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Dynamic microwave-assisted extraction

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Abstract

An apparatus for extraction of solid matrices has been constructed which utilizes a microwave technique for heating in a dynamic mode. During the extraction, fresh solvent is continuously pumped through the extraction cell, which is maintained at a slight overpressure in order to keep the solvent in a liquid state. The extraction efficiency, which can be easily monitored, has been investigated in a factorial design and validated for polycyclic aromatic hydrocarbons in a reference sediment sample (EC-1). Important parameters were found to be temperature and duration of extraction. Flow-rate had no significant first-order effect on the recovery, but interaction effects with flow-rate were found to be significant. The dynamic microwave-assisted extraction apparatus was demonstrated to yield recoveries equivalent to Soxhlet extraction, but in a much shorter time. Each extraction of EC-1 typically takes 40 min.

Keywords: Microwave-assisted extraction; Extraction methods; Factorial design; Instrumentation; Polynuclear aromatic hydrocarbons

1. Introduction

Extraction is one of the most crucial points in the analytical chain in the effort of achieving a complete recovery of target compounds [1]. It is also one of the most complex steps to treat mathematically, and it rarely yields reproducible results [2–9]. This is mainly because properties of the matrix, to which the compounds are attached, are very difficult to predict and will differ even if samples are collected from almost identical points at a single site, using the same sampling technique. Adsorption, which is the most common mechanism by which molecules become attached to a matrix, is reasonably well understood, but it has not been precisely defined mathematically [10]. Langmuir adsorption equation, for instance, presupposes that there is a consistent unimolecular layer of adsorbed compounds that do not interfere with each other. These simplifications of adsorption/desorption processes permits simple mathematical treatment, which often conform acceptably well to experimental results. There are also many multi-layer adsorption models, with expressions of varying complexity for deriving the adsorption isotherm [10].

It may be the above-mentioned inconsistency of target matrices that has hampered the instrumental and theoretical development of extraction techniques, while the much more predictable chromatographic techniques used later in the analytical chain have received much more attention. Thus, the largest sources of error are to be found in the extraction step often because of deficiencies in experimental design, or in variations in the sampling step. An impressive,

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and rather astonishing fact related to these observations, is that the Soxhlet extraction technique, introduced by Franz Von Soxhlet almost a century ago, is still one of the most commonly used extraction techniques in organic analytical chemistry. A number of modern and more costly, but not often more efficient, extraction techniques have been developed. Concepts like supercritical fluid extraction (SFE) [11], pressurized liquid extraction (PLE) [12], solid-phase extraction (SPE) [13,14], solid-phase microextraction (SPME) [15], microwave-assisted extraction (MAE) and ultrasonic extraction [16] have evolved. These techniques have a range of advantages, including rapidity and reductions in solvent consumption. They also use less environmentally hazardous solvents, and offer better possibilities for controlling the extraction, for automation and possibilities for coupling the extraction on-line with other analytical techniques.

However, a limitation shared by all of the techniques listed above is that the extraction rarely is monitored, resulting in a high level of uncertainty concerning the point at which the extraction process is complete or can be considered quantitative. This is a significant problem because the extraction of different sample matrices will not necessarily yield the same elution profile of extracted compounds, even if the origin of the matrices is almost the identical. Thus, there is considerable difficulty in establishing fixed times for extracting standard reference materials. The practical solutions to this problem are usually to use excessively large extraction times in order to ensure complete extraction, or to accept possible losses of compounds due to variations in the sample matrices.

Another way to overcome this obstacle is to introduce efficient extraction techniques that can monitor the extraction process. In this work, we introduce dynamic microwave-assisted extraction (DMAE), which enables the extraction process to be monitored with the aid of a high-performance liquid chromatography (HPLC) detector. In addition this technique also permits the possibility of a more selective extraction of compounds due to the dynamic approach. This is because fresh solvent is pumped through the extraction cell throughout the entire extraction stage, producing a process that resembles chromatography with a rather undefined solid-phase. Using a dynamic procedure, the partition equilibrium does not demand that the solutes are forced into the solvent with almost 100% efficiency, i.e., k_d does not need to be extremely large compared to k_a. Finally, the use of microwaves for heating in extraction purposes is very efficient, accurate and energy saving. This has been confirmed by Pare and co-workers in the extraction of phenols and polycyclic aromatic hydrocarbons (PAHs) from soils with MAE [17–20]. The drawback with different types of microwave-assisted extractions is that completely non-polar solvents cannot generally be used, although the sample matrix can sometimes be used as an energy absorber.

2. Experimental

2.1. Set-up of the dynamic microwave-assisted extractor

The dynamic microwave extractor (Fig. 1) was assembled in our laboratory. It consists of a Merck 655A-12 solvent delivery system, an Electrolux EMM2361 microwave oven, an extraction cell, a Eurotherm temperature set-point controller with a type K thermocouple supplied by Pentronic, Sweden, a Shimadzu RF-535 HPLC fluorescence detector and a 300 mm×0.25 mm I.D. fused-silica restrictor.

