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Journal of Chromatography A, 1025 (2004) 41–49
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Comparison of different trapping methods for pressurised hot water extraction

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Abstract

Four trapping methods for pressurised hot water extraction were compared in terms of recovery and selectivity. Also, robustness, repeatability and solvent consumption of the trapping systems were investigated. The trapping methods were collection into solvent following liquid–liquid extraction, solid-phase trapping into Tenax TA (SPE), flat sheet microporous membrane liquid–liquid extraction and hollow fibre microporous membrane liquid–liquid extraction. Polycyclic aromatic hydrocarbons were extracted with these systems from four soil and sediment matrices and the extracts were analysed by GC–MS and size-exclusion chromatography. Clear differences were observed in the selectivity and extraction efficiencies of the trapping systems.

Keywords: Pressurised hot water extraction; Extraction methods; Microporous membrane liquid–liquid extraction; Soil; Sediments; Environmental analysis; Polynuclear aromatic hydrocarbons

1. Introduction

Efficient and reliable novel extraction methods such as supercritical fluid extraction (SFE) [1–5], pressurised fluid extraction with organic solvents (accelerated solvent extraction) [4,6] and pressurised hot water extraction (PHWE) [7–9] have recently been under intensive study for the analysis of solid samples. The major advantages of PHWE are the low cost and environmental friendliness of water. Furthermore, the solvating properties of water are easily altered through change in temperature and pressure. At high temperatures the physico-chemical properties of water, especially the relative permittivity (ε), are favourable to the solubility of less polar compounds [10]. Pressure, on the other hand, has only a minor effect on the relative permittivity and the value of ε increases only slightly with pressure. Low values of ε are desirable in the extraction of non-polar compounds.

Since PHWE is a dynamic extraction method, the extract (about 20–50 ml) has to be concentrated before analysis. The level of concentration depends on the analytical technique. After PHWE, analytes are usually collected into solvent (liquid–liquid extraction, LLE) or a solid-phase trap (solid-phase extraction, SPE) [11–13]. Microporous membrane liquid–liquid extraction (MMLLE) [14,15] with both flat sheet and hollow fibre membrane units has also been used in the trapping of analytes.

The principles of LLE and SPE are well known [16]. The benefits of these methods are the availability of the equipment and a wide application range as well as the high extraction yields. In LLE, however, organic solvents are heavily consumed and intensive manual work is usually needed. In SPE, careful selection of the adsorbent and the elution solvent is required to achieve adequate selectivity and to assure that all the analytes are removed from the trap. MMLLE is continuous LLE proceeding via a hydrophobic membrane placed between two immiscible liquid phases, one aqueous and the other organic. This technique is based on the difference in the partition coefficients of the analytes between the donor and the acceptor solvents, which means that the driving force for the separation is a concentration gradient across the membrane [17–20]. Mass transfer occurs by diffusion across the liquid–liquid interface. In addition to the LLE process, also size-exclusion takes place in MMLLE, increasing the selectivity of the extraction [21]. As MMLLE is dynamic in nature, extraction yields are lower than with LLE and SPE.

We compared four trapping systems for PHWE (LLE, SPE, hollow fibre MMLLE, flat sheet MMLLE) and extracted four different sediment and soil samples. The analysis was made by gas chromatography–mass spectrometry

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doi:10.1016/j.chroma.2003.08.057

(GC–MS) and size-exclusion chromatography (SEC). Special emphasis was paid to the selectivity and the advantages as well as disadvantages of the different trapping methods. The quantitative results obtained with PHWE were compared with results achieved with Soxhlet extraction and with reference values.

2. Experimental

All solvents were of HPLC quality. Toluene, ethyl acetate and cyclohexane were from Lab Scan Analytical Sciences (Dublin, Ireland). Water was distilled, deionised and filtered before use. Acid-washed sea-sand was from Riedel-de Haën (Seelze, Germany). The internal standard, 4,4′-dibromooctafluorobiphenyl, and the recovery standard, 1,1′-binaphthyl, were from Aldrich (Gillingham, UK). The polycyclic aromatic hydrocarbon (PAH) standard mixture (Z-014G-R) contained 16 US Environmental Protection Agency (EPA) PAH compounds and was from Accu-Standard (New Haven, CT, USA). The 2.0 mg/ml stock solution was in dichloromethane– benzene (1:1). Further dilutions were made in toluene or cyclohexane.

