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Effect of moisture on the extraction efficiency of polycyclic aromatic hydrocarbons from soils under atmospheric pressure by focused microwave-assisted extraction

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Abstract

The effects of the moisture content in the original, air-dried and re-moistened matrices as well as solvent have been studied on the recovery of polycyclic aromatic hydrocarbons (PAHs) from soil by a focused microwave-assisted extraction (FMAE) method. Solvents selected for the extractions were cyclohexane–acetone (1:1), hexane–acetone (1:1) and dichloromethane. On the extraction of 20-day aged spiked soil, the highest recovery was found by applying hexane–acetone mixture. Spiked soil sample, quality control sample and real soil sample were used for the evaluation of moisture effect. It indicated that the presence of water in the soil is important for the recovery enhancement of PAHs and with this presence it is possible to avoid drying step with the FMAE technique. A comparison between microwave and 16-h Soxhlet methods has been made. It evidenced that the microwave-assisted extraction under ambient atmospheric pressure is a suitable alternative to Soxhlet extraction for the analysis of PAHs in soils. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Extraction methods; Microwave-assisted extraction; Soil; Environmental analysis; Polynuclear aromatic hydrocarbons

1. Introduction

Sample preparation is a critical step in most analytical cycles. Reliable trace-level analysis begins with the quantitative extraction of the analytes from the sample matrix in a manner, which is compatible with the rest of the analytical procedure. The most widely used liquid–solid extraction such as the Soxhlet technique requires 6 to 48 h, consumes a large volume of organic solvents and is laborious. In

the past few years, methods established, such as supercritical fluid extraction (SFE) [1,2], pressurized liquid extraction (PLE) [3] and microwave-assisted extraction (MAE), have been used to reduce the volume of solvents required, improve the precision of analyte recoveries, reduce extraction time and decrease costs. MAE has been reported as an alternative sample preparation technique for various solid samples by Granzler and co-workers [4,5]. The application of microwave energy to the sample preparations may be performed in two-ways: pressurized microwave-assisted extraction (PMAE) in a closed-system under pressure and focused microwave-assisted extraction (FMAE) in an open-system

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under atmospheric pressure. Most of the studies have dealt with closed vessels and few studies have been reported on the extraction of organic pollutants in a focused open-vessel system. The former technology (PMAE) has been employed for the extractions of different environmental pollutants such as hydrocarbons (HCs) [6], polycyclic aromatic hydrocarbons (PAHs) [7,8], organochlorine pesticides (OCPs) [5,9–13], polychlorinated biphenyls (PCBs) [14], dioxins/furans [15], triazines [16] and alkyl/aryl phosphates [17], in soil, sediment and sludge sample matrices. The disadvantage of the closed vessel method is that the sample must be sealed well inside the microwave and pressure compatible vessel before extraction takes place. In addition, once the extraction is finished, the vessels must be cooled to room temperature before they can be opened. These steps considerably increase the overall sample treatment time. The latter technology (FMAE) has also been applied to the extractions of PAHs [18], PCBs [14], pesticides [19], organometallic compounds [20–23], and dioxins/furans [24] from spiked, real, and reference material samples.

PAHs, a widely distributed extensive group of compounds, are serious and ubiquitous environmental contaminants [25]. Because of their high mutagenicity and carcinogenicity, the existent level of PAHs in a wide range of environmental samples has brought high interest among analytical chemists [26]. The parameters studied in the optimization of MAE of PAHs are: temperature, pressure (for closed vessel system), extraction time, microwave power, solvent nature, and solvent quantity. As an example, an extraction time increase from 5 to 10 min at 30 W in an open vessel resulted in higher recoveries of PAHs from certified sediment [27]. A contrary result was observed for PCBs from sludge samples indicating the longer extraction time had no enhancement on recoveries [14]. Budzinski and co-workers [28,29] reported experimental conditions have been optimized with different parameters, such as time and power of irradiation, nature of solvent, percentage of water, adjusted using the SRM 1941a as a test matrix. Among all the parameters, the quantity of re-moistened water added to the dry sample matrix is of primary importance to maximize the recoveries.

Applications of this technique have been evaluated in our research projects such as determination of

PAHs [7,8,30], PCBs [31], and chlorinated dioxin/furans [15] from environmental samples. In the present work, stability of PAHs in the presence of sample matrix and effect of moisture and solvent on the extraction efficiency of aged PAHs spiked soil in an open vessel focused microwave system were studied. The best condition from the experiment was applied to the reference material and real samples. In the study of moisture effect, soil with original water content, air-dried soil and remoistened soil was used. The results were compared with Soxhlet method developed by the Environmental Technology Centre [32], Environment Canada.

2. Experimental

2.1. Solvents and reagents

Solvents used in this study were cyclohexane (non-UV, Caledon, Canada), hexane (HPLC/Spectro, Tadia, USA), acetone (HPLC/Spectro, Tadia), dichloromethane (HPLC/Spectro, Tadia) and benzene (distilled in glass, Caledon). Glasswool is loosely placed in a column (30 cm×2.5 cm I.D.) and eluted with two column volumes of dichloromethane followed by two columns of hexane. The clean glasswool is then placed in a pre-cleaned beaker, covered loosely with hexane-rinsed aluminum foil and allowed to air dry; overnight in a fumehood. The dry glasswool is kept in an oven at temperature between 110 and 130°C until ready for use. The glass fiber filter is rinsed with 3 ml hexane before use. Granular, anhydrous sodium sulfate (Riedel-de Haen, Germany), prewashed with hexane and dichloromethane, in a solvent rinsed aluminum foil covered beaker was oven-dried 50°C for at least 1 h before conditioning overnight at 225°C. Silica gel (0.063–0.2 mm, Merck, Germany) was washed with hexane and dichloromethane as described and oven-dried at 50°C for a minimum of 1 h in a foil-covered beaker, then conditioned at 225°C for 5 h.

