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Dynamic microwave-assisted extraction coupled on-line with solid-phase extraction: determination of polycyclic aromatic hydrocarbons in sediment and soil

Magnus Ericsson, Anders Colmsjö*

Department of Analytical Chemistry, Stockholm University, 106 91 Stockholm, Sweden

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Abstract

This paper describes a new extraction tool for the determination of polycyclic aromatic hydrocarbons (PAHs) in soil and sediment samples, using dynamic microwave-assisted extraction combined with solid-phase extraction (DMAE–SPE). The critical variables for DMAE–SPE are investigated and optimized in an experimental design. The technique proved to be fast, accurate and able to yield quantitative extraction of PAHs from naturally contaminated sediment and soil samples. The set-up is fully automated and features monitored extraction, which facilitates rapid optimization of the method. In addition, only small quantities of solvent and sample are required.

Keywords: Microwave-assisted extraction; Solid-phase extraction; Polynuclear aromatic hydrocarbons

1. Introduction

Efficient and quantitative extraction of compounds from complex matrixes is often difficult to achieve. Compounds are adsorbed in different ways and are more or less difficult of access due to both morphology of the matrix and the adsorption isotherms of the analyte–matrix systems. Varying properties of almost similar sample matrices makes recoveries of compounds from unknown samples almost impossible to calculate. Spiked samples will thus rarely give the same recoveries as real samples under identical extraction conditions.

In order to speed up the analysis, while maintaining high recovery and good precision, and to reduce the quantities of toxic solvents used, a number of techniques, based on dynamic systems and the use of elevated temperatures and pressures, have been developed. Commercially available systems with the ability to heat and pressurize liquids include pressurized liquid extraction (PLE) [1,2], microwave-assisted extraction (MAE) [3–7] and supercritical fluid extraction (SFE) [8,9]. These techniques take advantage of the greater solubility in pressurized and heated liquids that organic solutes usually exhibit [10].

Using a dynamic approach to extraction is generally advantageous, especially with respect to the partitioning of the solute into the extraction media. This can be highly efficient when fresh solvent is continuously introduced into the extraction cell, i.e., the rate constant for desorption does not need to be

*Corresponding author. Tel.: +46-8-167-197; fax: +46-8-156-391.

E-mail address: anders.colmsjo@anchem.su.se (A. Colmsjö).

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large in comparison with the rate constant for adsorption for efficient removal of the target solute.

Dynamic microwave-assisted extraction (DMAE) has been found to be an efficient technique [11], combining dynamic extraction with the use of microwaves as a heat source. In Ref. [11] extractions under relatively high temperatures and pressures (130 °C, 15 bar) were performed. In addition, the extractions were continuously monitored in an instrument that resembled one used for SFE. Another technique to monitor the extraction of polycyclic aromatic hydrocarbons (PAHs) from solid samples was presented by Garcia-Ayuso et al. [12]. In their approach, a commercial device for focused microwave-assisted Soxhlet extraction was modified to include a flow injection manifold and a fluorescence detector. In order to monitor the extraction, triplicates of 500 μl of the extract was injected into the flow line of the detector for each finished extraction cycle. Their conclusion was that the system was good for screening of unknown samples and for studies of the extraction kinetics. Cresswell and Haswell presented a different form of a dynamic microwave-assisted extractor. With their technique PAHs were extracted from a sediment using an instrument made in their laboratory [13]. In this, the sediment sample was slurried in water or acetone and introduced, through a PTFE tube, into a microwave field prior to filtration. Analytes were extracted, then trapped on a C_{18} cartridge. Trapped solutes were eluted from the cartridge directly onto an analytical high-performance liquid chromatography (HPLC) column. Recoveries were in the range 62–93%.

In this paper, the technique presented in Ref. [11] is further developed. The coupling of DMAE to SPE via a series of valves, in order to include monitored extraction, cleaning and elution of PAHs, is described. A reduced factorial design was used to determine the critical system variables and further optimization was achieved using a central composite design. Tests were conducted with PAHs from naturally contaminated sediment and soil.

