME and MAE-DLLME including limit of detection (LOD), limit of quantification (LOQ), precision, accuracy, relative extraction recovery and relative extraction factor were validated and compared. The LOD of DLLME and MAE-DLLME were in the range of 0.040-0.400 and 0.0200-0.080 µg/L, respectively. For DLLME, precision and accuracy were 1.22-7.50% (RSD) and 71.77% to 90.93%, respectively; while for MAE-DLLME, were 0.77%-3.07% (RSD) and 83.65-98.42%, respectively. The relative extraction recovery was improved from 70.81% – 85.41% in DLLME to 85.79% - 99.61% in MAE-DLLME. The relative enrichment factors were ranged from 126-156 and 165 to 202 for DLLME and MAE-DLLME, respectively. The volume of extraction solvent was reduced from 50 µL to 30 µL in MAE-DLLME. The overall analytical performances of MAE-DLLME is better than DLLME. The application of proposed MAE-DLLME in real samples was also investigated and discussed.

Keywords: dispersive liquid-liquid microextraction, microwave-assisted extraction, polycyclic aromatic hydrocarbons, extraction solvent

Abstrak

Pengekstrakan berbantukan mikrogelombang (MAE) gandingan dengan pengekstrakan mikro cecair-cecair serakan (DLLME) yang diikuti dengan gas kromatografi-pengesan nyalaan ion (GC-FID) bagi penentukan 13 jenis hidrokarbon aromatik polisiklik (PAHs) dalam sampel sayur-sayuran telah dibangunkan dalam kajian ini. Analisis prestasi optimum DLLME dan MAE-DLLME seperti had pengesanan (LODs), kepersisan, kejituan, perolehan semula pengekstrakan secara relatif dan faktor-faktor pengayaan secara relatif telah disahkan dan dibandingkan. Had pengesanan (LODs) bagi DLLME dan MAE-DLLME adalah dalam lingkungan 0.040-0.400 dan 0.0200-0.080 µg/L, masing-masing. Bagi DLLME, kepersisan dan kejituan adalah dalam lingkungan 1.22-7.50% dan 71.77-90.93%, masing-masing; manakala bagi MAE-DLLME, adalah dalam lingkungan 0.77-3.07% dan 83.65-98.42%, masing-masing. Perolehan semula pengekstrakan secara relatif telah ditingkatkan daripada 70.81-85.41% pada DLLME hingga 85.79 - 99.61% pada MAE-DLLME. Faktor-faktor pengayaan secara relatif adalah 126-156 dan 165-202 bagi DLLME dan MAE-DLLME, masing-masing. Jumlah pengekstrakan pelarut yang digunakan telah dikurangkan daripada

50 µL di DLLME kepada 30 µL di MAE-DLLME. Prestasi keseluruhan analisis MAE-DLLME adalah lebih baik daripada DLLME. Penggunaan MAE-DLLME dalam analisis sampel sebenar juga disiasat dan dibincangkan.

Kata kunci: pengekstrakan mikro cecair-cecair serakan, pengekstrakan berbantukan mikrogelombang, hidrokarbon aromatik polisiklik, pelarut pengekstrakan.

Introduction

Vegetables and fruits are essential elements of a healthy daily diet. They provide a large amount of vitamins, fibres and minerals. However, the occurrence of polycyclic aromatic hydrocarbons (PAHs) exposure on vegetables has been reported [1-3]. The contamination of PAHs on vegetables are primarily from human activities. Previous studies reported that the vegetables that grew in vicinity of contaminated sources were contaminated with high levels of PAHs sufficient to threaten human health [1, 2]. PAHs are a group of hydrocarbons with fused aromatic rings that form during the incomplete combustion of organic compounds. Numerous studies have confirmed their carcinogenicity. Therefore, PAHs have been declared as carcinogens and genotoxins by Scientific Committee on Food (SCF) [4] and the Joint FAO/WHO Expert Committee on Food Additives (JECFA) [5]. Since vegetables are an important part of human daily diets, it is necessary to ensure that vegetables are not exposed to high levels of PAHs.