2.2. Standards, reference materials and natural matrices

The 16 native PAHs {solutions of naphthalene

(NP), acenaphthylene (AL), acenaphthene (AE), fluorene (FL), phenanthrene (PHE), anthracene (AN), fluoranthene (FLT), pyrene (PY), benzo[*a*]anthracene [B(*a*)A], chrysene (Chry), benzo[*b*]fluoranthene [B(*b*)F], benzo[*k*]fluoranthene [B(*k*)F], benzo[*a*]pyrene [B(*a*)P], indeno[1,2,3-*cd*]pyrene (IP), dibenzo[*a,h*]anthracene [D(*ah*)A] and benzo[*ghi*]perylene [B(*ghi*)P]} were purchased from Supelco and AccuStandard. The internal standard ($[^2\text{H}_{10}]$ fluoranthene) and seven surrogates ($[^2\text{H}_{10}]$ acenaphthene, $[^2\text{H}_{10}]$ anthracene, $[^2\text{H}_{10}]$ pyrene, $[^2\text{H}_{12}]$ benzo[*a*]anthracene, $[^2\text{H}_{12}]$ benzo[*a*]pyrene, $[^2\text{H}_{14}]$ dibenzo[*a,h*]anthracene, and $[^2\text{H}_{12}]$ benzo[*ghi*]pyrene) were obtained from Cambridge Isotope (USA) or C/D/N Isotopes (Canada). The internal standard and surrogate solutions used to spike all the samples prior to the extraction were prepared at the 10 $\mu\text{g}/\text{ml}$ level in benzene for each component.

Uncontaminated soil used for spiking was collected from an uncultured hill site in central Taiwan. Soils were transported to the laboratory and sieved to 300–500 μm grain size without any drying process to maintain its original moisture content. Half a portion of the sieved soil was dried outdoors under ambient condition for 3 days and used as “air-dried soil”. Both original and dry soils were kept in amber vials inside a nitrogen-filled plastic bag and refrigerated until required. Characteristics of this uncontaminated soil are: pH, 7.6; organic carbon content, 3.38%; sand, 9%; slit, 81%; clay, 10%; and moisture, 18.5% (original) and 1.0% (air-dried). Preparation of spiked soil was as follows: adding 100 μl of the 10 ppm PAH solution evenly onto 1.0 g of uncontaminated soils (both original and dry soils) that were then stored in a screw-capped amber bottle at ambient temperature for 20 days equilibrium. The contaminated soil KS1 (pH, 7.3; organic carbon content, 2.93%; sand, 12%; slit, 79%; clay, 9%; and moisture, 15.3% and 1.6% after air drying) was sampled from a petroleum industrial zone, and KS2 (pH, 5.7; organic carbon content, 1.81%; sand, 22%; slit, 68%; clay, 10%; and moisture, 15.2% and 2.1% after air drying) was obtained in an urban area beside a gas station in southern Taiwan. A quality control soil sample (moisture, 0.6%), with reference values, was provided by the Environmental Technology Center, Environment Canada.

2.3. Extractions

The samples were analyzed according to the procedures shown in the flow chart in Fig. 1. Reference material and real soils were spiked with 100 μl of the surrogates solution (1.0 $\text{ng}/\mu\text{l}$) prior to the extractions. All samples (1.0 g on the basis of dry mass) were subjected to microwave and Soxhlet extractions. The extracts were filtered through anhydrous sodium sulfate and concentrated to a volume of 3–5 ml by rotary evaporation under reduced pressure at 50°C for subsequent silica gel column cleanup.

2.3.1. Microwave extraction

A Prolabo microwave equipment (Soxwave 100, 2450 MHz) equipped with a programmable heating

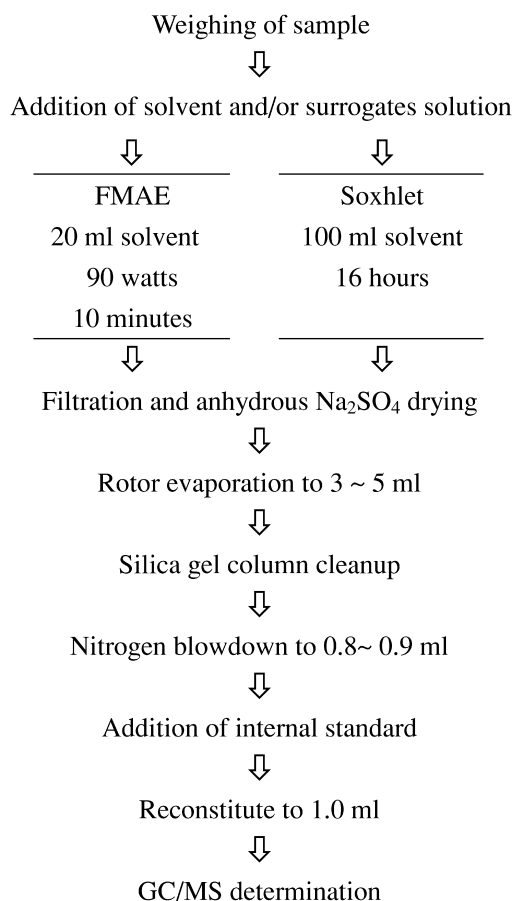


Fig. 1. The flow chart representing sample analysis procedure.

power from 0 to 300 W with 5% increments was used. Sample was weighed and placed in a pre-washed cellulose thimble and inserted into a 250-ml quartz extraction cell. All the microwave extractions were performed in a 20 ml of solvent (cyclohexane–acetone, 1:1, hexane–acetone, 1:1, or dichloromethane) under 90 W of irradiation power for 10 min.

2.3.2. Soxhlet extraction

Soxhlet extractions were performed using 1.0-g portions of soil to which 5.0 g of anhydrous sodium sulfate was added in a pre-washed cellulose thimble and inserted into a 50-ml Soxhlet extractor. The apparatus was fitted with a 150-ml flask containing 100 ml of cyclohexane that was boiled with a heating mantle and refluxed for 16 h with 5–6 cycles/h.