Four samples were used in the study: EC-1, JML and Setoc sediments and a soil sample from a gasworks site at Husarviken (Stockholm, Sweden). EC-1 was a certified reference material from Environment Canada, National Water Research Institute (Burlington, Canada). JML was collected from the Baltic Sea (59°34.89′N/23°37.83′E) on 19 October 1998 from the depth of 5–10 cm. The Setoc sample was a sediment sample 3 (98.4) from International Sediment Exchange for Tests of Organic Contaminants (The Netherlands). The Husarviken sample was collected from a decommissioned coal gasification plant in Husarviken (Stockholm, Sweden) where the contamination took place 1893–1972. The sample contained 79% dry substance of which 29% was organic carbon. The total amounts of PAHs in the samples were about 140 ± 25 μg/g for EC-1, 20 ± 4 μg/g for JML and Setoc samples and about 1700 ± 200 μg/g for Husarviken sample [14,15,22–24]. The samples had been air dried, sieved and ground. The Setoc sediment sample was kindly provided by Dr. Hanne Lund of SINTEF (Oslo, Norway), and the Husarviken soil sample was provided by Dr. Bert van Bavel (MTM Research Centre, Örebro University, Sweden). The sample size in the extractions was 200 mg. Before the sample was placed in the extraction vessel, it was mixed with 1 g sea-sand. Finally, a solution containing the internal standard (100 μl of 50 μg/ml 4,4′-dibromooctafluorobiphenyl) was added to the sample, the solvent was allowed to evaporate and the vessel was filled with sea-sand.

2.1. Apparatus

The PHWE system consisted of a GC oven (Chrompack CP 9000, Varian, CA, USA) and a Jasco PU-980 pump (Tokyo, Japan). Special laboratory-made high-temperature vessels of stainless steel (volume 2.8 ml, i.d. 10 mm) were used in the extractions [22]. Connections between pumps, valves and extraction vessel were made of 1/16 in. stainless steel tubing of 0.5 mm i.d. (1 in. = 2.54 cm).

A trapping column (5 cm × 2.1 mm i.d.) packed with Tenax TA (80–100 mesh) adsorbent (Alltech Associates, Deerfield, IL, USA) was used in the PHWE solid-phase trap experiments. There was a stainless steel frit with pore size of 10 μm in the inlet of the trapping column, and a frit of pore size 5 μm in the column outlet.

The flat sheet membrane extraction unit was constructed at Lund University (Lund, Sweden) and it consisted of two blocks, one made of PTFE and the other of PEEK (polyether ether ketone), clamped together with six bolts. The two blocks were identically grooved to form channels of 200 μl volume on either side of the membrane. The membrane was made of thin porous polypropylene (Celgard 2400, Hoechst Celanese, Charlotte, NC, USA). The thickness of the Celgard 2400 was 25.4 μm, the pore dimensions were 0.05 μm × 0.125 μm and the porosity was 0.4. The inlet and outlet tubings connecting the membrane unit to the PHWE pressure regulator were made of 1/16 in. PTFE tubing (0.3–0.5 mm i.d.).

The Celgard X-50-215 hollow fibre membrane was of polypropylene, the porosity was 40%, pore dimensions were 0.04 μm × 0.10 μm and effective pore size was 0.04 μm. Internal diameter was 220 μm, outer diameter 300 μm, wall thickness 40 μm and burst strength 15.5 kg/cm^2. The hollow fibre membrane extraction unit was laboratory-made [15]. It was constructed of an empty LC column (7.5 cm × 4.6 mm i.d.), to which capillaries for water inlet and outlet were welded. The original inlet and outlet of the column were used for the organic acceptor solvent. Ten pieces of Celgard X-50-215 hollow fibre (Celgard, Wiesbaden, Germany) of 8 cm length were glued to the column ends with Epo-Tek H77 epoxy glue (Micro Joining, Tyresö, Sweden). The glue consisted of two components in mixing ratio 100:15 (w/w).

The sample size in Soxhlet extraction was 200 mg. The samples were mixed with 1.0 g acid-washed sea-sand and they were extracted for 20 h with 100 ml of hexane–acetone (1:1) containing 100 μl of 50 μg/ml internal standard 4,4′-dibromooctafluorobiphenyl. The extracts were concentrated to 2 ml with a rotary evaporator and analysed by GC–MS.

Samples (2 μl) were injected in on-column mode to a GC–MS system (Hewlett-Packard 6890N gas chromatograph, 5973N quadrupole mass spectrometer, USA). The MS analysis was carried out in scan mode (scan range 50–550 u) with electron impact ionisation (EI, 70 eV). The temperature of the GC–MS interface was 300 °C, that of the ion source 230 °C and that of the analyser 150 °C. The analytical column of the gas chromatograph was a 30.0 m HP–5MS (Agilent Technologies, USA) with 0.25 mm i.d. and 0.25 μm phase thickness. A 3.0 m retention gap (BGB Analytik, Zurich, Switzerland) with 0.53 mm i.d. and 1,2-diphenyl-1,1,3,3-tetramethyldisilazane (DPTMDS) deacti-

vation was connected to the analytical column with a press-fit connector (BGB Analytik). The oven was programmed from 75 °C (5 min) to 300 °C (15 min) at 10 °C/min.

Hewlett-Packard 1100 equipment (Waldbronn, Germany) with diode array detection was used in size-exclusion chromatography (SEC). A PLgel Minimix column (Polymer Labs., Shropshire, UK) of cross-linked polystyrenedivinylbenzene (250 mm × 4.6 mm i.d., particle size 5 μm) was applied. The eluent was cyclohexane, the injection volume 20 μl and the flow-rate of the eluent 0.3 ml/min. Under these conditions the pressure was 38 bar. Detection was made at wavelengths of 220 and 225 nm. The data were collected and analysed with a Hewlett-Packard computing system (HP Chemstation for LC, Rev. A.06.03).