Most analytical instruments are unable to handle analytes directly in food sample with complex matrices and usually trace levels of PAHs are found in food samples [6]. Therefore, before chromatographic analysis, well- designed sample preparation is necessary for the extraction and preconcentration of analytes from the food sample. There are several sample preparation methods available for extraction of PAHs from vegetable samples. Dispersive liquid-liquid microextraction (DLLME) is one of the successful sample preparation techniques developed by Rezaee et al. [7]. The DLLME technique showed several advantages such as miniaturized solvent consumption, simplicity, rapidity and high extraction efficiency [8]. However, DLLME has several drawbacks. Chlorinated solvents which are highly toxic usually chosen as extraction solvents due to their high efficiency [9]. Previous studies have employed DLLME for extraction of PAHs from vegetables and the presence of matrix interference was reported [9]. Even though dilution was used to reduce the effect of matrix interference, matrix components were still present and mixed with extraction solvent. This caused difficulty in transferring the clean extraction phase for chromatographic analysis and a high volume of extraction solvent was required to reduce this problem. In order to overcome the matrix interference of DLLME, it is imperative to introduce a clean-up step before chromatographic analysis of PAHs.

Recently, microwave-assisted extraction (MAE) has been developed for food samples preparation. MAE helps to isolate the organic analytes from food matrices. MAE gained noticeable attraction due to its extraction time minimization, low volumes of organic solvents consumption and increased extraction recovery [10]. MAE has been successfully used in previous studies to clean up food samples [11-13]. In the previous study [14], two extraction methods, which are DLLME and MAE coupled with DLLME (MAE-DLLME), have been used for the determination of 13 PAHs in vegetables followed by gas-chromatography-flame ionization detector (GC-FID). Various parameters such as extraction solvent, dispersion solvent, extraction time, microwave power and the irradiation time of MAE-DLLME have been studied and optimized. To overcome the limitations of using toxic chlorinated solvents as extraction solvents in conventional DLLME, the study selected low toxic brominated and alcohol solvents for extraction. The main objective of this study was to validate and compare analytical performances of DLLME and MAE-DLLME. The efficiency of both methods for extraction of 13 PAHs in different vegetable samples was also investigated.

Materials and Methods

Reagents and materials

Standard formulations of 13 PAHs (EPA 525 PAH Mix B, 500 µg/ml in acetone), containing acenaphthylene (ACY), phenanthrene (PHE), fluorine (FLU), anthracene (ANT), benzo[a]anthracene (BaA), pyrene (PYR), benzo[a]pyrene (BaP), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[ghi]perylene (BghiP), dibenz[a,h]anthracene (DahA), indeno[1,2,3-cd]pyrene (IcP) and biphenyl solution (2000 µg/ml in methanol) were purchased from Sigma-Aldrich (USA). Acetone, hexane and acetonitrile were

purchased from Fisher Scientific (Loughborough, UK). Highest purity bromobenzene, 1-bromo-3-methylbutane, 1-bromobutane, 2-ethyl-1-hexanol, 2-heptanol, 2-bromo-2-methylbutane and 2-octanol were purchased from Merck (Darmstadt, Germany). All the reagents used were HPLC grade or analytical reagent grade.

Mixed working solutions (10 mg/L) of 13 PAHs and biphenyl as internal standard were prepared in acetone and methanol, respectively. Stock solutions were stored at 4°C in a refrigerator prior to use. Diluted solution was prepared daily for further studies.

Instrumentations

The mixture of PAHs was separated and identified using a gas chromatograph (GC, Agilent 7890A) with a split/splitless injector system, Agilent 7683B automatic liquid sampler and a flame ionization detector (FID). The SLB-5ms capillary column (30 m×0.25 mm ID, 0.25 µm film thickness) was used for PAHs separation. The carrier gas was high purity helium gas (99.9995%, Air products, UK), with a flow rate of 1.67 mL/min. It was passed through an Agilent Big Universal Trap-Helium purge (model RMSN-2) to remove water, oxygen and hydrocarbons. The injection port was kept at 290 °C and splitless mode was used. The PAHs separation was conducted with the following programmed temperatures: initial 70 °C held for 1 minute, 20 °C/min to 120 °C held for 1 minute; 120 to 258 at 10 °C/min held for 1 minute; 258 °C to 262 °C at 1 °C/min held for 2 minutes; and 262 °C to 280 °C at 5 °C/min and held for 5.1 minutes. The total time for one GC run was 36 minutes. The FID temperature was maintained at 300 °C, hydrogen gas (Air products, UK) and nitrogen gas (makeup flow) (Air products, UK) were regulated at a flow of 35 mL/min. The air flow (Air products, UK) for FID was at 350 mL/min. Agilent Chemstation (B.04.02 version) was used as an instrumental controller and for data analysis.