2.4. Cleanup

An open column (25 cm×1.4 cm I.D.) plugged with clean glasswool. The column was filled with approximately 7 g of activated silica gel and topped with 2 g of anhydrous sodium sulfate. A 10-ml volume of hexane was used to pre-wash the column and allowed to drain to bed level. The raw extract was transferred quantitatively to the column. The column was eluted with 5 ml of hexane, followed by 5 ml of benzene. The PAH fraction was then eluted with 10 ml of benzene into a calibrated centrifuge tube. The PAH fraction was concentrated by nitrogen blow-down at ambient temperature in a fumehood to just below 800 μ l. After addition of 100 μ l of [$^2\text{H}_{10}$]fluoranthene (10 ng/ μ l), the solution was reconstituted to 1.0 ml with benzene prior to analysis by gas chromatography–mass spectrometry (GC–MS).

2.5. Determination

A 1- μ l volume of the aliquot was directly injected into a Hewlett-Packard 5890 Series II GC system which was equipped with a HP-5 capillary column (30 m×0.25 mm, 0.25 μ m thickness of 5% phenyl–95% methylsilicone) and a 10 m×0.5 mm deactivated fused-silica precolumn. The GC oven program started at 90°C with a 1-min hold, 90°C to 200°C at 20°C/min, 200°C to 210°C at 3°C/min, 210°C to 290°C at 5°C/min, 10 min isothermal. A Hewlett-

Packard 5971 mass-selective detector was operated at 70 eV electron energy with a source temperature at 280°C to monitor PAHs in the selected ion monitoring (SIM) mode. The instrument was tuned daily with perfluorotributyl amine (PFTBA) introduced via the calibration gas valve. Data were collected by a HP G1034C MS ChemStation Software.

The linear dynamic range was established by five-point calibration curve (e.g., 10.0, 5.00, 0.50, 0.01, and 0.001 ng/ μ l). The calibration solutions consist of an internal standard [$^2\text{H}_{10}$]fluoranthene at a level of 1.0 ng/ μ l. A daily calibration standard (1.00 ng/ μ l) was used to quantitate sample analyte concentration.

3. Results and discussion

3.1. PAH recovery of concentration steps and stability during microwave irradiation

Fig. 2 represents the PAHs (100 μ l of 10.0 ng/ μ l standard solution in 20 ml of solvent) recovered from concentration, column cleanup and exposure under microwave irradiation. The recoveries of PAHs in these extraction solvents exhibit similar trends. The concentration steps with or without microwave irradiation (processes I and II in Fig. 2) showed no significant difference. The lower recoveries and higher standard deviations of acenaphthylene, acenaphthene and fluorene might be due to their higher volatility. Relatively higher percentage losses of dibenzo[*a,h*]anthracene, benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene were observed after silica gel cleanup (process III). This loss may be related to the structures of the compounds that are heavy and suffer from some interaction in the column. The overall recoveries of 3–6-membered rings are used for comparison and subsequent discussion.

3.2. Matrix interference on the PAH quantification

The quantification of PAHs in the presence of sample matrix may also be affected in terms of matrix interference. A non-spiked uncontaminated soils were extracted by both FMAE and Soxhlet methods based on the procedures shown in Fig. 1. The PAHs standard was then spiked into the obtained