2.2. Procedures

Previously optimised extraction conditions were applied in PHWE [25]. The extraction temperature was 300 °C, extraction time 30 min, water flow-rate 1.0 ml/min and pressure 9 bar (except in the SPE trapping where the pressure often rose above 50 bar). Four different trapping methods were investigated: LLE, SPE, flat sheet MMLLE and hollow fibre MMLLE. The conditions for the various trapping methods were chosen according to literature and previous studies [14,15,22–26].

2.2.1. LLE

For LLE, the water flow from the PHWE was directed to an extraction funnel containing 3 ml of ethyl acetate–cyclohexane (10:90, v/v) or toluene. After the first liquid–liquid extraction the water phase was extracted with a further 3 ml of organic solvent. The two fractions were combined and the extract was dried with sodium sulphate (Na_2SO_4) and concentrated to 0.5 ml under nitrogen flow.

2.2.2. SPE

During the PHWE the water flow was directed through the SPE trap. After the 30 min PHW extraction the oven was cooled, the water flow was turned off and the solid-phase trap was dried with nitrogen (9 bar) for 15 min. The extract was eluted from the trap with 3 ml of ethylacetate–cyclohexane (10:90, v/v) (6 min × 0.5 ml/min) and then was dried and concentrated as in LLE trapping.

2.2.3. FS–MMLLE

During the PHWE the water flow was directed to the donor channel of the membrane unit, while the acceptor phase [ethyl acetate–cyclohexane (10:90, v/v) or toluene] on the other side of the membrane remained stagnant. After the 30 min PHW extraction the oven was cooled, the water flow was turned off and the extract was eluted from the acceptor channel with a flow-rate of 0.5 ml/min for 1 min to yield the volume of 0.5 ml. The elution volume was based on our previous study [14] and elution of subsequent fractions from the acceptor channel. To ensure the elution of all the analytes, a fraction of 0.5 ml was eluted (analysis off-line, no upper elution limit unlike in the previous on-line method [14]).

2.2.4. HF–MMLLE

The water flow from the PHWE was directed through the donor cavity inside the hollow fibre membrane module while the organic acceptor [ethylacetate–cyclohexane (10:90, v/v)] inside the fibres was stagnant. After the oven was cooled and the water flow turned off, the extract was eluted from the acceptor cavity with a flow-rate of 0.5 ml/min for 1.5 min to yield the volume of 0.75 ml. In our previous study [15] an elution volume of 0.4 ml was found sufficient but a larger volume was eluted since in off-line analysis no upper elution limit exists.

3. Results and discussion

The efficiency of a trapping method is dependent on the chemistry of the analytes, the nature of the matrix, the objectives of the analysis and the limit of determination. The important factors related to the suitability of a trapping method in connection with PHWE are, besides efficiency, the selectivity and repeatability, the number of manual steps required in the pre-treatment, total extraction time and the robustness of the whole system. Three replicate PHW extractions of each sample were carried out with all four trapping methods. The conditions were chosen according to previous optimisation [14]. It was also verified by eluting subsequent fractions from the solid-phase trap that the whole analyte fraction was eluted in 3 ml. The samples were analysed by both GC–MS and SEC.

3.1. Choice of solvent

As a means of achieving comparative results, initially the same solvent, ethyl acetate–cyclohexane (10:90, v/v), was used with all trapping methods. In LLE the trapping solvent should extract the analytes efficiently and it should not mix with water. Benzene, toluene, *n*-hexane, cyclohexane and dichloromethane have typically been used in LLE of PAHs [26]. MMLLE places some additional requirements on the solvent: it should wet the membrane, it should have sufficient surface tension and it should not be overly volatile. In SPE, the solvent should efficiently elute the retained compounds from the trap. On the basis of these considerations, and the fact that cyclohexane is noncarsinogenic, ethyl acetate–cyclohexane (10:90, v/v) was chosen as the trapping solvent for the study. Ethyl acetate (10%) was added to increase the polarity of the solvent, something that was especially necessary when the analytes were eluted from the SPE trap [25]. Toluene is another good solvent for PAHs. Although useful in LLE and flat sheet MMLLE systems, however, it is unsuitable as an extraction solvent in hollow fibre MMLLE because it dissolves the epoxy glue. In SPE

Table 1
Average recoveries (%) obtained with different trapping methods compared to results obtained with Soxhlet extraction, volatiles from naphthalene to fluorene excluded, $n = 3$

	LLE	FS–MMLLE	HF–MMLLE	SPE
JML	159 ± 77	101 ± 23	105 ± 20	121 ± 31
Setoc	123 ± 14	102 ± 26	88 ± 11	151 ± 42
EC-1	95 ± 12	108 ± 29	70 ± 14	111 ± 17
Husarviken	108 ± 14	65 ± 19	47 ± 11	83 ± 30

it causes problems in contact with the Tenax TA solid-phase material. After comparison of the trapping methods with ethyl acetate–cyclohexane as the solvent, the effect of solvent choice on the results was studied by extracting certified EC-1 sediment by PHWE–LLE and PHWE–FS–MMLLE with trapping into toluene.