Sample preparation

The vegetable samples (cabbage) were purchased from a local hypermarket and washed with running tap water. The mass of 25 g vegetable was weighted, added with 300 mL distilled water, and homogenized using food processor (Philips, HR2001/70). Then, the homogenized sample was sieved using sift followed by filtration using Whatman filter paper (Grade 1, 110 mm). The filtered sample were then centrifuged using Spinplus Centrifuge (Topscien) at 4000 rpm for 5 minutes. After that, the supernatant was filtered using 0.22 µm pore size nylon membrane filters (Jinlong) and appropriate volume of filtered sample was transferred into glass bottle. The sample was spiked with appropriate concentrations of PAHs and biphenyl (internal standard) before extraction with DLLME or MAE-DLLME.

DLLME extraction

The parameters effecting the DLLME extraction such as extraction solvent, dispersion solvent, extraction time have been studied and optimized [14]. The mixture of extraction solvent (1-bromo-3-methylbutane), dispersive solvent (acetone) and internal standard (biphenyl) was rapidly injected into centrifuge tube containing spiked sample using a microvolume syringe in one minute extraction time. The mixture was gently shaken and centrifuged at 4000 rpm for 3 minutes. After centrifugation, organic phase was collected with syringe and sent for GC-FID analysis. The extraction was conducted in triplicate (n = 3).

MAE-DLLME extraction

Parameters such as microwave power, extraction solvent and irradiation time were optimized in the previous study [14]. The volume of 4 mL extraction solvent (acetone) was added into glass bottle containing 10 mL spiked sample. Then, it was closed with cap and microwaved at 200 W for 1.5 minutes. After it was cooling down to room temperature, the spiked sample was shifted into centrifuge tube and centrifuged at 4000 rpm for 5 minutes. Then, 5 mL aqueous phase was transferred into another centrifuge tube and immediately used for DLLME extraction process as described above.

Analytical Performances of DLLME and MAE-DLLME

Analytical parameters including sensitivity, limits of detection (LOD) and limits of quantification (LOQ), precision, accuracy, relative enrichment factor (EF) and relative extraction recovery (ER) were investigated and compared. The validation methods used were followed guideline set by International Conference on Harmonization (ICH) [15]. The validation was conducted in triplicate (n = 3). In this study, the calculation of LOD was performed by analyzing

blank samples which spiked with decreased concentration of PAHs until a peak height of three time higher than the noise level was achieved (S/N=3). For the calculation of LOQ, the blank samples which spiked with decreased concentration of PAHs were analyzed until a peak height of ten time higher than the noise level was achieved (S/N=10).

Accuracy was evaluated by spiking the vegetable sample with the standard solutions of PAHs at three different concentrations in triplicate. The results of spiked samples and spiked distilled water were compared. The precision was studied in terms of intra- and inter-day variability and evaluated at three concentration levels of PAHs. The precision was studied in triplicate (n = 3) during the same day (repeatability) and three different days (intermediate precision) in a week. The precision was expressed as the percentage of relative standard deviation (RSD%).

The extraction recovery (ER) was defined as the ratio of the amount of analyte in sedimented phase (n_{sed}) with the initial amount of analyte in the sample (n_0). The enrichment factor (EF) was defined as the ratio between the concentration of analytes in the sedimented phase (C_{sed}) with the initial concentration of analyte (C_0) within the sample [16]. The relative ERs (or EFs) were defined as ratio of ERs (or EFs) attained by spiking vegetable sample and spiked distilled water. Relative enrichment factor (EF) was defined as ratio of EF obtained by spiked vegetable sample and spiked distilled water within the working range [16].