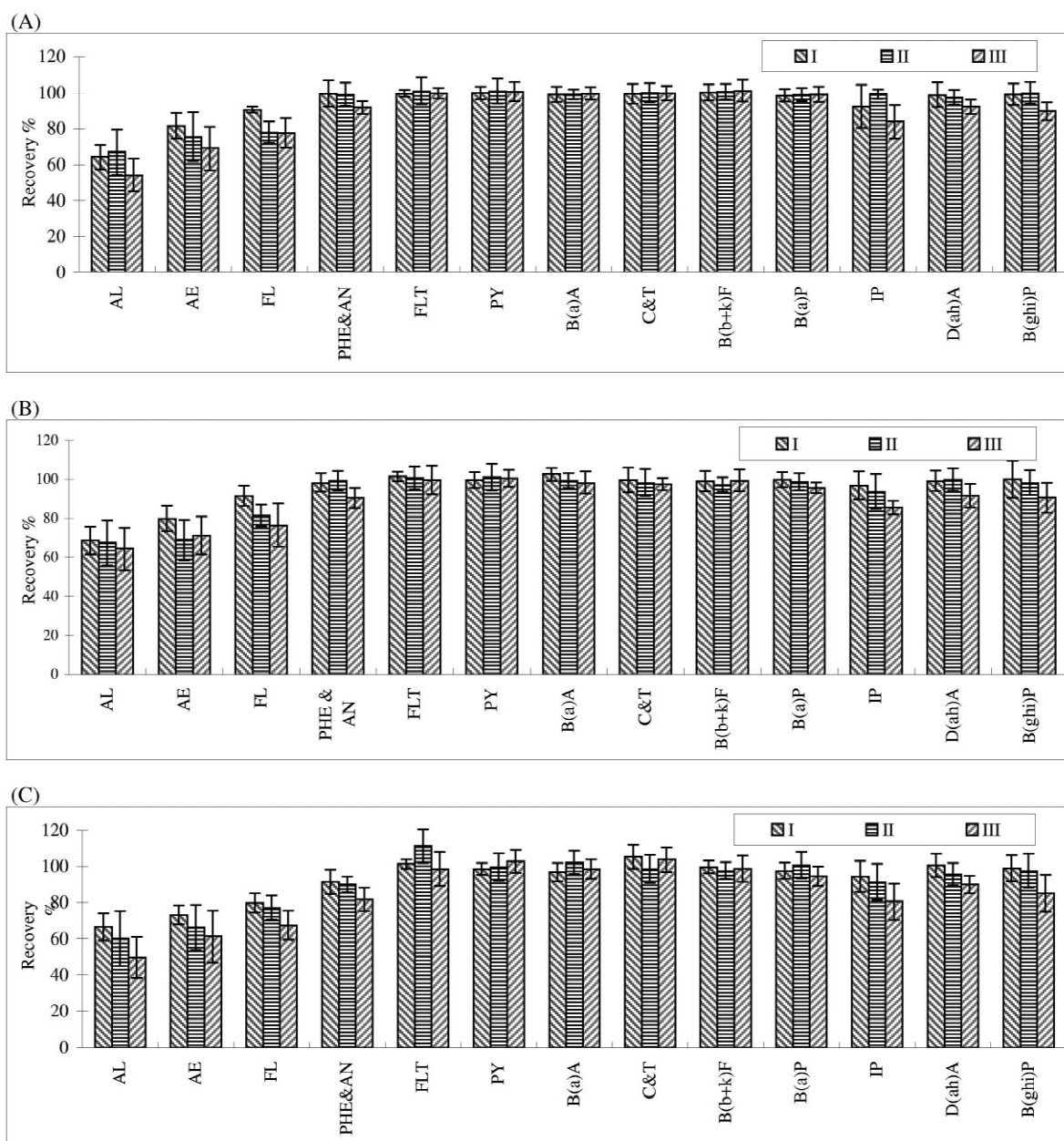


Fig. 2. PAH recoveries for individual step: (A) in cyclohexane–acetone (1:1); (B) in hexane–acetone (1:1) and (C) in dichloromethane. (I, With rotor evaporation to 3–5 ml followed by nitrogen blowdown to 1.0 ml; II, under 90 W microwave irradiation for 10 min followed by process I; III, process II followed by silica gel cleanup and nitrogen blowdown).

final column cleaned extract before GC–MS quantification. Comparison of the original and dry soil matrix effect, revealed no significant difference observed on the recovery. The average recoveries of

3–6-membered ring PAHs were in a range between 96.0 and 100.5% with standard deviations smaller than 7.0%. A higher interference was observed in the early eluting of three 2-membered ring PAHs.

Table 1
Stability test of PAHs in the presence of soil matrix suspension under microwave irradiation

PAH	Recovery (%) (based on spiked amount 1.0 µg/g and triplicate analysis) (average±SD)							
	FMAE						Soxhlet, cyclohexane	
	Cyclohexane–acetone (1:1)		Hexane–acetone (1:1)		Dichloromethane			
	Original matrix	Air-dried matrix	Original matrix	Air-dried matrix	Original matrix	Air-dried matrix	Original matrix	Air-dried matrix
AL	55.6±5.6	65.7±7.8	61.7±17.9	51.3±3.5	28.2±3.5	33.8±8.5	18.9±12.1	22.1±5.9
AE	63.6±7.6	72.3±8.5	68.7±15.6	77.3±6.5	37.9±3.7	43.1±8.9	45.7±5.9	38.9±6.9
FL	57.3±3.4	76.8±9.5	70.5±5.2	75.7±5.7	28.9±4.6	58.9±6.5	37.1±5.8	53.2±9.6
PHE and AN	91.5±7.9	88.5±10.1	99.7±6.0	79.8±4.4	63.9±7.5	58.9±6.0	85.3±8.9	94.5±10.6
FLT	91.7±6.6	110.3±3.5	101.3±8.1	95.1±3.8	87.9±3.2	84.3±6.9	101.2±9.1	98.3±8.7
PY	90.4±7.3	96.5±9.4	106.5±4.3	104.2±7.9	90.7±2.7	99.6±4.4	92.4±6.7	99.5±8.9
B(a)A	95.0±8.7	108.3±7.5	108.3±5.6	111.5±11.2	102.8±1.6	98.6±5.8	102.3±6.3	97.1±3.6
Chrysene and Triphenylene	91.2±6.5	101.6±4.4	115.5±5.7	103.6±9.1	101.5±6.4	93.8±7.6	99.2±8.9	105.6±6.8
B(b+k)F	85.3±9.4	97.9±13.8	107.5±4.3	85.6±13.4	81.3±8.9	103.4±8.5	93.1±5.7	99.4±6.7
B(a)P	91.2±9.5	98.8±6.1	106.7±6.7	71.5±8.8	110.6±1.1	108.9±4.1	98.5±5.6	105.3±9.9
IP	89.3±5.3	109.2±5.2	99.5±5.4	71.2±6.7	100.6±5.5	95.7±2.5	87.6±7.8	95.8±6.3
D(ah)A	85.8±7.7	83.5±3.3	90.3±5.7	75.8±7.6	85.1±5.7	71.2±5.3	95.3±10.1	81.7±5.8
B(ghi)P	87.6±10.6	87.4±8.5	88.6±3.5	72.3±12.6	77.3±4.4	67.8±7.3	87.8±7.3	86.5±6.7
Average of 3~6-ring PAHs	89.9±7.9	98.2±7.2	102.4±5.5	87.1±8.6	90.2±4.7	88.2±5.8	94.3±7.6	96.4±7.4

Table 2
PAHs recovered from 20-day aged spiked soil by focused microwave-assisted and Soxhlet extractions