2. Experimental

2.1. Chemicals and samples

Methanol was used as an extraction media in the DMAE (BDH, Poole, UK). The water added to retain the chosen target solutes was pre-cleaned by a UHQII system (Elga, High Wycombe, UK). The SPE cartridges were PLRP-S 15–20 μm, 100 Å (Spark Holland, AJ Emmen, The Netherlands), a highly crosslinked polymeric stationary phase made of polystyrene–divinylbenzene. The SPE eluent used was methyl-*tert*.-butyl ether (MTBE) (Rathburn Chemicals, Walkerburn, UK). Dichloromethane (Riedel-de Haen, Seelze, Germany) was used as the solvent for the external and internal standards. All solvents were of analytical-reagent grade. The PAH type reference substances ranged, in order of increasing retention time, from phenanthrene up to benzo[*ghi*]perylene, and were at a concentration of ~10 ng/μl. The internal standard spiked onto the samples was 2,2′-binaphthyl at a concentration of 100.8 ng/μl. All the standard substances were supplied by Larodan Fine Chemicals (Malmö, Sweden).

Two types of samples were used in this study, a standard reference material (SRM) EC-1 (National Water Research Institute, Environment Canada, Burlington, Canada) and a heavily contaminated soil from the site of the Värtan-harbor gas plant in Stockholm. The SRM was a freeze–dried particulate sediment, contaminated with PAHs and other chemicals. It was collected from Hamilton Bay, an industrialized part of the Lake Ontario shore. The certified PAH levels in this material had not been confirmed by previous studies, so our results were compared with Soxhlet data obtained elsewhere [11,14]. The contaminated soil was air dried at 20 °C for 48 h and grind thoroughly. The soil was then mixed and sieved through a 710 μm sieve.

2.2. Dynamic microwave-assisted extraction combined with solid-phase extraction

The extraction system (Fig. 1) was assembled in our laboratory. It consisted of a solvent delivery system (Merck 655A-12; Fig. 1a, P1) that pumped extraction media through a preheating column (Jour Research, Onsala, Sweden; Fig. 1, 2) into the extraction cell (Jour Research; Fig. 1, 3). Both the column and the cell were heated by a microwave-assisted oven (EMM2361, Electrolux, Stockholm, Sweden; Fig. 1, 1). The temperature of the solvent was measured using a grounded thermocouple, type

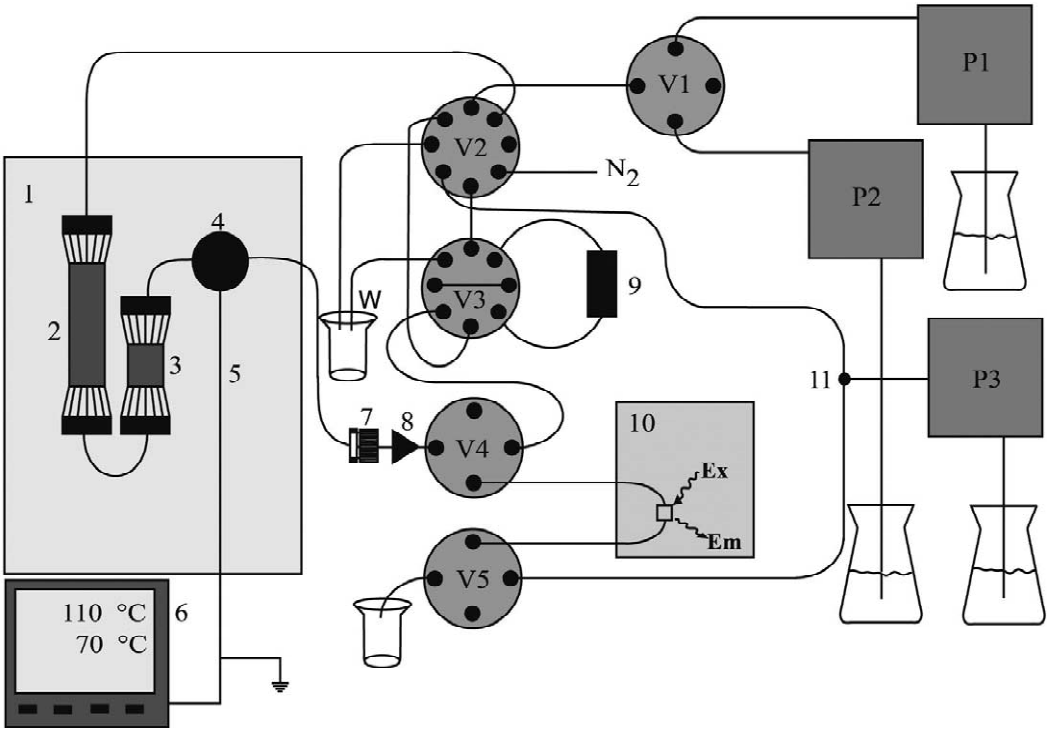

Fig. 1. The DMAE–SPE system: 1, Microwave oven; 2, pre-heating column; 3, extraction cell; 4, three-way PEEK connector; 5, grounded thermocouple type K; 6, temperature set point controller; 7, in-line particulate filter; 8, fused-silica restrictor; 9, SPE column; 10, fluorescence detector; 11, mixing tee, V1–V4, Valco valves; P1–P3, HPLC pumps.