The extraction cell was made out of PTFE (polytetrafluoroethylene) and had an internal volume of 8 ml. It was designed to fit a Soxhlet-type extraction thimble made out of cellulose. The tubes and the finger-tight fittings were made out of PEEK (polyether ether ketone) and were of HPLC-standard, with O.D. 1/16 mm. All tubing had an internal diameter of 0.5 mm. The eluent monitoring system, i.e., the fluorescence detector was set at an optimum for pyrene, with an excitation wavelength of 330 nm and an emission wavelength of 372 nm. A personal computer-based laboratory data system (ELDS Pro, Chromatography Data Systems, Svartsjö, Sweden) was used for registering and storing the detector signals. The fused-silica restrictor served to increase the pressure in the extraction cell and thereby keep the solvent in a liquid state.

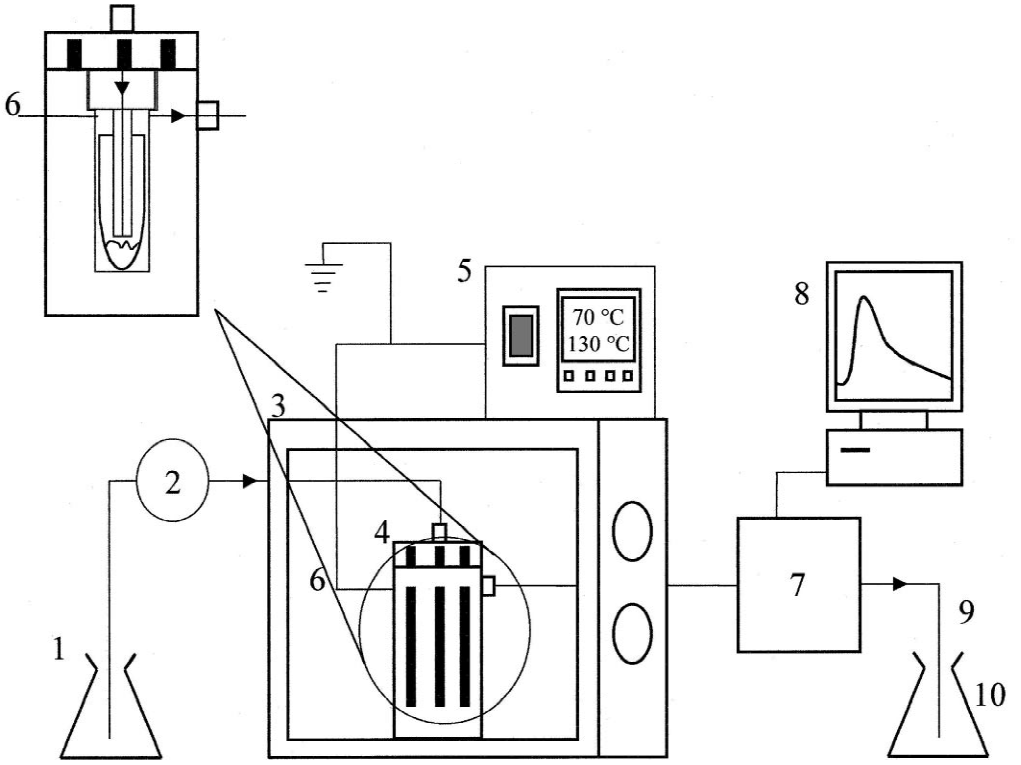

Fig. 1. System for dynamic microwave-assisted extraction, 1=solvent, 2=pump, 3=microwave oven, 4=extraction cell, 5=temperature set point controller, 6=thermocouple, 7=fluorescence detector, 8=registering device, 9=restrictor, 10=extract.

2.2. Chemicals and standards

Solvents used for extraction and clean-up were methanol, cyclohexane and dichloromethane, all of analytical-reagent grade, supplied by Merck, and dodecane (>99%) supplied by Janssen. The PAH type reference substances ranged, in order of increasing retention time, from phenanthrene up to benzo[*ghi*]perylene, and were provided by Larodan Fine Chemicals (Malmö, Sweden). 2,2′-Binaphthyl was used as internal standard.

2.3. Samples

A standard reference material (SRM) EC-1, (National Water Research Institute, Environment Canada, Burlington, Canada) was used throughout this study. This SRM is a freeze–dried particulate sediment, contaminated with PAHs. It was collected from Hamilton Bay, an industrialized part of Lake Ontario. The PAH concentrations in this material were determined by 72 Soxhlet extractions carried out in our laboratory, followed by gas chromatography (GC) analysis with flame ionization detection (FID) and mass spectrometry (MS), or HPLC with UV/fluorescence detection. Fourteen laboratories across Canada have provided a thorough collaborative evaluation of the concentrations for the selected PAHs in this material [21].

2.4. Extraction procedure

About 1-g portions of sediment were weighed accurately and placed into each of a series of cellulose extraction thimbles (50×10 mm). A 250-μl volume of a solution of the internal standard dissolved in dichloromethane was applied with a syringe to the top of each of these samples. They were allowed to dry overnight (15 h) in a refrigerator, and were then extracted in the microwave extractor, one

at a time, for 40 min at a temperature of 140°C. A constant flow of methanol (2 ml/min) was pumped through the extraction cell and the fluorescence detector. The extract was finally eluted via the restrictor, and was collected in a 100-ml pear shaped flask for further pre-treatment.