PAH	Recovery (%) (based on spiked amount 1.0 µg/g and triplicate analysis) (average±SD)									
	FMAE							Soxhlet, cyclohexane		
	Cyclohexane–acetone (1:1)		Hexane–acetone (1:1)			Dichloromethane				
	Original matrix	Air-dried matrix	Original matrix	Air-dried matrix	Re-moistened matrix ^a	Original matrix	Air-dried matrix	Original matrix	Air-dried matrix	Re-moistened matrix ^a
AL	45.5±7.7	21.3±8.9	42.7±6.0	20.0±5.6	38.6±6.8	20.2±9.8	20.8±6.5	15.2±7.5	14.6±7.4	10.3±8.8
AE	39.6±4.6	23.4±10.4	48.7±8.9	24.1±7.2	47.4±9.5	19.1±11.2	34.5±2.3	17.2±4.7	13.8±8.7	15.6±10.6
FL	50.3±8.4	44.1±8.6	55.8±6.0	67.0±4.3	46.9±8.4	36.9±3.6	34.4±13.9	25.2±2.7	31.7±6.7	40.1±8.4
PHE and AN	61.2±8.7	50.4±11.7	76.8±2.8	44.6±7.1	68.8±3.7	44.1±4.8	28.2±2.2	34.7±2.9	32.9±8.9	36.9±7.5
FLT	77.2±2.6	77.5±4.5	87.9±4.9	82.2±6.5	81.3±7.2	91.5±5.9	58.3±1.5	85.6±4.2	61.7±6.2	55.4±12.1
PY	80.7±6.9	73.0±8.9	98.1±6.5	75.9±8.4	82.5±6.1	88.6±5.1	54.9±5.6	76.7±4.3	48.7±9.6	58.6±7.1
B(a)A	85.3±9.2	80.8±7.9	91.3±4.3	79.6±9.5	85.6±5.5	89.4±11.9	50.8±8.5	106.9±2.8	53.6±6.4	47.3±7.4
Chrysene and Triphenylene	75.5±4.7	77.8±3.2	85.6±5.2	67.7±6.3	80.3±3.1	81.7±4.4	59.2±5.5	84.3±5.3	49.2±7.5	43.5±5.1
B(b+k)F	78.5±7.1	88.4±15.2	83.4±6.6	71.1±9.7	79.2±10.1	75.7±4.3	59.1±5.3	67.3±9.5	47.0±1.7	45.6±4.3
B(a)P	81.2±3.8	78.0±10.7	77.3±5.9	58.9±11.7	57.3±8.9	47.5±7.7	39.8±4.1	61.2±6.5	42.9±9.1	39.8±7.8
IP	77.8±1.1	61.5±6.5	81.3±13.5	57.1±3.7	65.4±5.2	74.5±11.7	34.2±12.5	77.2±2.5	34.4±6.8	38.7±8.9
D(ah)A	75.6±11.6	68.3±11.1	72.3±5.1	61.5±7.3	73.8±2.8	63.4±18.2	42.3±16.7	68.2±9.8	39.0±10.1	43.1±9.2
B(ghi)P	69.8±5.9	51.9±5.3	82.7±3.0	64.1±2.0	69.1±5.6	58.3±15.5	23.6±12.1	50.1±5.6	23.3±11.6	41.6±13.5
Average of 3~6-ring PAHs	76.3±6.2	70.8±8.5	83.7±5.8	66.3±7.2	74.3±5.8	71.5±8.9	45.0±7.4	71.2±5.3	43.3±7.8	45.1±8.3

^a Air dried soil was remoistened by adding water to 18.5% before extraction.

3.3. Stability of PAHs in the presence of matrix under microwave irradiation

Decomposition, transformation and catalytic reaction of compounds may take place while using microwave radiation to irradiate the solvent–matrix suspension [11]. Exposure to temperature, interaction of analyte and/or solvent, and catalytic reactions induced by the matrix inside the microwave cavity may influence the recoveries. To determine whether or not the microwave extraction conditions pose a problem, PAH standard was spiked into the mixture of soil matrix–solvent suspension immediately following the microwave irradiation. Results of the PAH stability test are listed in Table 1. The original matrix yielded the highest recovery whereas the lowest recovery was found in the air-dried soil suspension while using hexane–acetone as a solvent. In cyclohexane–acetone, the dry matrix suspension

showed higher recovery than that in original wet matrix. No significant matrix effect could be observed among these experimental conditions.

3.4. Solvent and moisture effects

Due to the mechanism of microwave heating the selection of the solvent is dependent upon its degree to absorb microwave energy, i.e., dissipation factor $\tan \delta$ [33]. In this study, cyclohexane–acetone, hexane–acetone and dichloromethane were selected for the evaluation of PAH extraction efficiency from spiked soils. Based upon the results in Table 2, hexane–acetone mixture was the solvent chosen to extract the quality control and real samples.

In most of the reported environmental analysis studies, solid samples are dried before extraction. After being sampled, soils and sediments are pre-treated with freeze–drying in order to obtain

Table 3
PAHs found in quality control sample by focused microwave-assisted and Soxhlet extraction methods

PAH	$\mu\text{g/g}$ (RSD, %)				Reference value ($\mu\text{g/g}$)
	FMAE		Soxhlet		
	Original matrix	Re-moistened ^a matrix	Original matrix	Re-moistened ^a matrix	
AL	1.7 (8.5)	1.3 (12.7)	2.9 (9.8)	1.2 (25.9)	
AE	2.2 (5.7)	3.9 (23.3)	3.3 (11.3)	2.9 (18.6)	
FL	5.5 (5.6)	5.8 (6.3)	6.7 (7.6)	6.4 (11.6)	
PHE and AN	18.9 (10.8)	17.7 (3.9)	15.3 (8.7)	15.1 (5.6)	16.8 ^b
FLT	15.9 (6.3)	17.1 (3.2)	16.6 (8.4)	14.8 (4.4)	17.3
PY	14.5 (7.2)	15.1 (8.5)	13.5 (6.6)	14.2 (6.7)	13
B(a)A	6.9 (7.9)	6.1 (3.1)	5.6 (11.8)	6.3 (4.2)	6.1
Chrysene and Triphenylene	6.6 (10.5)	7.2 (4.7)	7.4 (9.5)	8.1 (8.5)	
B(b+k)F	9.7 (6.8)	10.2 (6.4)	11.2 (13.2)	12.5 (7.6)	9.6 ^c
B(a)P	5.5 (7.1)	4.3 (5.3)	4.9 (9.3)	3.9 (3.8)	5.7
IP	5.2 (5.1)	4.9 (6.7)	5.1 (3.4)	4.3 (7.4)	
D(ah)A	1.9 (10.7)	2.2 (9.2)	0.6 (5.8)	2.6 (7.1)	
B(ghi)P	3.4 (8.2)	3.1 (10.5)	2.8 (15.1)	2.7 (9.6)	
Total (3–6 ring)	91.4 (8.1)	90.7 (5.6)	86.3 (9.3)	88.6 (6.4)	
% Surrogate recovered (average) \pm SD					
AE*	56.8 \pm 11.3	79.2 \pm 12.5	93.6 \pm 13.6	83.2 \pm 16.4	
AN*	79.9 \pm 16.5	85.6 \pm 8.9	125.3 \pm 21.3	102.5 \pm 7.6	
PY*	95.6 \pm 11.7	91.3 \pm 3.6	119.8 \pm 9.8	109.6 \pm 11.5	
B(a)A*	109.4 \pm 8.5	89.7 \pm 7.4	103.4 \pm 13.1	116.5 \pm 7.8	
B(a)P*	110.5 \pm 10.9	106.8 \pm 6.8	113.8 \pm 10.5	125.7 \pm 10.8	
D(ah)A*	83.1 \pm 7.3	89.2 \pm 8.5	120.6 \pm 8.2	129.8 \pm 13.6	
B(ghi)P*	78.6 \pm 8.4	81.5 \pm 3.2	116.7 \pm 16.7	108.9 \pm 9.7	

^a Soil sample was remoistened to 18.5% of water before extraction.