K (Pentronic, Sweden; Fig. 1, 5) mounted in a modified tee (Jour Research; Fig. 1, 4) and regulated by a temperature set-point controller (Eurotherm, Sweden; Fig. 1, 6). An in-line filter (Jour Research; Fig. 1, 7) was used as a particulate filter for the extract. In order to retain pressure over the DMAE system and to keep the methanol in a liquid state, the flow of extract was restricted, using a piece of raw fused-silica of 50 mm×0.1 mm I.D. (J&W Scientific, Folsom, CA, USA; Fig. 1, 8) at the entrance to the SPE system. The extraction and elution was monitored using a HPLC–fluorescence detection system (RF-535 Shimadzu, Japan; Fig. 1, 10). To deliver the SPE eluent and the water, two separate HPLC pumps (Fig. 1, P2 and P3) were used (LC-6A, Shimadzu and prostar 220, Varian, Palo Alto, CA, USA, respectively). The flows of methanol and water were combined in a mixing tee (Jour Research; Fig. 1, 11). The SPE was performed using a Cartridge holder (Spark Holland) designed for 10×2 mm disposable cartridges (Fig. 1, 9). Nitrogen gas was passed over the cartridge in order to dry the solid phase prior to GC analysis. The gas was purified using two gas cleaning filters, one of charcoal and the other a moisture filter (Chrompack; Varian). Four- and six-port valves were used (VICI AG, Valco International, Switzerland; Fig. 1, V1–V5) to switch solvents and gas streams, as appropriate.

The pre-heater, the extraction cell, the particulate filter all the tubing and the finger-tight fittings were made of PEEK (polyether ether ketone). The extraction cell had an internal volume of 0.5 ml. The tubes were of HPLC-standard, with O.D. ≈1.59 mm. All tubing had an internal diameter of 0.25 mm. The extraction monitoring system, was set at an optimum for pyrene, with an excitation wavelength of 330 nm and an emission wavelength of 372 nm. A personal computer (PC)-based laboratory data system (ELDS Pro, Chromatography Data Systems, Svartsjö, Sweden) was used to register and store the detector signal. The same software was also used to program a relay card for switching the valves.

2.3. Experimental design

Four variables influencing the DMAE–SPE were investigated by means of experimental design. The variables were: the total volume of the SPE eluate ($V_{E\text{-}SPE}$=100–500 μl); the drying time (T_{DRY}=5–15 min), i.e., the time used to remove any residual water and methanol from the SPE cartridge using nitrogen gas; the flow-rate of the added water (Φ_w=100–1100 μl/min); and the duration of the microwave assisted extraction (T_{MAE}=20–30 min). Approximately 60 mg of the SRM was used as the matrix. Initially, a reduced factorial design was performed. The variables found to be significant in the screening experiments were further investigated and optimized using a central composite design.

A total of 11 experiments, including three central points and four axial points, were performed using a central composite design. The distance to the axial points was slightly modified from 1.414 to 1.200 in normalized mode for greater simplicity. The concentrations (μg/g) of four PAHs found in the SRM were used to represent the responses. These compounds were chosen in order to cover most of the range of the chromatographic retention time. They were phenanthrene, pyrene, benzo[*a*]pyrene and benzo[*ghi*]perylene. Multiple linear regression (MLR) was performed using Modde 4.0 software (Umetri, Umeå, Sweden) installed on a personal computer.