For comparison of the laboratory-obtained DMAE values, the sediment samples were extracted for 24 h with 50 ml dichloromethane in a Soxhlet apparatus equipped with a 100-ml round flask.

2.5. Clean-up and analysis

Following the extraction, 300 μl of dodecane was added. Extracts were evaporated in a rotary evaporator until only the dodecane keeper remained.

Pre-cleaning was performed with open column chromatography on a 60×6 mm glass column, slurry packed with silica gel 60, d=0.063–0.2 mm (Merck). The silica was heated to 450°C for 24 h and subsequently deactivated with 10% (w/w) distilled water. The deactivated silica was stored in cyclohexane prior to use. The dodecane extract was applied to the silica gel, and a fraction containing paraffins, olefins, mono- and dicyclic aromatic compounds and PAHs were eluted with 8 ml of cyclohexane.

A HPLC system for backflush-liquid chromatography, including a Varian Pro Star pump, a Waters automatic valve station for injection and switching flow, and a Valco valve, was used to purify the PAH fraction. Portions (100-μl) of the extracts were injected and separated on a nitrophenylpropylsilica (Nucleosil 5 NO_2, 5 μm, 150×4 mm) column. Eluting compounds were detected by a Varian 9050 UV–Vis detector. As the mobile phase, cyclohexane was used isocratically. Registering of the detector signal and operating of the switch valves was accomplished by a personal computer-based data system with the software ELDS Win Pro (Chromatography Data Systems). Alkanes, alkenes, olefins, mono- and dicyclic aromatic compounds elute before PAHs in this system, thus making it possible to switch flow direction and elute all PAHs in one backflush peak. The time for starting the backflush was determined by the retention time of anthracene, the first eluting PAH. The backflush fraction was collected and reduced to 100 μl under a stream of nitrogen gas.

2.6. Gas chromatography

Final separation of the extracts was accomplished with a gas chromatograph equipped with a photo ionization detection (PID) system (Carlo Erba mega series, Italy). The PID system used a 9.6 eV lamp and the detector temperature was 325°C. The GC system was equipped with a DB5-MS (J & W, 30 m×0.25 mm I.D.; phase, 0.25 μm) column with nitrogen as carrier gas. The GC-oven temperature program was as follows: 60°C (2 min), 25°C/min, 155°C (1 min), 7°C/min, 325°C (15 min). Parameters for the splitless injection were: splitless time, 1.5 min; injection volume, 1 μl; injector temperature, 325°C. Registering of the detector signal and processing of chromatogram was achieved with a personal computer-based data system with the software ELDS Win Pro.

2.7. Factorial design

In order to investigate and visualize the effects of some of the different system parameters and their interactions, a two-level factorial design with center points was applied. The investigated parameters were: temperature, flow-rate and time of extraction. Eight cube and six center point experiments were made. The high and the low values for the variables were chosen as follows: temperature: 110/130°C; flow-rate: 2/6 ml/min; time of extraction: 10/20 min. As response, a sum of extracted fluoranthene, pyrene, benzo[*a*]anthracene and chrysene was used. The data were processed using Codex 2.6 beta5 software from SumIT System, Solna, Sweden, equipped with the multiple linear regression (MLR) calculation feature.

3. Results and discussion

3.1. Monitoring the extraction

In most extraction systems, the time of the extraction is settled empirically. This is usually an uncertain factor that can lead to loss of compounds

or much longer than necessary extractions. With DMAE it is possible to visually determine the evolution of the extraction. Fig. 2a illustrates the complete extraction of a sediment sample (EC-1) as monitored by HPLC–fluorescence detection, which gives the possibility of selectively monitoring individual compounds, or more general monitoring, depending on the excitation and emission wavelengths and slit widths chosen. Great care has to be taken when choosing parameters for monitoring the extraction, however. Different target compounds can be expected to extract with quite different time