Real sample analysis

To evaluate the feasibility of the proposed MAE-DLLME in real sample analysis, three types of popular salad organic vegetables, namely cabbage, tomato and carrot, purchased from a local market, were analyzed. The samples were prepared, extracted and analyzed using optimized MAE-DLLME-GC-FID. Relative ER was used to express the efficiency of proposed MAE-DLLME.

Results and Discussion

In this study, the one-at-a-time design has been employed to study the effects of parameters affecting the efficiency of MAE-DLLME. Relative extraction recovery (ER) and relative enrichment factor (EF) were used to express the extraction efficiency.

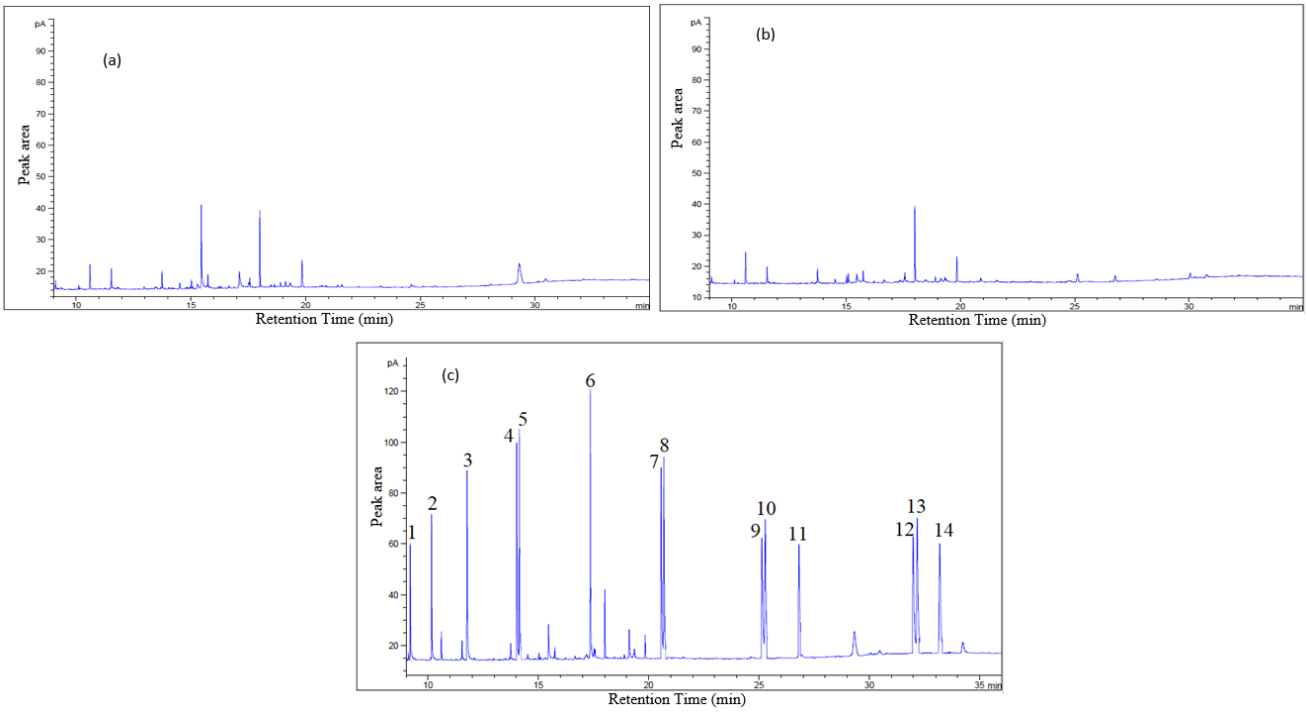
Optimization of DLLME and MAE-DLLME

The optimization of DLLME and MAE-DLLME extractions followed by a gas chromatography-flame ionization detector (GC-FID) for the determination of 13 PAHs in vegetables was discussed in a previous paper [14]. The extraction solvent of 1-bromo-3-methylbutane was found to be the most efficient in extracting the 13 investigated PAHs because of its nonpolar and water-insoluble nature which able to form nonpolar interaction with PAHs. Besides that, the solvent of 1-bromo-3-methylbutane is low toxic and less viscous than other extraction solvents. Low viscosity is more favorable for the extraction of PAHs because high viscosity would slow down the mass transfer thus reduce extraction efficiency [8, 17].