2.4. Analysis procedure for DMAE–SPE

The optimized DMAE–SPE procedure was performed as follows. Portions of approximately 60 mg of sediment or contaminated soil were weighed and placed into the extraction cell in between two small plugs of glass fiber wool. A volume of 5.0 μl of the internal standard mixture was added using a positive displacement pipette (Socorex, Switzerland). Prior to extraction, a new SPE cartridge and a clean in-line filter were loaded into the system, which had been rinsed through with methanol. The solid phase was first cleaned with 7.5 ml of methanol, and then activated with 9.0 ml of water. The flow of extraction media (i.e., methanol) and water was halted while the extraction cell was mounted with finger tight connections into the system (see Fig. 1). The flow of the extraction media and water, the relay program and recording of the fluorescence signal were started simultaneously (Fig. 2a). The microwave heating was started after a 1-min delay, to ensure that the extraction cell was properly filled with extraction media. The parameters investigated were set as determined by the central composite and the screening designs: the water flow-rate was 800 μl/min; the duration of microwave-assisted extraction was 30 min; the drying time was 15 min at a flow-rate of 100 ml/min; and an SPE eluent volume of 400 μl MTBE at a flow-rate of 130 μl/min was used. The pressure over the extraction cell was about 30 bar, with a slight oscillation due to the bistable (on/off) nature of the microwave heating. The flow-rate of the extraction media (0.5 ml/min) and the temperature of the extraction (110 °C) had been investigated previously [11] and were empirically adjusted for this new use of DMAE. Pressure was measured using the HPLC pump that delivered the extraction media.

When the microwave-assisted extraction was complete, after 30 min, the microwave heating and the flow of extraction media and water were terminated, and the eluent pump was started. Simultaneously, valves 1, 2 and 4 were switched (Fig. 2b) to start the nitrogen drying of the solid-phase, and the cleaning of the rest of the system with the SPE eluent, MTBE. Prior to elution of trapped solutes, the system was rinsed with methanol, and simultaneously a stream of nitrogen gas was passed through the cartridge in order to remove the remaining water (Fig. 2b). After a drying and cleaning period of 15 min, valves 3 and 5 were switched (Fig. 2c), and the trapped components were backflushed from the solid-phase using the eluent, then collected manually in a vial ready for GC–photo ionization detection (PID) or mass spectrometry (MS).

2.5. Static microwave-assisted extraction and Soxhlet extraction

Static microwave assisted extraction of the gas plant soil was performed in order to compare extraction yields with the dynamic mode method. A Q max 4000 (Questron, USA) was used for this purpose. The modified MAE reference method was based on a process outlined by Pineiro-Iglesias et al.