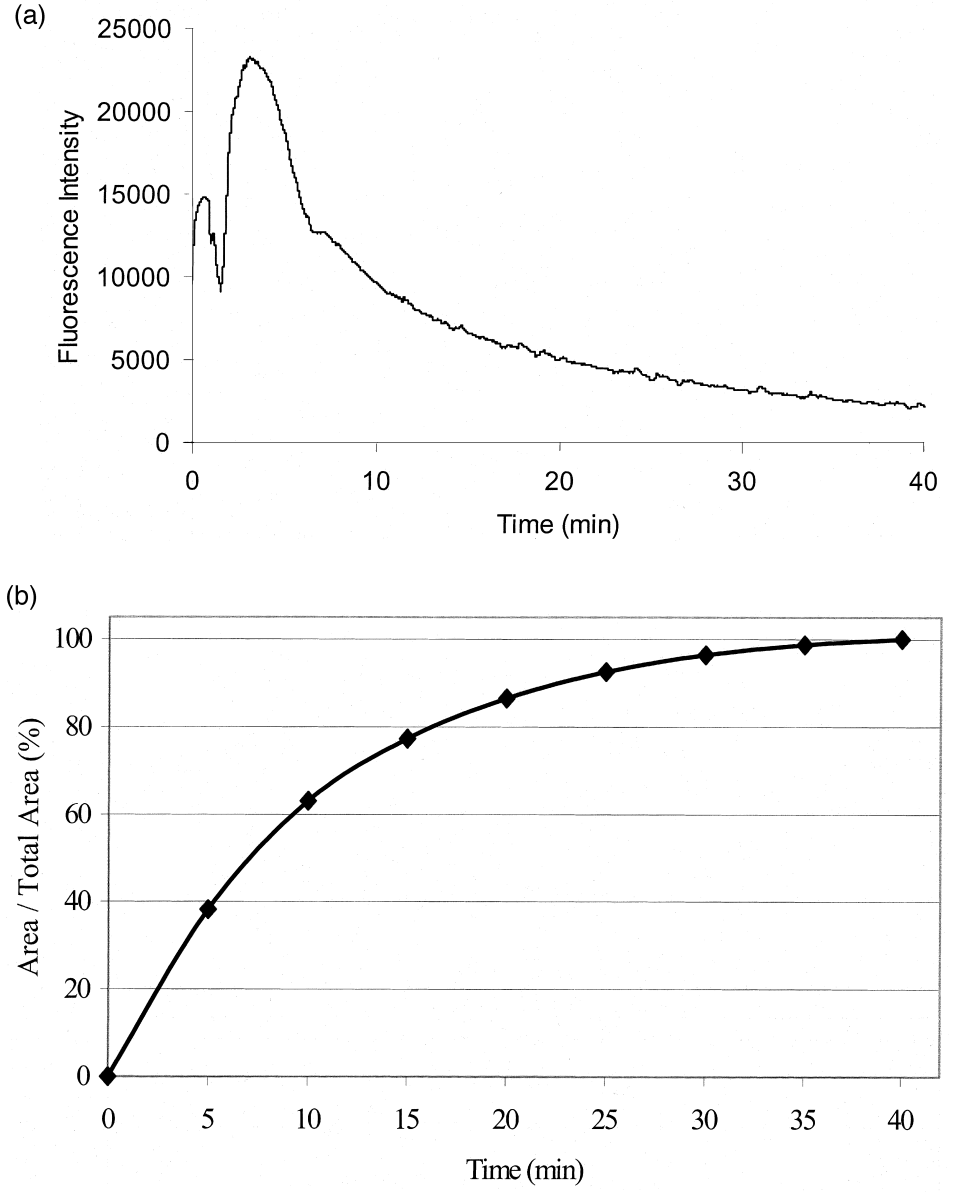

Fig. 2. (a) Profile for the DMAE extraction of EC-1. Fluorescence detection: excitation, 330 nm; emission, 372 nm. Cell parameters: temperature, 140°C; time of extraction, 40 min; methanol flow-rate, 2 ml/min. (b) Eluted amount in (a) expressed as area/total area of the monitored extraction profile.

profiles. In this particular case the wavelengths were chosen to fit excitation and emission wavelengths of pyrene selectively. The elution profile initially rises steeply, then declines exponentially, showing that most of the pyrene elutes prior to 20 min. This can be seen in Fig. 2b, which shows the recovery of pyrene, extracted by DMAE applied to the same sample. In this case, almost 90% of the compounds were extracted after 20 min. In Fig. 3, a gas chromatogram is shown following a dynamic microwave-assisted extraction for 40 min and clean-up. Compared to Soxhlet extraction, no significant loss of high-molecular-mass PAHs can be discerned in spite of the short time of extraction. More or less sophisticated methods can be used in order to scan both excitation and emission wavelengths during the extraction. This will ultimately generate data that has to be treated by chemometric methods. An extensive investigation of these treatments is beyond the scope of this paper.

3.2. Recovery

In order to gain more extensive knowledge of the factors influencing the DMAE method, a full factorial design was conducted. In the extractor there are several parameters that can be varied. In this work, the effects of temperature (T), flow-rate (Φ) and time of extraction (t) were chosen for study. In a factorial design this will give a first approximation following the general equation:

$$\text{Yield} = b_1T + b_2\Phi + b_3t + b_4T\Phi + b_5Tt + b_6\Phi t \quad (1)$$

The importance of these parameters was calculated from experimental data derived from the DMAE of a sediment sample with emphasis on PAHs. In Table 1,

Table 1
Regression coefficients derived from the MLR calculations

Variable	Regression coefficient	Confidence limit ($P=0.05$)
Temperature	9.0	±2.0
Flow-rate	0.9	±2.0
Time	10.8	±2.0
Temperature·Flow	5.6	±2.0
Temperature·Time	2.7	±2.0
Flow·Time	−4.7	±2.0