3.2. Recovery

The recoveries of the PHW extractions obtained with the different trapping methods were compared with those achieved with Soxhlet extraction (Table 1). The average extraction percentages are reported with volatiles from naphthalene to fluorene excluded. The extraction yields (PHWE) for the volatiles were high compared with the Soxhlet results since the Soxhlet extracts had to be concentrated with a rotary evaporator and a considerable fraction of the volatiles was lost in the concentration step. For PHWE–LLE the average recoveries excluding volatiles varied from 95% (EC-1) to 159% (JML). For PHWE–FS–MMLLE they were in the range 65–108% (minimum: Husarviken/maximum: EC-1); for PHWE–HF–MMLLE they were 47–105% (minimum: Husarviken/maximum: JML) and for PHWE– SPE 83–151% (minimum: Husarviken/maximum: Setoc). In general, highest recoveries were obtained with PHWE–LLE and PHWE–SPE. The average recoveries taking all four samples into account were 121% for PHWE–LLE, 94% for PHWE–FS–MMLLE, 78% for PHWE–HF–MMLLE and 117% for PHWE–SPE. It is clear that, because of the dynamic nature of MMLLE, 100% extraction is not typically reached with PHWE–FS–MMLLE or PHWE–HF–MMLLE. Reliable results can be obtained, however, if a recovery standard is used or if the extractions are, for example, coupled on-line to GC (transfer of the whole extract) and the calibration is made with the whole on-line system. PHWE results for PAHs in the certified EC-1 sediment with the different trapping systems are presented in Table 2 together with reference values. A recovery standard was used in the calculation of the results.

The sample matrix and the amount of PAHs in the sample have an effect on the recovery. If the analytes are present in large quantities, their solubility in pressurised hot water can be a limiting factor in the extraction. This may explain why recoveries were lowest (except with PHWE–LLE) for the Husarviken sample, which contained the largest amount of PAHs. The capacity of the SPE trap may also be a limiting factor and break through from the trap may occur with large PAH amounts. An equilibrium process takes place in MMLLE and with high PAH amounts not all the analyte molecules have sufficient time to diffuse through the membrane, and this leads to lower extraction yields. With the samples containing smaller amounts of PAHs (the JML and Setoc samples) the ability of water to dissolve PAHs and the capacity of the trap are not limiting factors and the recoveries are higher. The high recovery of anthracene is most probably due to its poor chromatographic behaviour. Baseline separation between phenanthrene and anthracene is not fully reached and since the amount of phenanthrene is clearly higher than that of anthracene, deviation from the reference value occurred.

Extraction yields obtained with the PHWE–FS– MMLLE were improved over the results of our recent study [14]. The extraction unit employed was now larger (100 μl grooves replaced with 200 μl grooves) and the donor flow-rate could be increased from 0.5 to 1.0 ml/min.

3.3. Repeatability

R.S.D. values are generally large (about 10–30%) in the analysis of complex environmental samples containing only trace amounts of analytes [23]. For example, the R.S.D.

Table 2
Amounts of PAHs (μg/g) determined in sediment EC-1 with different trapping methods, $n = 3$

Compound[a]	LLE	FS–MMLLE	HF–MMLLE	SPE	Reference
Phe	15.6 ± 1.4	17.0 ± 3.4	14.4 ± 3.1	17.7 ± 3.0	15.8 ± 2.0
Ant	5.0 ± 1.2	4.3 ± 1.1	4.8 ± 1.2	3.1 ± 0.7	1.2 ± 0.4
Fla	21.2 ± 1.7	21.3 ± 4.7	21.7 ± 5.2	22.4 ± 4.8	23.2 ± 2.3
Pyr	17.2 ± 1.4	16.0 ± 3.7	14.2 ± 3.3	16.3 ± 3.3	16.7 ± 1.5
BaA + Chry	17.4 ± 2.1	17.5 ± 4.0	17.0 ± 3.4	18.8 ± 3.9	17.9 ± 2.3
BbkF	12.4 ± 3.8	13.0 ± 3.1	12.5 ± 2.5	13.0 ± 2.0	12.3 ± 2.2
BaP	5.3 ± 0.7	5.0 ± 1.2	5.4 ± 1.1	5.3 ± 0.9	5.3 ± 0.3
IdP + DbA	6.1 ± 0.5	6.3 ± 1.5	6.1 ± 0.5	6.3 ± 0.4	7.0 ± 0.4
Bghi	5.0 ± 0.5	5.0 ± 1.0	5.4 ± 1.4	5.0 ± 0.7	4.9 ± 0.3

[a] Phe, phenanthrene; Ant, anthracene; Fla, fluoranthene; Pyr, pyrene; BaA + Chry, benz[*a*]anthracene + chrysene; BbkF, benzo[*b*] + [*k*]fluoranthene; BaP, benzo[*a*]pyrene; IdP + DbA, indeno[1,2,3-*cd*]pyrene + dibenz[*a*,*h*]anthracene; Bghi, benzo[*ghi*]perylene.

values reported for the certified EC-1 sediment are in the range 7.5–25% and on average 12.7% [24]. Reference values for the volatiles (naphthalene, acenaphthylene and acenaphthene) are not reported [24]. We investigated the average R.S.D. values of the PHW extractions with the different trapping methods. With PHWE–LLE the average R.S.D. ranged from 11.5% (Setoc sample) to 48.5% (JML). With PHWE–FS–MMLLE the average R.S.D. were in the range of 22.7–29.7% (minimum: JML/maximum: Husarviken). With PHWE–HF–MMLLE they ranged from 13.0% (Setoc) to 25.2% (Husarviken) and with PHWE–SPE from 16.0% (EC-1) to 37.3% (Husarviken).