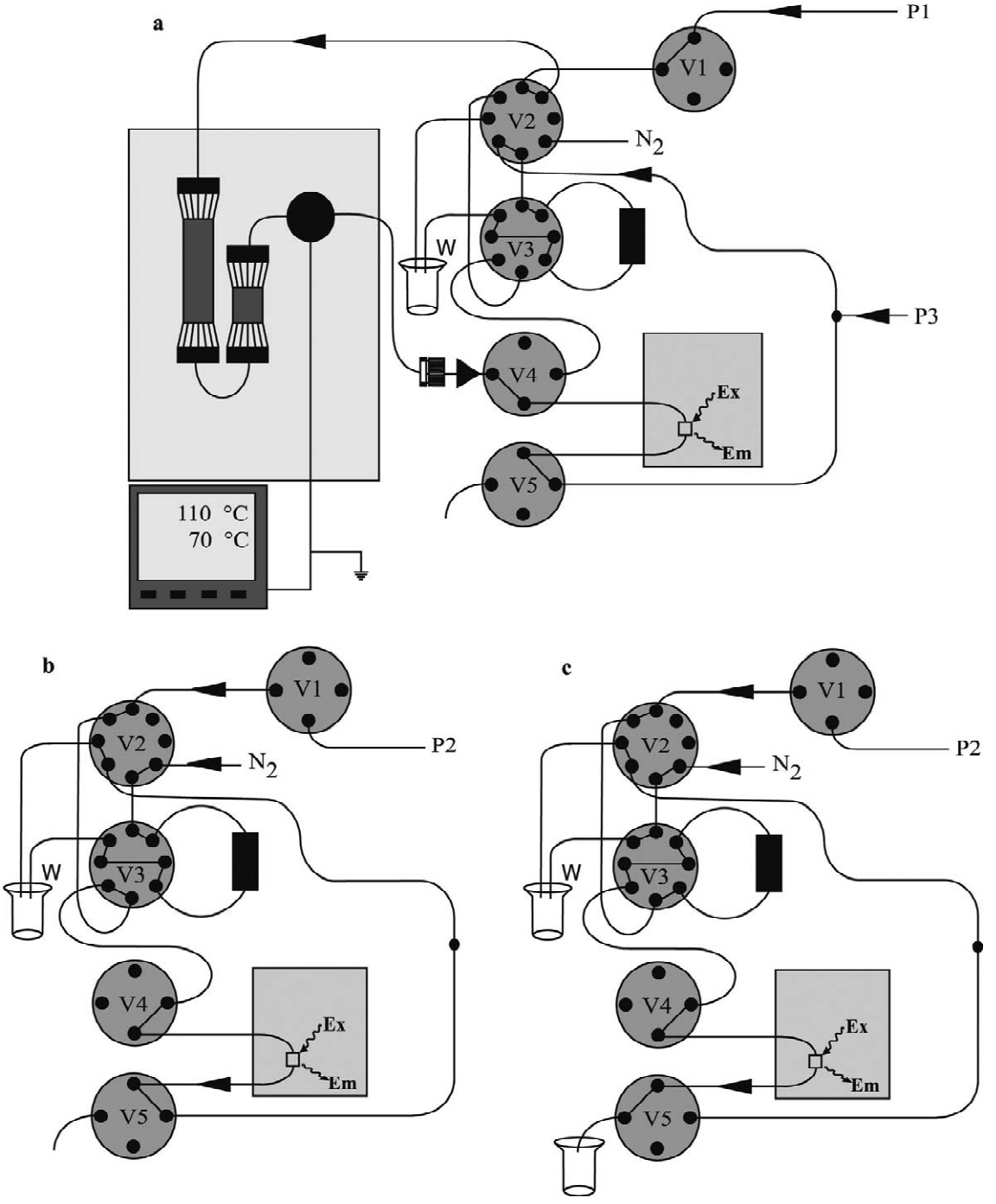

Fig. 2. Positions of the valves and the flow directions during: (a) extraction; (b) drying and system clean-up; (c) SPE elution.

[15]. Samples of approximately 100 mg of soil were weighed and placed in the MAE cells. A 25 μl volume of the internal standard was added using a positive displacement pipette (Socorex). Extractions were made using 15 ml of cyclohexane–acetone (1:1) at 120 °C for 20 min. The supernatant of each extract was filtered through pre-washed glass fiber wool inside a pipette. Extracts were then reduced to a volume of 200 μl in a rotary evaporator. Further clean-up prior to GC analysis is described elsewhere [11]. For comparison of the PAH levels in the sediment samples achieved with DMAE–SPE, approximately 1 g portions of the sediment was extracted with 50 ml of dichloromethane for 24 h in a Soxhlet apparatus. Results and clean-up is described in Ref. [11].

2.6. Gas chromatography

The final separation of the extracts was accomplished using gas chromatography. For PAHs, the GC system was equipped with either a PID system (Carlo Erba mega series, Italy) or an MS system (Hewlett-Packard, GC 5890, MS 5971A). The PID system used a 8.4 eV lamp and the detector temperature was set to 325 °C. MS was conducted in the selected ion-monitoring mode at a temperature of 190 °C. Both the Carlo Erba and the Hewlett-Packard GC systems were equipped with a DB5-MS (J & W, 30 m×0.25 mm I.D.; phase, 0.10 μm) column. Hydrogen was used as the carrier gas for GC–PID at 50 cm/s and helium was used in the GC–MS at 40 cm/s. The GC oven temperature program was as follows: 60 °C (1 min), 25 °C/min to 155 °C, which was held for 1 min, 7 °C/min to 325 °C, which was held for 15 min. The parameters for the splitless injection were: splitless time, 0.5 min; injection volume, 1 μl; injector temperature, 325 °C. A personal computer-based data system with ELDS Win Pro software (Chromatography Data Systems, Svartsjö, Sweden) was used to record the PID signal and to process the chromatograms. The software HP-Chemstation was used to process and to control the GC–MS system. GC–PID was used for all analysis except for the experimental design experiments.

3. Results and discussion

The aim of this work was to construct and validate a system that could dynamically extract analytes from different matrices using microwave heating of the solvent and sample, followed by entrapment on an SPE column. The second step was accomplished by introducing water into the eluate, so that the analytes were retained on the solid phase. In addition, the SPE column was dried with gaseous nitrogen, and a small amount of MTBE was sufficient to elute the trapped solutes.

3.1. Monitoring the extraction and elution

The advantage of using a monitored extraction method is that it allows the investigator to check on a routine basis the time needed to recover compounds, and simultaneously to monitor the elution profile of particular analytes [11]. In addition, the amount of solvent needed for the extraction and pre-cleaning of the system can be controlled. In Fig. 3, the fluorescence trace of an extraction of soil collected from the gas plant is shown. Initially, compounds extracted from the extraction cell appear as a hump on the chromatogram (Fig. 3a). Following this, there is a drying period of 15 min (Fig. 3b). Finally, the compounds trapped on the SPE are eluted. This area