The optimum DLLME conditions were 5.0 mL of sample solution, 30 μL of 1-bromo-3-methylbutane (extraction solvent) and 800 μL of acetone (dispersive solvent) in one minute extraction time. In the MAE-DLLME, the sample was extracted by microwave power of 200 W in acetone for 1.5 minutes of irradiation time at room temperature followed by optimized DLLME [14].

Analytical performances of DLLME and MAE-DLLME

The sensitivity of DLLME and MAE-DLLME were evaluated by comparing chromatograms of blank sample obtained using optimized DLLME, optimized MAE-DLLME and chromatogram of spiked cabbage sample obtained using optimized MAE-DLLME. The results were illustrated in Figure 1. Based on Figure 1(a) and (b), some interferences were not fully abated in MAE-DLLME because there were some peaks still appear on the chromatogram (Figure 1b). However, their peak's number and height were lesser and lower than the interference peaks in DLLME (Figure 1a). Furthermore, no interference in MAE-DLLME was overlapped with the peak of PAHs. Therefore MAE-DLLME has better sensitivity than DLLME.



*Peak No. 1-Biphenyl (Internal Standard), 2-Acenaphthylene, 3-Fluorene, 4-Phenanthrene, 5-Anthracene, 6-Pyrene, 7-benzo[a]anthracene, 8-Chrysene, 9-benzo[b]fluoranthene, 10-benzo[k]fluoranthene, 11-benzo[a]pyrene, 12-Dibenz[a,h]anthracene, 13-Benzo[ghi]perylene, 14-Indeno[1,2,3-cd]pyrene.

Figure 1. Chromatograms of (a) blank cabbage sample using optimized DLLME (b) blank cabbage sample using optimized MAE-DLLME and (c) spiked cabbage sample using optimized MAE-DLLME.
No. 1-Biphenyl (Internal Standard), 2-Acenaphthylene, 3-Fluorene, 4-Phenanthrene, 5-Anthracene, 6-Pyrene, 7-benzo[a]anthracene, 8-Chrysene, 9-benzo[b]fluoranthene, 10-benzo[k]fluoranthene, 11-benzo[a]pyrene, 12-Dibenz[a,h]anthracene, 13-Benzo[ghi]perylene, 14-Indeno[1,2,3-cd]pyrene

The results of the analytical performance of DLLME and MAE-DLLME were summarized in Table 1 and 2. The LOD range was between 0.040 µg/L and 0.400 µg/L in DLLME and 0.020 µg/L and 0.080 µg/L in MAE-DLLME. For LOQ, the range was varied from 0.100 µg/L to 1.200 µg/L in DLLME and 0.080 µg/L to 0.250 µg/L in MAE-DLLME.

Table 1. Analytical performance of DLLME

Analytes	**LOD[a]**	**LOQ[b]**	**Accuracy[c]**	**RSD[d]**	**Relative ER[e]**	**Relative EF[e]**
ACY	8	20	88.16	2.94	88.16	192
FLU	8	20	90.93	4.59	90.93	202
PHE	10	80	82.99	2.79	82.99	195
ANT	10	30	89.40	7.19	89.40	182
PYR	15	100	79.28	4.93	79.28	168
BaA	4	10	77.08	4.89	77.08	179
CHR	4	10	78.52	4.66	78.52	174

Table 1 (cont'd). Analytical performance of DLLME

Analytes	LOD[a]	LOQ[b]	Accuracy[c]	RSD[d]	Relative ER[e]	Relative EF[e]
BbF	40	120	71.77	2.06	71.77	180
BkF	10	20	76.46	1.22	76.46	174
BaP	40	100	77.28	7.50	77.28	166
DahA	10	40	76.50	3.18	76.50	165
BghiP	10	30	80.22	2.84	80.22	166
IcP	10	40	78.56	2.40	78.56	167