The widest variation in the recoveries was obtained with the Husarviken sample containing the largest amount of PAHs. Probably the dirtiness of the extract made the GC analysis less repeatable because there were a number of co-eluting compounds. The co-eluting matrix compounds and the very low amounts of the PAHs in the JML sample were also the probable reasons for the poor repeatability of the PHWE–LLE system.

In our earlier studies with on-line coupled PHWE–FS–MMLLE–GC and PHWE–HF–MMLLE–GC (Husarviken sample), the average R.S.D. values were 10.6 and 8.3%, respectively. Analysis of the less contaminated Setoc sample gave an average R.S.D.% of about 20% [15]. When the whole cycle of extraction and analysis is carried out in a closed system, no manual interference is present and the possibility of sample loss and contamination is minimised. The on-line systems, where no concentration steps are needed, generally give better repeatability than the off-line systems, where only small part of the (concentrated) extract can be injected to GC.

3.4. Selectivity of the trapping methods (cleaning effect)

The selectivity of the four trapping methods was studied by measuring the total peak area in GC chromatograms (relative to the internal standard 4,4′-dibromooctafluorobiphenyl, Table 3) and by recording SEC profiles (Fig. 1). The GC–MS chromatograms for the PHW extracts trapped with the four different systems are presented in Fig. 2. The total GC area gives an estimate of the amount of total organic compounds in the extract, whereas the SEC profile gives an estimate of the molecular mass distribution of the compounds in the extract.

Table 4
Spectral match (%) of selected PAHs with library MS spectra, sediment EC-1

Compound	LLE	FS–MMLLE	HF–MMLLE	SPE
Naphthalene	90	91	90	91
Fluorene	70	96	93	60
Phenanthrene	83	95	95	92
Benz[*a*]anthracene	60	95	70	46
Benzo[*k*]fluoranthene	86	96	83	89

In GC, the largest total areas relative to the area of the internal standard were obtained with PHWE–LLE and PHWE–SPE. The lower total areas with PHWE–FS–MMLLE and PHWE–HF–MMLLE showed the membrane units to provide a positive cleaning effect. Compounds larger than the pore size of the membrane (40 nm in HF–MMLLE and 50 nm in FS–MMLLE) cannot pass through the membranes.

The results of the analysis by SEC confirmed that a significant cleaning effect is obtained with the membrane extraction units. Co-extracted matrix components with high-molecular-mass are a problem in GC analysis because they tend to contaminate the GC system and cause problems in injection and quantitative analysis (matrix and memory effects). If the extract is not cleaned in the trapping step, larger matrix compounds may dirty the GC column. Molecular mass standards (4800–20 000 g/mol) and PAH standards were analysed to determine the retention time window in SEC. Fig. 1 presents the extracts of the JML sediment. As can be seen in the figure, the amount of high-molecular-mass compounds relative to the amount of low-molecular-mass compounds was highest in PHWE–LLE, indicating non-selective trapping. The amount of high-molecular-mass compounds was second highest in the extract obtained by PHWE–SPE (some cleaning effect). A clear cleaning effect was observed with the two membrane extractions. Furthermore, fewer high-molecular-mass compounds were present in the chromatogram obtained with PHWE–HF–MMLLE than in the one obtained with PHWE–FS–MMLLE. This is as expected since the membrane pore size is smaller (40 nm) in HF–MMLLE than in FS–MMLLE (50 nm).

3.5. Spectral match in mass spectrometry

The spectral match of the analyte spectra with MS library spectra was investigated. As an example, Table 4 presents

Table 3
Total peak areas in GC relative to the area of the internal standard for the different trapping methods

	JML	Setoc	EC-1	HUSAR
PHWE–LLE	337 ± 237	102 ± 15	48 ± 2	259 ± 109
PHWE–FS–MMLLE	72 ± 38	68 ± 30	49 ± 8	212 ± 114
PHWE–HF–MMLLE	63 ± 36	82 ± 35	35 ± 14	238 ± 171
PHWE–SPE	100 ± 52	136 ± 49	50 ± 10	380 ± 14
Soxhlet	123 ± 8	136 ± 29	44 ± 2	537 ± 7

Husar, soil sample from Husarviken, Sweden, $n = 3$.