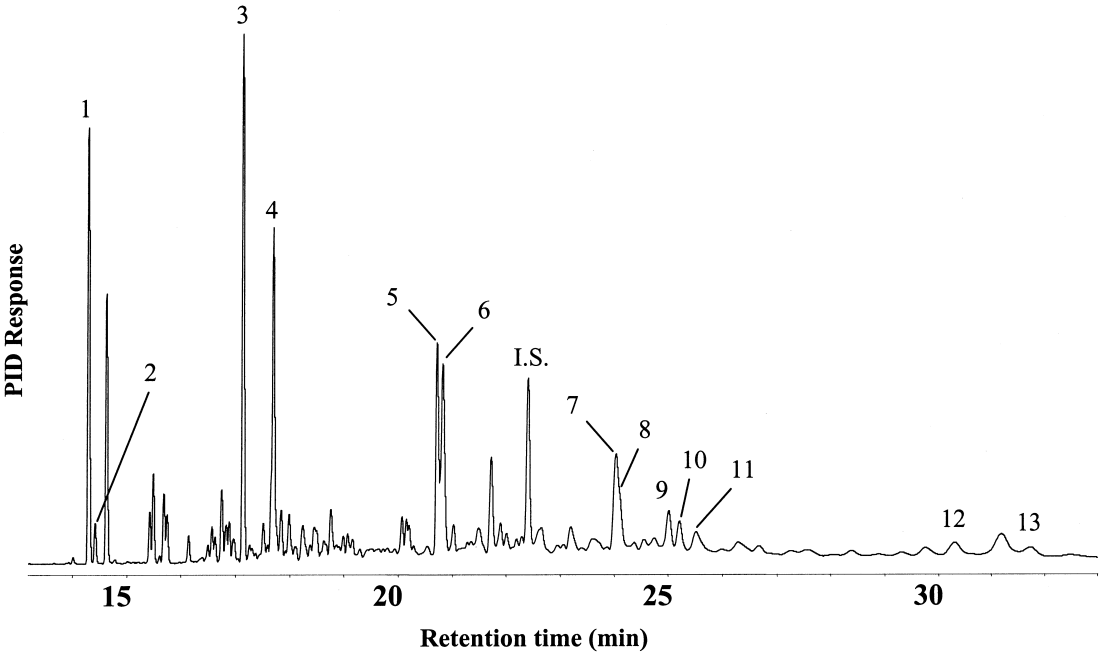

Fig. 3. GC–PID chromatogram of the cleaned up DMAE extract of EC-1. Compound numbers correspond to Table 2.

the size, the confidence limit and sign of the regression coefficients are shown, based on an experimental domain that covered temperatures from 110 to 130°C, flow-rates from 2 to 6 ml/min, and extraction times varying from 10 to 20 min. The magnitude of the coefficients for temperature and time of extraction indicate that these factors are important and, consequently, they have a strong influence on the model. Likewise, all interaction effects seem to be of importance when considering the extraction yield, whereas flow-rate is of minor importance. It is usually difficult to make physico–chemical interpretations from the magnitude of the coefficients, as small variations in one parameter affect the values of the others. However, the importance of temperature can probably be related to two factors. Firstly, an increase in temperature will increase the vapor pressure of any volatile substance, and thus increase its solubility [22]. Secondly, according to the Arrhenius equation, a rise in temperature will reduce the activation energy barrier of dissociation, thus decreasing the energy required to overcome the many different activation energy barriers present in real samples [23]. The significance of the extraction time can be presumed to be related to the time required for the desorption process to take place. Thus, a need for prolonged extraction may be an indication of slow desorption kinetics. The flow-rate has little or no influence on the model, and thus cannot be considered an important factor. The effects of the interaction between temperature and time are of importance for the model, as can be seen from the response surfaces (Figs. 4 and 5). When flow-rate and temperature are varied and the time of extraction