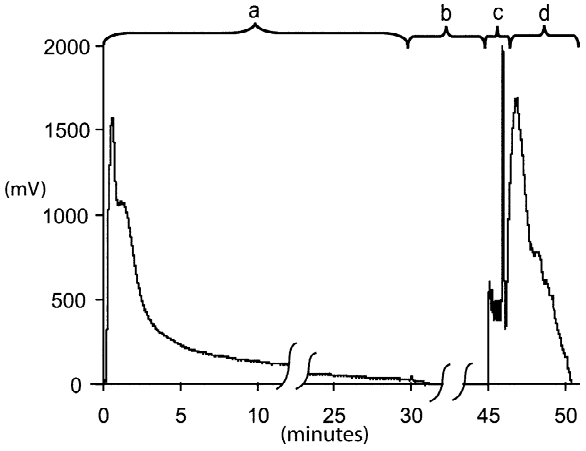

Fig. 3. The fluorescence extraction profile of the contaminated soil: (a) microwave assisted extraction; (b) drying period; (c) gas remainders; (d) eluted components.

in the chromatogram consists of two parts (Fig. 3c and d), the first corresponding to the phase when the remaining nitrogen gas leaves the system, followed by the analytes dissolved in MTBE.

3.2. Drying procedure

In order to establish the minimum drying period for the solid phase, following the DMAE extraction, the SPE eluate was introduced into 1 ml of hexane. If water is present, the solution turns opaque. This method is described by Vreuls et al. [16]. A drying period of 5 min at a gas flow-rate of 100 ml/min was found to be sufficient to remove all residual water from the cartridge. No effects on the recovery of PAHs were observed after 5 min of drying at a gas flow-rate of 100 ml/min. In the following experimental design, a drying period of 5–15 min was chosen.

3.3. Experimental design

The problem of optimizing an analytical system for a number of substances, within a range of physical properties, can be difficult and always results in compromises. For the particular compounds selected in this study this included the possibility that PAHs with different properties, primarily large differences in boiling point and hydrophobicity, require different extraction conditions for optimum extraction performance. However, high recoveries were found for all the compounds at one particular combination of variable settings.

Initially, a screening design of n chosen variables was performed. This was achieved using a reduced factorial design with 2^{n-1} experiments [17]. Following this, an optimization was performed, in this case, a central composite design (CCD) [17]. To achieve a CCD, a full factorial design is used with 2^n experiments, including a number of additional central points and $2n$ axial points. The axial points are selected at a distance of $\pm(2^n)^{1/4}$ from the central point in a normalized variable domain (± 1). This results in an equation for a response y (recovery) and nx-variables with coefficients β:

$$y = \beta_0 + \beta_1 x_1 + \ldots + \beta_n x_n + \beta_{11} x_1^2 + \ldots + \beta_{nn} x_n^2 + \beta_{1n} x_1 x_n + \ldots + \beta_{n1} x_n x_1$$

3.3.1. Screening design

The extraction efficiency for DMAE–SPE of the SRM sediment sample from Hamilton Bay was evaluated in two steps. First, a reduced factorial design was performed incorporating eight experiments. The levels of the parameters are defined in Table 1. From the magnitude of the resulting β-coefficients and their confidence intervals (Table 2), it was concluded that the drying time and the duration of extraction were not significant within the chosen domain. This is valid since only values higher than the 95% confidence interval have a significant influence on the model. The elution volume and the water flow-rate were significantly correlated to the yield of the four target compounds. These two significant parameters were investigated further in a subsequent optimization.

It was concluded from the results of the investigation that varying the drying period between 5 and 15 min had no effect on the recovery, and produced a visually dry extract. However, since the intention is to couple DMAE–SPE to large volume injection, using the retention gap technique on a gas chromatograph, extremely dry extracts are required. There-

Table 1
Experimental design variables and levels

Variable	Levels	
	Low	High
Water flow-rate (μl/min), Φ_w	100	1100
Duration of microwave-assisted extraction (min), T_{MAE}	20	30
SPE drying time (min), T_{DRY}	5	15
SPE eluent volume (μl), $V_{E\text{-}SPE}$	100	500

Table 2
Coefficients from the screening design (figures in parentheses are the ±95% confidence interval)

	Coefficients			
	Phenanthrene	Pyrene	Benzo[*a*]pyrene	Benzo[*ghi*]perylene
Constant	27.6 (4.3)	26.2 (4.2)	5.3 (0.3)	4.0 (0.1)
$V_{\text{E-SPE}}$	−0.9 (4.9)	−0.2 (4.8)	0.2 (0.4)	0.2 (0.1)
T_{DRY}	1.4 (4.9)	1.1 (4.8)	0.1 (0.4)	0.0 (0.1)
Φ_{w}	12.3 (4.9)	9.4 (4.8)	0.5 (0.4)	0.0 (0.1)
T_{MAE}	−5.1 (4.9)	−4.2 (4.8)	−0.3 (0.4)	0.1 (0.1)

fore, the longest drying period was used for all subsequent experiments.