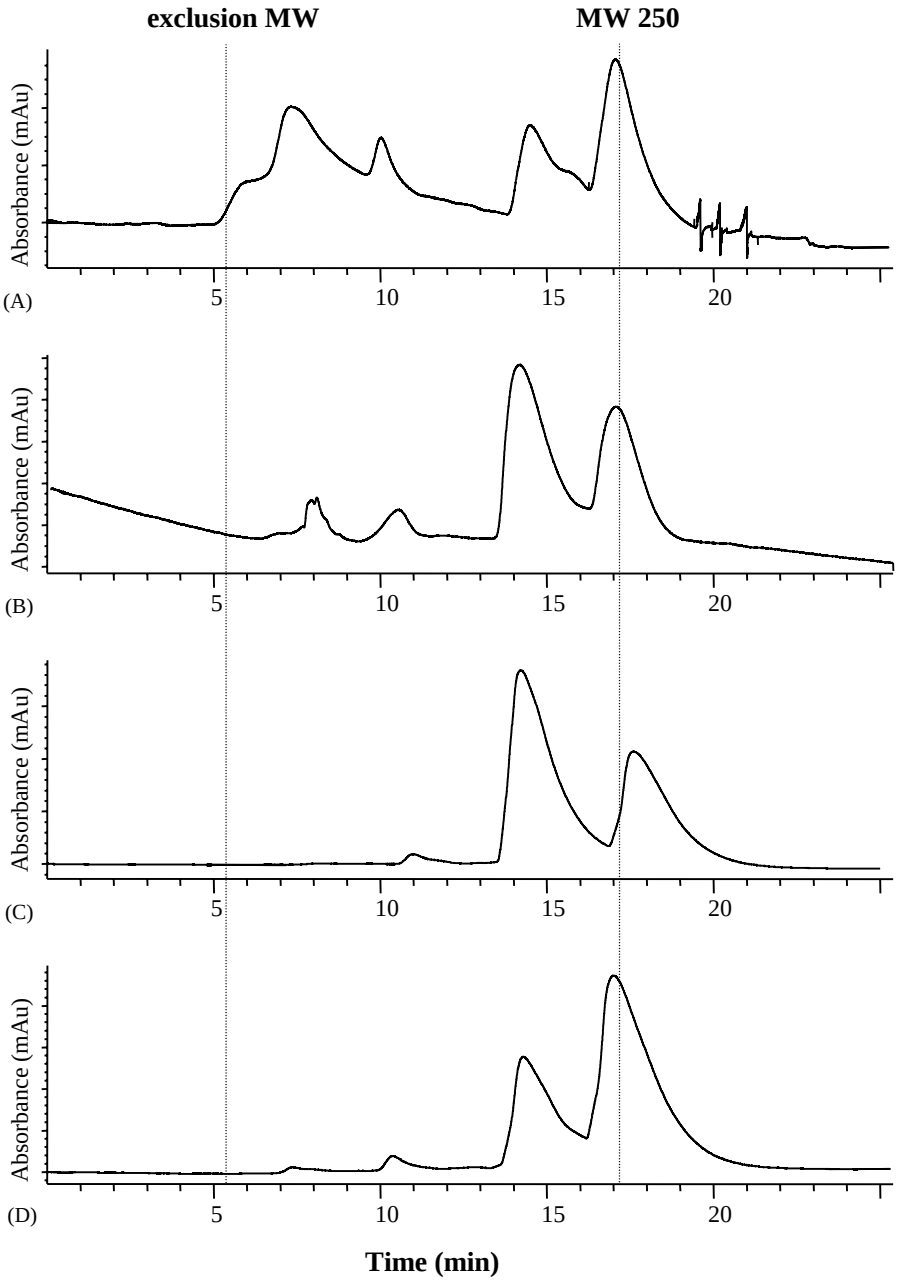

Fig. 1. SEC analysis of JML sediment extract: (A) trapping in ethyl acetate–cyclohexane (10:90) following liquid–liquid extraction; (B) trapping in solid-phase trap containing Tenax TA; (C) trapping by hollow fibre membrane liquid–liquid extraction; (D) trapping by flat sheet membrane liquid–liquid extraction.

the results for five PAH compounds with different molecular masses in the certified EC-1 sediment. Overall, the best spectral matches were obtained with the membrane trapping methods (PHWE–FS–MMLLE and PHWE–HF–MMLLE) in keeping with the more selective trapping with these systems. For the Husarviken sample, which contained high concentration of PAHs, all spectral matches were >95% for all trapping methods. With the Setoc sample the spectral matches varied from 70 to 95% and the percentage of matches also varied within the same trapping method. The PAH levels in the Setoc sample are relatively low and the peaks were not as clearly separated from the background noise as in the case of the Husarviken sample.