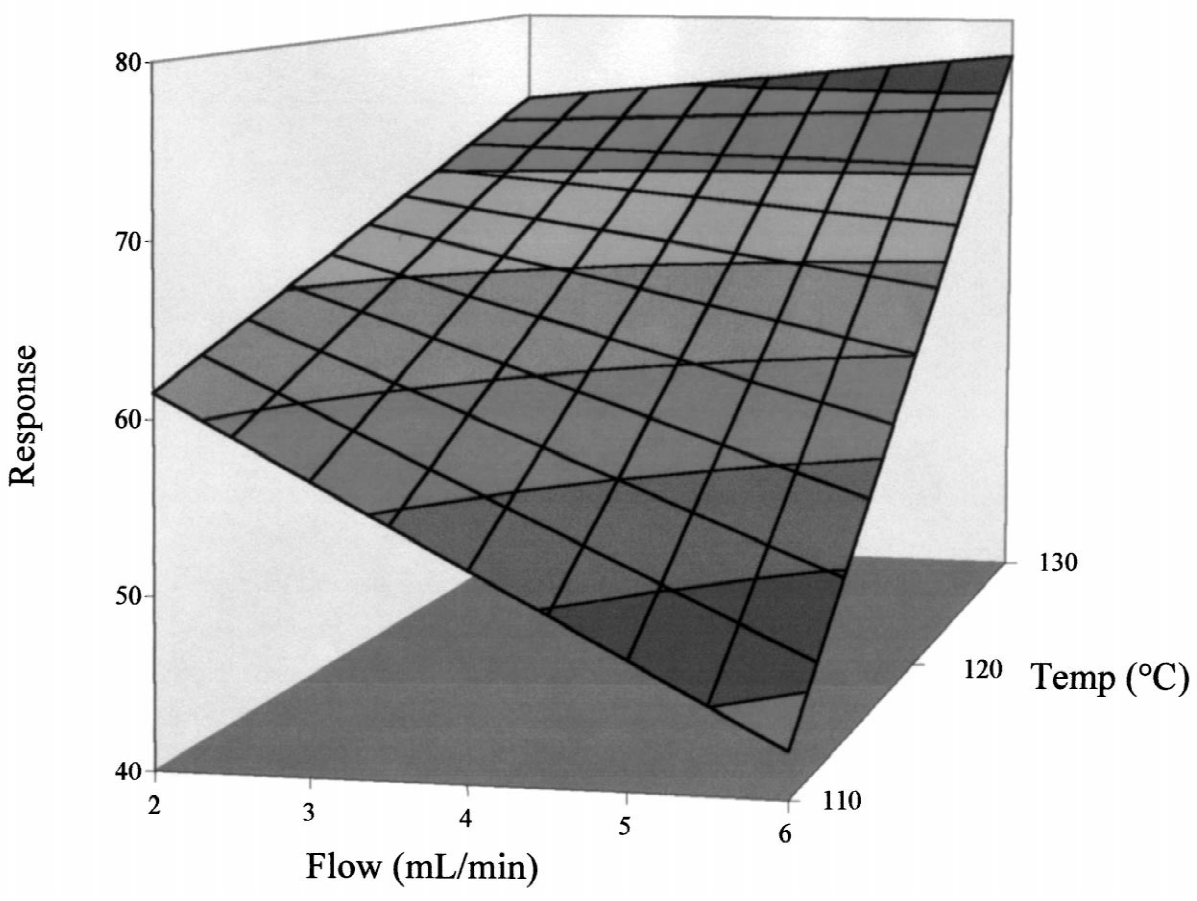

Fig. 4. Response surface for flow and temperature, with the time of extraction held constant at 20 min.

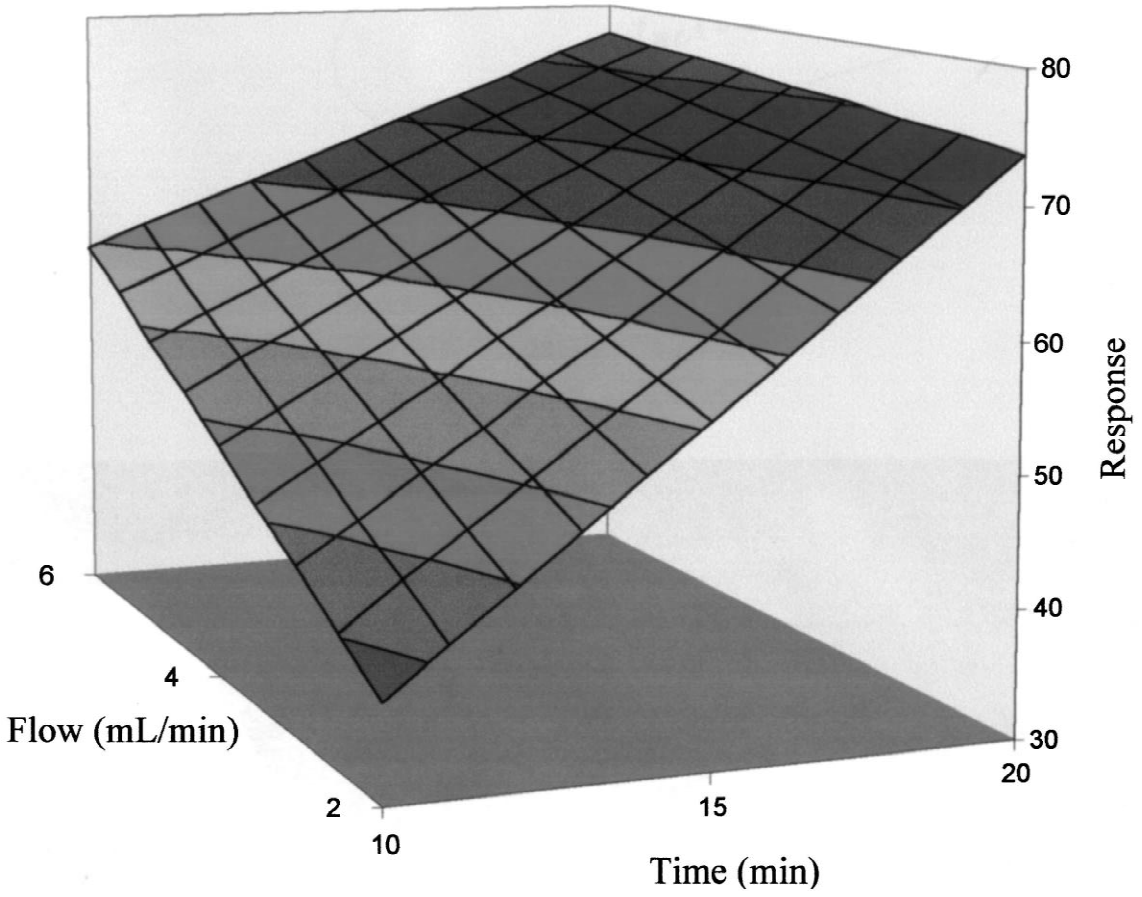

Fig. 5. Response surface for flow and time of extraction, with the temperature held constant at 130°C.

is held constant at 20 min (Fig. 4), the response surface flattens out as the temperature is elevated. This indicates that solvent flow-rate and the consumption of solvent can be kept low, while maintaining satisfactory recoveries, by increasing the temperature. If flow-rate and time of extraction are varied, and the temperature is held constant at 130°C (Fig. 5), the slope of the response surface along the flow axis becomes flatter as the time of the extraction is increased. This is due to rapid initial elution of loosely bound substances, and the effect can also be seen in the extraction profile (Fig. 2a). In this case, by prolonging the extraction it is also possible to reduce the solvent flow-rate and still preserve the high levels of recovery. Pressure is not a consideration in this study, but it can also be varied by changing the length or the internal diameter of the restrictor. It has been shown that pressure does not have a strong influence on extraction recovery [24], and that the main purpose of elevating the pressure is to preserve the extraction media in a liquid state.