[a]: LOD, limit of detection (S/N = 3), 10^{-2} µg/L
[b]: LOQ, limit of quantification (S/N = 10), 10^{-2} µg/L
[c]: Accuracy was obtained by calculating ratio of relative ER of cabbage sample and distilled water sample spiked with 120 µg/L in DLLME and 80 µg/L in MAE-DLLME respectively
[d]: Precision was obtained by calculating ratio of RSD of cabbage sample and distilled water sample spiked with 120 µg/L in DLLME and 80 µg/L in MAE-DLLME respectively
[e]: Relative ER and EF were obtained by calculating the ratio of EF obtained by spiked cabbage sample and spiked distilled water

Table 2. Analytical performance of MAE-DLLME

Analytes	LOD[a]	LOQ[b]	Accuracy[c]	RSD[d]	Relative ER[e]	Relative EF[e]
ACY	2	10	94.74	1.25	94.74	131
FLU	2	8	88.45	2.77	88.45	134
PHE	2	10	92.60	3.07	92.60	126
ANT	2	8	94.09	1.83	94.09	141
PYR	2	8	98.42	2.61	98.42	143
BaA	2	10	94.06	1.79	94.06	136
CHR	2	8	84.12	2.49	84.12	138
BbF	5	20	86.78	2.16	86.78	144
BkF	8	25	93.49	0.77	93.49	145
BaP	5	25	86.46	1.30	86.46	136
DahA	2	8	92.38	1.48	92.38	135
BghiP	4	10	87.46	1.43	87.46	142
IcP	2	8	83.65	1.86	83.65	156

The abbreviations are same as described in Table 1

The precision and the accuracy performances were attained by spiking cabbage sample at 80 µg/L of 13 PAHs in MAE-DLLME and 120 µg/L in DLLME. The precision and accuracy were ranged from 1.22% to 7.50% and 71.77% to 90.93% respectively in DLLME. For MAE-DLLME, the precision was ranged from 0.77% to 3.07% and accuracy was between 83.65% and 98.42%. These results demonstrated that MAE-DLLME is more accurate and repeatable than DLLME. Besides, the relative ERs and EFs of MAE-DLLME were higher than the relative ERs and EFs of DLLME. It may due to the low volume usage of extraction solvent and reduction of matrix interference in MAE-DLLME.

Based on the results in Table 1 and 2, the proposed MAE-DLLME showed better analytical performance than DLLME. This might due to the good sample preparation that eliminated the large matrix impurities from the sample. During the microwave process, the thermal labile matrix impurities would be degraded thus enable high

mass transfer of PAHs from samples into organic phase. Furthermore, the minimum volume of extraction solvent (50 μL) used in DLLME was higher than the minimum volume of extraction solvent (30 μL) used in MAE-DLLME. The reduction of extraction solvent minimized the exposure risk of organic solvent to operator and environment. MAE-DLLME is more cost-effective if large amounts of sample are required to be analysed.

Comparison of analytical performance of MAE-DLLME with other studies

The method performance of developed MAE-DLLME was compared with other methods from literature studies for the determination of PAHs in vegetables. Table 3 shows some analytical features and parameters of the previous studies and developed MAE-DLLME.

Table 3. Comparison of the developed MAE-DLLME with other methods for the determination of PAHs in vegetable samples

Method	Types of ES*	LD_{50} of Solvent (oral, mg/kg)	Organic Solvent Consumption (mL)	Extraction Time (min)	RSD %	Ref
CD-LLE-CC-HPLC-FLD[a]	Cyclohexane, N,N-dimethylformamide–water	>5000, 3000	> 150	>2	NA	[18]
CD-Soxhlet-HPLC-UVD[b]	Cyclohexane/acetone (2:1, v/v)	>5000, 5800	NA	480	4.5-11	[19]
CD-HOLLE-HPLC-FLD[c]	Tetrachloroethane	2629	< 10	0	1.1–8.5	[20]
MAE-DLLME-GC-FID	1-bromo-3-methylbutane	6150	4.83	1	0.77–3.07	This study