3.6. Effect of the trapping solvent

To study the effect of solvent on the trapping, the EC-1 sediment was extracted by PHWE–LLE and PHWE–FS–MMLLE with toluene as well as with ethyl acetate–cyclohexane. No significant differences between the solvents were observed in the total areas divided by the areas of the internal standard: in both systems the

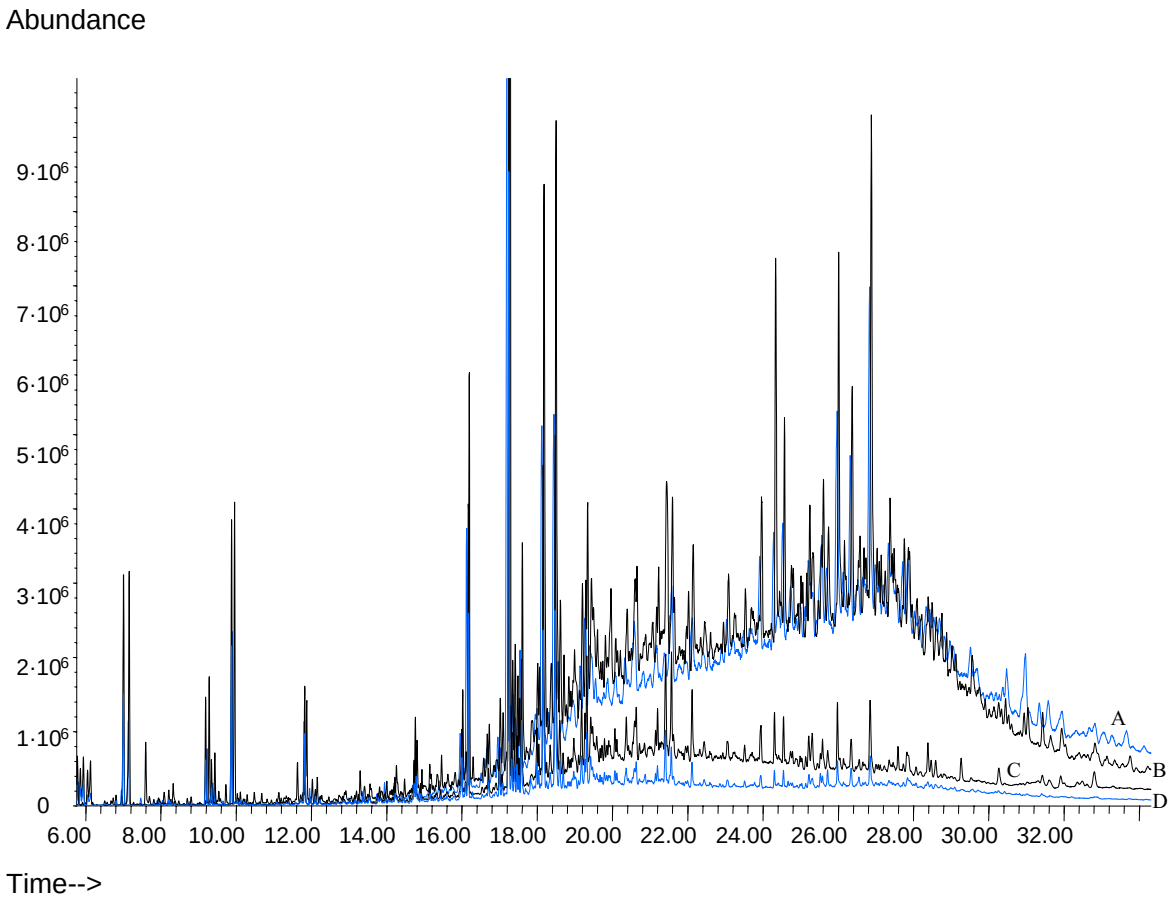

Fig. 2. GC–MS analysis of sediment EC-1: (A) trapping in solid-phase trap containing Tenax TA; (B) trapping in ethyl acetate–cyclohexane (10:90) following liquid–liquid extraction; (C) trapping by flat sheet membrane liquid–liquid extraction; (D) trapping by hollow fibre membrane liquid–liquid extraction.

recoveries of PAHs were generally only slightly better with toluene than with ethyl acetate–cyclohexane (10:90, v/v). The average recoveries relative to those obtained in Soxhlet extraction (excluding volatiles naphthalene to fluorene) were 97.8% (EtAc–cyclohexane) and 98.4% (toluene) for PHWE–LLE and 116.1% (EtAc–cyclohexane) and 118.1% (toluene) for PHWE–FS–MMLLE. Taking into account the standard deviations of the measurements the differences were not significant.

Differences in the repeatability of PHWE–FS– MMLLE were observed. The R.S.D.% with toluene trapping was 6.1%, while it was 26.6% with ethyl acetate–cyclohexane (10:90, v/v) trapping. With PHWE–LLE, on the other hand, the R.S.D.% values for toluene and ethyl acetate–cyclohexane (10:90, v/v) were 17.3 and 12.9%, respectively.

3.7. Solvent consumption

The trapping methods requiring smallest amounts of solvent were the membrane extractions. About 0.5 ml of elution solvent was needed in FS–MMLLE and about 0.75 ml in HF–MMLLE. The extract was eluted with 3 ml of organic solvent in PHWE–SPE and with 6 ml in PHWE–LLE. In all methods, organic solvent was also used in the cleaning of the metal and PTFE tubings.