3.3. Validation

Extraction recovery by the DMAE system was validated by comparison with certified values, and with values obtained from Soxhlet extraction. Extraction conditions selected, with guidance from the factorial design, were as follows: temperature, 140°C; flow-rate, 2 ml/min and extraction time, 40 min. In Table 2, recoveries of PAHs extracted from a sediment sample (EC-1) are shown. The certified values [21] and results from Soxhlet and DMAE extractions are shown in columns A, B and C,

Table 2
Recoveries of PAHs from a certified reference sediment (EC-1) presented in gas chromatographic elution order (figures in parentheses are standard deviations)

No.	PAH	(A) Certified value[a] (μg/g)	(B) Soxhlet value[b] (μg/g)	(C) DMAE value[c] (μg/g)
1	Phenanthrene	15.8 (1.2)	23.3 (2.8)	22.7 (1.7)
2	Anthracene	1.2 (0.3)	2.2 (0.2)	2.3 (0.4)
3	Fluoranthene	23.2 (2.0)	36.9 (3.5)	35.3 (2.0)
4	Pyrene	16.7 (2.0)	29.4 (2.6)	28.2 (2.1)
5	Benzo[*a*]anthracene	8.7 (0.8)	10.8 (0.6)	10.2 (1.5)
6	Chrysene/triphenylene[d]	9.2 (0.9)	12.3 (0.7)	11.5 (1.5)
7	Benzo[*b*]fluoranthene	7.9 (0.9)	11.3 (1.2)	11.1 (2.6)
8	Benzo[*k*]fluoranthene	4.4 (0.5)	6.4 (0.3)	5.2 (1.3)
9	Benzo[*e*]pyrene	5.3 (0.6)	6.3 (0.3)	7.5 (2.0)
10	Benzo[*a*]pyrene	5.3 (0.7)	6.5 (0.3)	5.2 (1.3)
11	Perylene	1.1 (0.2)	1.6 (0.1)	2.1 (0.3)
12	Indeno[123-*cd*]pyrene	5.7 (0.6)	5.0 (0.6)	5.1 (1.3)
13	Benzo[*ghi*]perylene	4.9 (0.7)	4.4 (0.4)	4.4 (1.4)

[a] Weighted average of pooled the laboratory-obtained results established by Lee et al. [21].
[b] Average of five results.
[c] Average of four results.
[d] Coeluting peaks, recovery expressed as a sum of chrysene and triphenylene.

respectively. Relative standard deviations range from 4 to 13% for the Soxhlet extraction and somewhat higher, from 6 to 32%, for the DMAE extraction (Table 3). The corresponding range for the certified values is 8 to 25%. This range is basically derived from a rather stable absolute standard deviation applied on peaks of varying size (given in parentheses in Table 2). The most striking effects shown in Table 2 are the generally good agreement between the Soxhlet and DMAE, and the relatively poor agreement between these and the certified values. This anomaly is further explored in Table 4, where the certified and the DMAE values are given as percentages of the Soxhlet recoveries.

Thus, the results show there is good agreement between the two extraction techniques used in our laboratory, DMAE and Soxhlet. These results are highly comparable, as the same method of quantification has been used in both cases, i.e., all laboratory work following the extraction step is the same. This reduces the risk of introducing systematic errors between the methods. The considerable deviation

Table 3
Recovery of PAHs (%) from EC-1, relative certified values

No.	PAH	Soxhlet, % recovery (% RSD, $n=5$)	DMAE, % recovery (% RSD, $n=4$)
1	Phenanthrene	147.5 (12.0)	143.7 (7.5)
2	Anthracene	183.3 (9.1)	191.7 (17.4)
3	Fluoranthene	159.1 (9.5)	152.2 (5.7)
4	Pyrene	176.0 (8.8)	168.9 (7.4)
5	Benzo[*a*]anthracene	124.1 (5.6)	117.2 (14.7)
6	Chrysene/triphenylene[a]	133.7 (5.7)	125.0 (13.0)
7	Benzo[*b*]fluoranthene	143.0 (10.6)	140.5 (23.4)
8	Benzo[*k*]fluoranthene	145.5 (4.7)	118.2 (25.0)
9	Benzo[*e*]pyrene	118.9 (4.8)	141.5 (26.7)
10	Benzo[*a*]pyrene	122.6 (4.6)	98.1 (25.0)
11	Perylene	145.5 (6.3)	190.9 (14.3)
12	Indeno[123-*cd*]pyrene	87.7 (12.0)	89.5 (25.5)
13	Benzo[*ghi*]perylene	89.8 (9.1)	89.8 (31.8)

[a] Coeluting peaks, recovery expressed as a sum of chrysene and triphenylene.