^b Reference value of PHE.

^c Sum of reference value of B(b)F (6.0 $\mu\text{g/g}$) and B(k)F (3.6 $\mu\text{g/g}$). All analyses were performed in triplicate.

homogenous matrices, convenient storage, avoidance from sample's evolution and improvement in the efficiency of conventional extraction processes such as Soxhlet method [34]. For a solid sample such as soil and sediment that contain residue water, formation of gas bubbles of the moisture existing inside the sample which has resulted from local superheating by microwave irradiation, this might cause the expansion of pores that results in the extraction solvent penetrating into matrix and/or liberation of target molecules out to the solvent [20,33]. In the present work, it has appeared interesting to study the influence of the moisture content on the recovery of PAHs using FMAE under ambient pressure. Comparisons were made between original wet soil and air-dried counterparts. However, the original and air-dried moieties might exhibit different characteristics in terms of the interaction between soil matrix

and PAHs, mass transfer rate and possible intrinsic microbial activity [35]. Therefore, remoistening of the original soil after air-dried was also used for comparison.

Results of the extractions of 20-day aging spiked original, air-dried and remoistened matrices by different solvents are listed in Table 2. In all experimental conditions, PAHs recovered from original matrix were higher than that from air-dried soil. Within the results in FMAE: the highest recovery of PAHs occurred after the extraction of original matrix in hexane–acetone; the lowest recovery was found on the extraction of air-dried soil in dichloromethane; and, the recovery was enhanced by the remoistening of the air-dried soil before extractions took place. In Soxhlet extraction, the remoistening procedure did not show any significant increase on PAH recovery.

Table 4
PAHs found in contaminated soil sample KS1 by focused microwave-assisted and Soxhlet extraction methods

PAH	$\mu\text{g/g}$ (RSD, %)					
	FMAE			Soxhlet		
	Original matrix	Air-dried matrix	Re-moistened matrix*	Original matrix	Air-dried matrix	Re-moistened matrix*
AL	23.6 (15.6)	10.3 (27.1)	9.7 (21.2)	16.5 (29.5)	11.4 (31.4)	8.5 (19.6)
AE	11.2 (21.3)	6.5 (15.4)	3.8 (13.5)	8.6 (16.8)	9.5 (24.1)	9.1 (20.5)
FL	4.4 (16.2)	3.9 (11.5)	2.9 (9.6)	3.6 (11.3)	3.8 (13.5)	4.1 (12.1)
PHE and AN	15.9 (7.9)	11.8 (12.8)	13.3 (7.5)	14.1 (10.8)	12.3 (15.4)	11.4 (17.2)
FLT	6.2 (7.4)	4.3 (11.6)	5.8 (9.7)	5.6 (8.5)	5.1 (9.6)	5.6 (10.2)
PY	5.1 (5.8)	4.1 (10.2)	4.7 (6.9)	4.3 (9.4)	4.9 (7.3)	4.2 (8.5)
B(a)A	1.9 (9.2)	2.2 (5.3)	2.0 (3.3)	2.5 (5.9)	2.2 (9.7)	1.9 (7.3)
Chrysene and Triphenylene	3.5 (8.7)	3.3 (7.8)	3.7 (2.1)	3.9 (8.7)	2.8 (10.1)	3.0 (8.4)
B(b+k)F	4.2 (9.5)	5.1 (5.7)	4.6 (3.9)	3.1 (5.8)	3.6 (7.4)	2.8 (6.3)
B(a)P	3.1 (8.2)	2.5 (13.6)	3.3 (9.7)	2.8 (14.4)	1.2 (16.9)	2.1 (12.5)
IP	1.0 (13.6)	0.6 (16.2)	1.3 (12.8)	0.7 (20.5)	0.5 (26.4)	0.7 (31.2)
D(ah)A	0.2 (15.9)	–	0.1 (28.3)	–	0.1 (39.5)	–
B(ghi)P	0.1 (19.5)	–	–	–	–	–
Total (3–6 ring)	45.6 (9.4)	37.8 (10.5)	41.7 (7.2)	40.6 (9.9)	36.5 (12.0)	35.8 (12.4)
% Surrogates recovered (average) \pm SD						
AE*	79.2 \pm 12.5	56.8 \pm 16.4	73.5 \pm 13.4	64.3 \pm 16.9	70.6 \pm 18.7	66.5 \pm 12.1
AN*	85.6 \pm 8.9	79.9 \pm 7.6	80.7 \pm 10.1	75.4 \pm 9.9	72.7 \pm 15.5	69.7 \pm 14.3
PY*	91.3 \pm 3.6	95.6 \pm 11.5	89.9 \pm 7.2	87.6 \pm 6.3	90.6 \pm 7.8	85.2 \pm 8.7
B(a)A*	89.7 \pm 7.4	109.4 \pm 7.8	95.3 \pm 5.6	112.6 \pm 10.5	96.8 \pm 8.4	89.4 \pm 6.8
B(a)P*	106.8 \pm 6.8	110.5 \pm 10.8	87.2 \pm 13.2	105.9 \pm 8.8	121.3 \pm 15.9	110.5 \pm 19.2
D(ah)A*	89.2 \pm 8.5	83.1 \pm 13.6	79.6 \pm 6.5	101.5 \pm 7.4	92.1 \pm 6.6	91.6 \pm 8.5
B(ghi)P*	81.5 \pm 3.2	78.6 \pm 9.7	73.5 \pm 5.3	85.8 \pm 6.7	90.1 \pm 7.1	79.8 \pm 10.3

*Air-dried soil was remoistened with water to 18.5% before extraction. All analyses were performed in triplicate.