A small increase in the recovery (4–5%) of benzo[*ghi*]perylene was observed when the duration of extraction was set at 30 min rather than 20 min. Consequently, the duration of the extraction was also kept constant in the subsequent optimization, at 30 min. Breakthrough of phenantrene in the SPE cartridge due to the extended duration of extraction was however not detected.

3.3.2. Central composite design

The results from the screening experiments indicated that the variables T_{DRY} and T_{MAE}, were not important factors affecting the overall yield. Interaction dependence between these variables and the others did not appear to be significant. A central composite design involving 11 experiments was conducted in order to optimize the two remaining variables ($V_{\text{E-SPE}}$ and Φ_{W}). A model was calculated that showed a coefficient of determination between observed and predicted measurements close to 0.98 for all the responses. The local optimum for all the responses was found to be at a water flow-rate of 0.8 ml/min and a minimum elution volume of 300 μl MTBE. The calculated model for all the responses suggested a strong influence of the water flow-rate (Φ_{W}) and the quadratic term, Φ_{W}^2 (Table 3). The interaction effect ($V^*_{\text{E-SPE}}\Phi_{\text{w}}$), the elution volume ($V_{\text{E-SPE}}$) and its quadratic term ($V^2_{\text{E-SPE}}$) were found to be non-significant (Table 3). The aim of achieving quantitative extraction of the target PAHs from the SRM was achieved using a DMAE extraction lasting 30 min. The additional flow-rate of water was adjusted to 0.8 ml/min and the drying time of the SPE cartridge was set to 15 min. Finally, the SPE elution volume was slightly increased from 300 to 400 μl of MTBE in order to allow for highly contaminated samples.

3.4. Extraction efficiency—applications with two samples

The extraction recovery for the optimized DMAE–SPE system was validated by comparing the results with data obtained from Soxhlet extraction and MAE. In Tables 4 and 5, concentrations are given for a number of polycyclic aromatic hydrocarbons in the Hamilton Bay sediment and in the gas plant soil. The recoveries achieved using DMAE–SPE are compared to the Soxhlet extraction for the sediment and to the MAE for the soil. For the sediment, a good

Table 3
Coefficients from the central composite design (figures in parentheses are the ±95% confidence interval)

	Coefficients			
	Phenanthrene	Pyrene	Benzo[*a*]pyrene	Benzo[*ghi*]perylene
Constant	21.7 (5.2)	29.3 (6.3)	5.6 (1.4)	4.7 (1.0)
$V_{\text{E-SPE}}$	2.8 (3.6)	3.8 (4.3)	0.8 (0.9)	0.5 (0.7)
Φ_{w}	9.7 (3.6)	12.2 (4.3)	2.5 (0.9)	1.8 (0.7)
$(V_{\text{E-SPE}})^2$	−4.2 (4.8)	−6.7 (5.8)	−1.2 (1.2)	−1.0 (1.0)
$(\Phi_{\text{w}})^2$	−7.2 (4.8)	−10.2 (5.8)	−1.8 (1.2)	−1.6 (1.0)
$V^*_{\text{E-SPE}}\Phi_{\text{w}}$	0.3 (4.7)	0.8 (5.7)	0.1 (1.2)	0.0 (0.9)

Table 4
The recovery of PAH relative Soxhlet for the reference sediment EC-1 (figures in parentheses are the relative standard deviations, %, $n=5$)

PAH	Soxhlet (μg/g)	DMAE–SPE (μg/g)	Recovery (%) (DMAE–SPE)/Soxhlet
Phenanthrene	23.3 (12)	23.1 (7)	99
Anthracene	2.2 (9)	2.2 (4)	100
Fluoranthene	36.9 (10)	36.6 (5)	99
Pyrene	29.4 (9)	29.0 (3)	99
Benzo[*a*]anthracene	10.8 (6)	9.9 (4)	92
Chrysene/triphenylene[a]	12.3 (6)	13.3 (7)	108
Benzo[*b*&*k*]fluoranthene[b]	23.6 (11)	21.1 (4)	89
Benzo[*e*]pyrene	6.3 (5)	5.7 (6)	90
Benzo[*a*]pyrene	6.5 (5)	5.9 (1)	91
Perylene	1.6 (6)	1.4 (10)	88
Indeno[1,2,3-*cd*]pyrene	5.0 (12)	5.2 (5)	104
Dibenz[*a,h*&*c*]anthracene[c]	1.9 (10)	1.8 (9)	95
Benzo[*ghi*]perylene	4.4 (9)	4.4 (4)	100