Table 4
Recovery of PAHs (%) from EC-1, relative Soxhlet laboratory-obtained values

No.	PAH	Certified, % recovery	DMAE, % recovery (% RSD, $n=4$)
1	Phenanthrene	67.8	97.4 (7.5)
2	Anthracene	54.5	104.5 (17.4)
3	Fluoranthene	62.9	95.7 (5.7)
4	Pyrene	56.6	95.9 (7.4)
5	Benzo[*a*]anthracene	80.6	94.4 (14.7)
6	Chrysene/triphenylene[a]	74.8	93.5 (13.0)
7	Benzo[*b*]fluoranthene	69.9	98.2 (23.4)
8	Benzo[*k*]fluoranthene	68.8	81.3 (25.0)
9	Benzo[*e*]pyrene	84.1	119.0 (26.7)
10	Benzo[*a*]pyrene	81.5	80.0 (25.0)
11	Perylene	68.8	131.3 (14.3)
12	Indeno[123-*cd*]pyrene	114.0	102.0 (25.5)
13	Benzo[*ghi*]perylene	111.4	100.0 (31.8)
	Overall average	76.6	99.5 (18.3)

[a] Coeluting peaks, recovery expressed as a sum of chrysene and triphenylene.

between the these values and the certified values is probably an effect of systematic errors. However, similar deviations were found by Suffet et al. [25], who also obtained significantly higher yields than the certified values. They ascertained that the dissimilarities are probably due to ''interlaboratory effects'', arising from differences in analysis techniques, standards or equipment between laboratories. To investigate the interlaboratory effect in the analysis of PAHs in EC-1, Lee et al. [21] organized a study with 14 participating laboratories in Canada. Some of the results they collated are summarized in Table 5, showing there was a wide range of calculated concentrations from the same sample, demonstrating that systematic errors had indeed occurred between the participating laboratories. This emphasizes the necessity of producing reference samples that have been thoroughly analyzed by many laboratories, using different methods of analysis.

3.4. Dynamic extraction methods

In Table 6, some of the properties of DMAE are compared to SFE and Soxhlet extraction. These three methods can be compared on the basis that they all use a dynamic extraction mode. The time needed to extract PAHs quantitatively from EC-1 by DMAE is approximately 40 min, with the flow-rate and temperature used. This is slightly faster than the 50 min required for an optimized SFE method [25], and much faster than a 24 h Soxhlet extraction. The solvents used in the comparative trials were metha-

Table 5
Interlaboratory results (μg/g) for selected[a] PAHs in EC-1

PAH	Range	Median	Mean (SD)	Certified	DMAE	Suffet Soxhlet
Phenanthrene	9.9–24.4	16.8	16.6 (4.6)	15.8	22.7	15.5
Anthracene	0.4–13.2	1.5	3.9 (4.7)	1.2	2.3	0.9
Fluoranthene	14.9–45.3	21.8	23.4 (7.4)	23.2	35.3	25.8
Benzo[*b*]fluoranthene	3.7–15.2	6.8	8.1 (3.6)	7.9	11.1	15.8
Benzo[*k*]fluoranthene	2.8–16.6	3.6	5.6 (4.2)	4.4	5.2	5.7
Benzo[*a*]pyrene	2.6–30.0	4.5	6.6 (6.8)	5.3	7.5	5.6
Perylene	1.1–2.2	1.2	1.5 (0.5)	1.1	2.1	–
Benzo[*ghi*]perylene	0.45–20.3	4.7	7.3 (6.5)	4.9	4.4	5.2

[a] For a complete listing of available data, refer to Lee et al. [21].

Table 6
Properties of DMAE, compared to SFE and Soxhlet extraction

Property	DMAE	SFE	Soxhlet
Time of extraction[a]	40 min	50 min[b]	24 h
Extraction media	Methanol	CO_2	Dichloromethane
Online possibilities	Yes	Yes	No
Monitored extraction	Yes	No	No

[a] That is, the time required to quantitatively extract the selected PAHs from EC-1.
[b] See Suffet et al. [25] for parameter settings.

nol for DMAE, CO_2 for SFE and dichloromethane for Soxhlet extraction. DMAE and SFE normally use elevated temperatures to create highly diffusive liquids, thus increasing extraction rates and promoting extraction efficiency [23].

The importance of choosing an optimized solvent decreases at higher extraction temperatures, as differences in solvent strength also decrease [26]. This makes it possible to use more environmentally lenient and cost-effective solvents such as methanol and CO_2 in DMAE and SFE. Soxhlet extraction, in contrast, uses large amounts of low-boiling-point solvents that are usually much more environmentally hazardous. Finally, the possibility of coupling the extraction on-line to a chromatographic method (another feature shared by DMAE and SFE) is highly advantageous, since it reduces both the manual handling required, and the risk of contamination.

4. Conclusions

Dynamic microwave-assisted extraction techniques offer the possibilities of speeding up extraction, while maintaining analyte recovery rates. As the technique uses standard laboratory equipment, it will probably be a cost-effective method compared to possible alternatives, such as supercritical fluid extraction. As it also offers the possibility of easily coupling the extraction technique to SPE or chromatographic systems, it has a great potential for integration into fully automated systems for chemical analysis.

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