3.5. Application to other matrices

FMAE (conditions: 20 ml of hexane–acetone, 1:1, 30 W microwave power, 10 min) and Soxhlet methods (conditions: 100 ml of cyclohexane, 16 h) have been applied to the extractions of PAHs from quality control soil sample and re-moistened counterpart (deuterated PAH surrogates have been added prior to extraction). The detailed results of triplicate analyses for each PAH and recovery of surrogate are listed in Table 3 and are in a good agreement with reference values. The total values of 3–6-membered ring PAHs obtained from both methods and both matrices are similar (in a range of 86.3 to 91.4 $\mu\text{g/g}$) with no difference is shown. The addition of water does not seem to affect extraction efficiency, which might be due to the fine grain size of the quality control (QC) sample [29]. Surrogate recovered from

Soxhlet method is higher than that from FMAE. However the percentage recoveries and relative standard deviations are ranged in an acceptable level.

The results of contaminated soil KS1 are summarized in Table 4. The total amount of 3–6-membered ring PAHs extracted from original, air-dried and re-moistened soils by FMAE are 45.6, 37.8 and 41.7 $\mu\text{g/g}$, respectively, and those extracted by Soxhlet are 40.6, 36.5 and 35.8 $\mu\text{g/g}$, respectively. Within the results of FMAE, PAHs recovered from re-moistened soil (41.7 $\mu\text{g/g}$) is 8.6% less than that from original soil (45.6 $\mu\text{g/g}$). This decrease might be due to the vaporization during the air-drying process [36]. The amount of PAHs recovered is 10% higher from remoistened matrix than that from air-dried counterpart by the microwave method (41.7 vs. 37.8 $\mu\text{g/g}$). However, this is not the case for Soxhlet extraction: the result obtained from re-moistened soil

Table 5
PAHs found in contaminated soil sample KS2 by focused microwave-assisted and Soxhlet extraction methods

PAH	$\mu\text{g/g}$ (RSD, %)					
	FMAE			Soxhlet		
	Original matrix	Air-dried matrix	Re-moistened matrix*	Original matrix	Air-dried matrix	Re-moistened matrix*
AL	2.11 (13.2)	1.17 (23.5)	1.79 (16.2)	3.02 (31.3)	1.82 (26.3)	2.26 (18.5)
AE	3.15 (15.9)	2.03 (19.7)	1.95 (15.4)	5.14 (18.7)	3.36 (20.5)	2.89 (26.4)
FL	0.71 (9.8)	0.64 (12.8)	0.60 (10.6)	0.67 (14.2)	0.59 (17.1)	0.54 (11.5)
PHE and AN	0.59 (11.4)	0.41 (9.7)	0.49 (8.8)	0.65 (18.1)	0.55 (13.4)	0.52 (10.6)
FLT	0.23 (3.2)	0.18 (8.9)	0.21 (7.5)	0.16 (8.9)	0.17 (10.6)	0.21 (8.7)
PY	0.17 (9.5)	0.22 (13.4)	0.15 (10.1)	0.21 (12.4)	0.14 (15.3)	0.19 (17.3)
B(a)A	0.08 (10.6)	0.11 (19.1)	0.13 (12.6)	0.03 (13.5)	0.06 (20.5)	0.08 (13.4)
Chrysene and Triphenylene	0.04 (7.6)	0.01 (18.3)	0.05 (9.8)	0.06 (12.7)	0.03 (19.1)	0.04 (21.2)
B(b+k)F	0.82 (7.9)	0.55 (4.8)	0.69 (8.3)	0.64 (7.9)	0.35 (6.8)	0.40 (8.8)
B(a)P	0.02 (21.3)	–	0.01 (17.2)	–	–	–
IP	–	–	–	–	–	–
D(ah)A	–	–	–	–	–	–
B(ghi)P	–	–	–	–	–	–
Total (3–6 ring)	2.66 (9.1)	2.12 (10.2)	2.33 (9.4)	2.42 (13.0)	1.89 (13.5)	1.98 (11.3)
% Surrogates recovered (average) \pm SD						
AE*	65.3 \pm 9.8	68.8 \pm 11.4	74.5 \pm 8.6	69.3 \pm 14.2	61.9 \pm 16.4	61.4 \pm 11.6
AN*	75.8 \pm 7.6	81.3 \pm 9.5	79.7 \pm 7.1	74.1 \pm 12.5	70.3 \pm 10.6	71.3 \pm 10.4
PY*	91.9 \pm 5.4	96.5 \pm 3.2	96.3 \pm 8.2	89.9 \pm 8.4	87.5 \pm 9.7	82.4 \pm 9.1
B(a)A*	93.6 \pm 5.6	92.4 \pm 6.3	100.1 \pm 3.8	95.3 \pm 7.6	98.3 \pm 3.8	90.5 \pm 5.7
B(a)P*	95.7 \pm 8.5	90.6 \pm 5.7	90.5 \pm 4.6	96.7 \pm 5.8	106.4 \pm 13.2	97.6 \pm 8.4
D(ah)A*	85.3 \pm 3.3	80.2 \pm 4.8	76.8 \pm 6.1	73.2 \pm 7.9	82.3 \pm 5.3	85.1 \pm 5.2
B(ghi)P*	81.7 \pm 4.1	75.6 \pm 3.6	80.5 \pm 5.5	70.1 \pm 9.2	80.7 \pm 8.2	76.6 \pm 7.9

*Air-dried soil was remoistened with water at 18.5% before extraction. All analyses were performed in triplicate.

does not demonstrate any enhancement compared with that from air-dried soil (35.8 vs. 36.5 $\mu\text{g/g}$). This indicates the moisture effect enhances the extraction efficiency under microwave heating process.

Amounts of PAHs extracted from KS2 are presented in Table 5. The results show a similar trend as those results obtained from KS1. In general, loss of some PAHs during air-drying process, enhancement of extraction efficiency with the presence of moisture and higher recovery of FMAE than Soxhlet are observed in the present experiment conditions.