"NA" indicating no data; "ES" indicating extraction solvent; [a.] CC-HPLC-FLD: Chemical digestion-liquid-liquid extraction-column chromatography-high performance liquid chromatography-fluorescence detector; [b.] CD-Soxhlet-HPLC-UVD: Chemical digestion-Soxhlet extraction-column chromatography-high performance liquid chromatography-ultraviolet detector; [c.] CD-HOLLE-HPLC-FLD: Chemical digestion-homogeneous liquid-liquid extraction-high performance liquid chromatography-fluorescence detector

It is evident that the developed MAE-DLLME has numerous advantages. No hazardous chemicals were used in developed MAE-DLLME for sample preparation prior to extraction. The matrix interferences in vegetable samples can be minimized by microwave heating without chemical digestion. Low lethal dose (LD_{50}) indicating that the solvent is low toxic and safe to use. The extraction solvent employed in present study is less toxic than literature studies. In addition, MAE-DLLME required small volume of solvent to clean-up and extract the PAHs from one vegetable samples. Moreover, the extraction time is short and the RSD value was very low. Thereby, the developed MAE-DLLME-GC-FID used in this study is a fast, cost-effective and environmentally friendly method for the determination of PAHs in vegetable sample.

Real sample analysis

There are different organic nutrient levels and pollutants in organic vegetables were reported [21]. These organic contents such as nonpolar chlorophylls and carotenes might cause matrix effect in extraction of PAHs from vegetables [22]. Three types of popular salad organic vegetables, namely cabbage, tomato and carrot were analyzed in this study to evaluate the feasibility of the proposed MAE-DLLME in real sample analysis. Relative ER was used to express the efficiency of proposed MAE-DLLME.

The result of extraction of PAHs from real samples is tabulated in Table 4. The spiked blank sample was used as control sample and the analysis was conducted in triplicate. The proposed MAE-DLLME was able to extract 13

PAHs from organic vegetables. The samples of carrot were found to have high concentration of high molecular weight PAHs. This might because high molecular weight PAHs are more likely to adsorb to the soils, thus increase the chance of contamination [23]. Cabbages were found to have the highest concentration of total PAHs compared to tomato and carrot. The large surface area of air exchange in cabbage could facilitate the adsorption of PAHs [23]. According to the product label on the vegetables, the vegetable samples were planted in Johor and Negeri Sembilan of Malaysia. After harvested, these vegetables were transported to local market in Klang, Selangor of Malaysia. The distance between plantation and market is more than 100 kilometers. Therefore, the contamination of PAHs in these vegetables were mainly due to the long distance transportation.

Table 4. PAHs concentrations (µg/kg, fresh weight) in organic vegetables (n = 3)

Sample	Cabbage	Tomato	Carrot
ACY	0.049	0.044	0.161
FLU	0.113	0.139	n.d.
PHE	0.090	n.d.	n.d.
ANT	0.157	0.199	n.d.
PYR	0.368	0.402	0.184
BaA	0.223	0.167	0.231
CHR	0.195	n.d.	0.116
BbF	0.356	0.345	0.410
BkF	0.322	n.d.	n.d.
BaP	0.372	n.d.	0.278
DahA	0.560	0.192	0.196
BghiP	n.d.	n.d.	0.086
IcP	0.214	n.d.	0.621
Σ13PAH	2.969	1.488	2.283

n.d.: not detected

Conclusion

In the present study, an analytical method of MAE-DLLME coupled with GC-FID for clean-up and extraction of 13 PAHs from vegetable samples has been developed. The analytical performances of DLLME and MAE-DLLME were validated and compared. The results showed that both methods exhibited low limits of detection and limits of quantification, good precision, accuracy, extraction recovery and enrichment factor. Although MAE-DLLME required the consumption of organic solvents and processing time in microwave process, the overall performance of MAE-DLLME is better than DLLME due to the thermal degradation of matrix components. In conclusions, MAE coupled with DLLME successfully increased extraction efficiency by degrading matrix interference and reducing volume of extraction solvent. The developed MAE-DLLME is preferable for analysis of PAHs in food sample with complex matrices. With the recent development of automation technology, the automated MAE-DLLME procedure should be developed in the future.

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