3.8. Extraction time (PHWE + trapping)

Total extraction times were different with the different trapping methods. With PHWE–LLE it took about 1 h to extract the sample: PHWE (30 min) followed by manual liquid–liquid extraction twice, drying the sample with Na_2SO_4 and concentration with N_2. With PHWE–FS–MMLLE and PHWE–HF–MMLLE the extract merely had to be eluted from the acceptor channel of the membrane module after PHW extraction and was then ready to be injected into the GC system. That took about 35 min altogether. With PHWE–SPE the solid-phase trap had to be dried for 10–15 min after the PHW extraction. After that the extract was eluted, dried and concentrated. Drying of the extract was necessary to remove possible traces of water, which could damage the GC column. The whole procedure took about 1 h. The evaporation in PHWE–LLE and PHWE–SPE could of course be done in parallel for several samples, which would slightly decrease the total extraction time.

Table 5
Comparison of characteristics of different trapping methods after PHWE

	PHWE–LLE	PHWE–FS–MMLLE	PHWE–HF–MMLLE	PHWE–SPE
Recovery vs. Soxhlet (%) (average)	95–158 (121)	65–108 (94)	50–105 (78)	83–150 (117)
R.S.D.%	11–48	22–29	13–25	16–37
Operation	Many manual steps required (LLE, drying, concentration with N_2)	Easy	Easy	Relatively easy, concentration with N_2 required
Robustness	Average	Good	Average	Poor
Number of manual steps after PHWE	3	0	0	2
Consumption of solvents	>5 ml	Elution with 0.5 ml	Elution with 0.5–1.0 ml	3 ml
Extraction time (PHWE + trapping)	∼1 h	35 min	35 min	∼1 h
Selectivity	−	++	++	+
On-line connection to GC	−	+	+	+
Special problems	Laborious manual work	Possible adsorption to PEEK and PTFE materials in the membrane block	Building of the HF–MMLLE unit	Blockage of the trap ≥ increasing pressure, memory effects

3.9. Challenges and advantages

The characteristics of the trapping methods are compared in Table 5.

3.9.1. PHWE–LLE

A multi-step procedure is carried out in PHWE–LLE. Considerable manual work is required and the procedure is laborious. The possibilities of human error and contamination also have to be taken into account. On the other hand, extraction yields are generally high.

3.9.2. PHWE–FS–MMLLE

Possible adsorption of the hydrophobic analytes onto the PTFE and PEEK materials of the membrane block may cause problems (memory effects, unrepeatable results in PHWE–FS–MMLLE). These problems can be minimised by careful cleaning of the tubings and extraction channels with organic solvents. One of the main advantages of this method is the fast collection of the extract requiring no further manual pre-treatment. Also, selectivity is enhanced relative to LLE and SPE. The membrane extraction unit is relatively robust and operation is easy. On-line connection to LC or GC is possible.

3.9.3. PHWE–HF–MMLLE

The gluing is challenging in the construction of the HF–MMLLE module, since the glue has to be compatible with the organic acceptor solvent. We chose epoxy glue and this limited the selection of the acceptor solvent as aromatic solvents cannot be used in contact with epoxy glue. The main advantages are the same as in PHWE–FS–MMLLE: fast collection of the extract, good selectivity and the possibility of on-line connection to LC or GC.

3.9.4. PHWE–SPE

The major problem with the solid-phase trap as a collection method is that it occasionally gets partly or fully blocked. The blockage causes a rise in pressure and, at worst, unrepeatable extractions. The pressure in PHWE was maintained at 9 bar for PHWE–LLE and PHWE–MMLLE, so the extraction was made with water vapour (steam), which has proven to be more efficient than liquid water [25]. The threshold value for steam/liquid water is 86 bar at 300 °C. In PHWE–SPE, the pressure occasionally rose rapidly, even over 86 bar, owing to partial blockage; the state of the water then changed from steam to liquid leading to unrepeatable results. Even though the trap was cleaned with organic solvent after each extraction, some memory effects were encountered. Also, alteration of the Tenax material was observed after several extractions. With dirty samples (the Husarviken soil), the filters in the column ends had to be changed or cleaned after some ten extractions to avoid blockage.

Advantages of PHWE–SPE are its good extraction efficiency and the possibility of on-line connection to LC or GC.

4. Conclusions

Considerably different results were obtained with the four trapping methods in PHWE; recoveries, R.S.D.%, selectivity and operation all differed. It follows that the trapping method should be selected with care. On the basis of this research it could be concluded that, for the best possible recovery, trapping into solvent may be the method of choice. If selectivity is important, membrane extraction will be best. In membrane extraction units, large matrix compounds can-

not pass through the membrane pores but they remain in the donor feed so that the extract is cleaner. Of the two membrane trapping systems, higher extraction yields were obtained with the flat sheet unit. This unit is also more robust than the hollow fibre unit and could therefore be recommended for use with PHWE.

Acknowledgements

Financial support was provided by the Academy of Finland (project 48867). The authors are grateful to Mr. Pekka Tarkiainen, Workshop of the Department of Chemistry, for technical support. Dr. J. Schneider (Celgard GmbH, Wiesbaden, Germany) is thanked for providing us with Celgard membrane samples.

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