4. Conclusions

The focused microwave-assisted extraction under an atmospheric open vessel system has been studied which reveals that this method is a good alternative to Soxhlet extraction for the analysis of PAHs in soil samples. With the current method developed, the addition of the water to the dry matrices enhances the recovery of PAHs from soil samples. The analysis of original moisture content matrix can be performed by FMAE without drying procedure with acceptable precision and reproducibility. This study demonstrates that the reduced solvent use and the reduced extraction time are important advantages of FMAE compared with the Soxhlet method.

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References

- [1] R.W. Vannoot, J.-P. Chervet, H. Lingeman, G.J. de Jong, U.A.Th. Brinkman, *J. Chromatogr.* 505 (1990) 45.
- [2] M.M. Schantz, J.J. Nichols, S.A. Wise, *Anal. Chem.* 69 (1997) 4210.
- [3] O.P. Heemken, N. Theobald, B.W. Wenclawiak, *Anal. Chem.* 69 (1997) 2171.
- [4] K. Granzler, A. Salgo, K. Valko, *J. Chromatogr.* 371 (1986) 299.
- [5] K. Granzler, I. Szinai, *J. Chromatogr.* 520 (1990) 257.
- [6] A. Pastor, E. Vazquez, R. Ciscar, M. de la Guardia, *Anal. Chim. Acta* 344 (1997) 241.
- [7] Z. Wang, M. Fingas, Y.Y. Shu, L. Sigouin, M. Landriault, P. Lambert, R. Turpin, P. Campagna, J. Mullin, *Environ. Sci. Technol.* 33 (1999) 3100.
- [8] R.C. Lao, Y.Y. Shu, J. Holmes, C. Chiu, *Microchem. J.* 53 (1996) 99.
- [9] K. Li, J.M.R. Belanger, M.P. Llompart, R.D. Turpin, R. Singhvi, J.R.J. Pare, *Spectroscopy* 13 (1996/97) 1.
- [10] V. Lopez-Avila, R. Young, W.F. Benedicto, P. Ho, R. Kim, *Anal. Chem.* 67 (1995) 2096.
- [11] V. Lopez-Avila, R. Young, *J. AOAC Int.* 81 (1998) 462.
- [12] I. Silgoner, R. Krska, E. Lombas, O. Gans, E. Rosenberg, M. Grasserbauer, *Fresenius J. Anal. Chem.* 362 (1998) 120.
- [13] H.M. Pylypiw Jr., T.L. Arsenault, C.M. Thetford, M.J.I. Mattina, *J. Agric. Food Chem.* 45 (1997) 3522.
- [14] G. Dupont, C. Delteil, V. Camel, A. Bermond, *Analyst* 124 (1999) 453.
- [15] C. Chiu, G. Poole, Y.Y. Shu, R. Thomas, *Organohalogen Comp.* 27 (1996) 333.
- [16] G. Xiong, B. Tang, X. He, M. Zhao, Z.P. Zhang, Z.X. Zhang, *Talanta* 48 (1999) 333.
- [17] H. de Geus, B.N. Zegers, H. Lingeman, U.A.Th. Brinkman, *Int. J. Environ. Anal. Chem.* 56 (1994) 119.
- [18] N. Saim, J.R. Dean, Md.P. Abdullah, Z. Zakaria, *J. Chromatogr. A* 791 (1997) 361.
- [19] L.E. Garcia-Ayuso, M. Sanchez, A. Fernandez de Alba, M.D. Luque de Castro, *Anal. Chem.* 70 (1998) 2426.
- [20] O.F.X. Donard, B. Lalere, F. Martin, R. Lobinski, *Anal. Chem.* 67 (1995) 4250.
- [21] T. Dagnac, A. Padro, R. Rubio, G. Rauret, *Anal. Chim. Acta* 364 (1998) 9.
- [22] I.R. Pereiro, V.O. Schmitt, J. Szpunar, O.F.X. Donard, R. Lobinski, *Anal. Chem.* 68 (1996) 4135.
- [23] B. Lalere, J. Szpunar, H. Budzinski, P. Garrigues, O.F.X. Donard, *Analyst* 120 (1995) 2665.
- [24] E. Eljarrat, J. Caixach, J. Rivera, *Chemosphere* 36 (1998) 2359.
- [25] R.G. Harvey, *Polycyclic Aromatic Hydrocarbons*, Wiley, New York, 1997.
- [26] M.L. Lee, M.V. Novotny, K.D. Bartle, in: *Analytical Chemistry of Polycyclic Compounds*, Academic Press, New York, 1992, p. 462.
- [27] H. Budzinski, A. Papineau, P. Baumard, P. Garrigues, *C.R. Acad. Sci. Paris* 321 (1995) 69.
- [28] H. Budzinski, M. Letellier, P. Garrigues, K. Le Menach, *J. Chromatogr. A* 837 (1999) 187.
- [29] M. Letellier, H. Budzinski, *Analyst* 124 (1999) 5.
- [30] Y.Y. Shu, R.C. Lao, C. Chiu, R. Turle, *Chemosphere* 41 (2000) 1709.
- [31] Y.Y. Shu, C. Chiu, R. Turle, G. Poole, T.C. Yang, R.C. Lao, *Org. Halogen Comp.* 31 (1997) 9.

- [32] Environment Technology Centre Method: Analytical Method for the Determination of PAHs in Soils/Sediments. Method No. 3.8/1.0/M, Environmental Technology Centre, Environment Canada, Ottawa, October 1997.
- [33] V. Camel, *Trends Anal. Chem.* 19 (2000) 229.
- [34] J.D. Haddock, P.F. Landrum, J.P. Glesy, *Anal. Chem.* 55 (1983) 1197.
- [35] T.N.P. Bosma, P.J.M. Middeldorp, G. Schraa, A.J.B. Zehnder, *Environ. Sci. Technol.* 31 (1997) 248.
- [36] S.B. Hawthorn, C.B. Grabanski, *Environ. Sci. Technol.* 34 (2000) 4348.