[a] Coeluting peaks, recovery expressed as a sum of chrysene and triphenylene.
[b] Coeluting peaks, recovery expressed as a sum of benzo[*b*]fluoranthene and benzo[*k*]fluoranthene.
[c] Coeluting peaks, recovery expressed as a sum of dibenz[*a,h*]anthracene and dibenz[*a,c*]anthracene.

correlation between the DMAE–SPE and the Soxhlet extraction was observed, $r^2=0.996$. Deviations from complete recovery were all within ±12%, with perylene being the most divergent (88%). The accuracy achieved with DMAE–SPE were in the range 1–10% (RSD). This result was slightly better than the 5–12% (RSD) achieved with Soxhlet extraction.

The gas plant soil samples were extracted without any alteration to the parameters of the optimized extraction method. In this case, extraction efficiencies for the DMAE–SPE method were close to, or

Table 5
The recovery of PAH relative MAE for the gas plant soil (figures in parentheses are the relative standard deviations, %, $n=5$)

PAH	MAE (μg/g)	DMAE–SPE (μg/g)	Recovery (%) (DMAE–SPE)/MAE
Phenanthrene	14.6 (3)	15.3 (4)	105
Anthracene	2.4 (12)	2.6 (3)	108
3-Methylphenanthrene	4.2 (10)	4.7 (14)	112
2-Methylphenanthrene	7.2 (6)	7.5 (13)	104
2-Methylanthracene	1.3 (14)	1.3 (14)	100
9-Methylphenanthrene	4.2 (16)	4.4 (15)	105
Fluoranthene	13.9 (9)	14.0 (6)	101
Pyrene	8.8 (6)	9.9 (4)	113
Benzo[*a*]anthracene	5.3 (8)	5.8 (6)	109
Chrysene/triphenylene[a]	10.0 (6)	10.3 (5)	103
Benzo[*b*&*k*]fluoranthene[b]	11.9 (9)	11.5 (6)	97
Benzo[*e*]pyrene	4.4 (10)	4.6 (6)	105
Benzo[*a*]pyrene	5.5 (10)	5.7 (5)	104
Perylene	1.4 (17)	1.5 (10)	107
Indeno[1,2,3-*cd*]pyrene	4.2 (20)	4.0 (14)	95
Dibenz[*a,h*&*c*]anthracene[c]	1.4 (19)	1.5 (10)	107
Benzo[*ghi*]perylene	3.1 (11)	3.3 (6)	106

[a] Coeluting peaks, recovery expressed as a sum of chrysene and triphenylene.
[b] Coeluting peaks, recovery expressed as a sum of benzo[*b*]fluoranthene and benzo[*k*]fluoranthene.
[c] Coeluting peaks, recovery expressed as a sum of dibenz[*a,h*]anthracene and dibenz[*a,c*]anthracene.

better than, those of the static MAE, with the highest deviation for 3-methylphenanthrene (112%). The coefficient of determination between the methods for this sample was $r^2 = 0.994$. In this case, a number of methylphenanthrenes were also quantified. The occurrence of a large number of compounds in the chromatographic elution area of methylphenanthrenes interfered with the quantification, thus yielding an increased standard deviation for some compounds (RSD = 11–14%). The overall accuracy was in the range of 3–15% (RSD) for DMAE–SPE and 3–20% (RSD) for MAE. For both samples, the DMAE method yielded slightly higher recoveries compared to the reference method (slope = 1.016 in the correlation plot for both samples).

4. Conclusions

The present work demonstrates that DMAE–SPE can easily be used for an efficient and reliable extraction of PAHs from complex matrices. It is likely that this combined system, with slightly altered parameters, could be used for the extraction of other types of compounds, such as flame retardants. Furthermore, the system could easily be combined with high-resolution chromatographic systems, such as gas or liquid chromatography with a variety of detectors, giving the potential for flexibility in the selection of system modules. The particular system described in this paper is, at present, being combined with both GC–nitrogen–phosphorus detection and GC–MS systems. The simplicity and cost efficiency of the system offers a number of attractive solutions for completely automated analysis, with a large sample throughput.

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