Supercritical carbon dioxide extraction of polycyclic aromatic hydrocarbons from sediments

Hing-Biu Lee* and Thomas E. Peart

National Water Research Institute, Environment Canada, P.O. Box 5050, Burlington, Ontario L7R 4A6 (Canada)

Robert L. Hong-You

Wastewater Technology Centre Laboratories, Burlington, Ontario L7R 4L7 (Canada)

Dennis R. Gere

Hewlett-Packard Company, Little Falls Site, 2850 Centerville Road, Wilmington, DE 19808 (USA)

ABSTRACT

A supercritical fluid extraction (SFE) method using carbon dioxide was developed for the determination of the 16 US Environmental Protection Agency polycyclic aromatic hydrocarbon (PAH) priority pollutants in naturally contaminated sediments. While carbon dioxide is less efficient for the heavier PAHs than other fluids such as nitrous oxide and Freon-22, its deficiency was remedied by the use of a mixture of water, methanol, and dichloromethane as modifiers, a higher extraction temperature of 120°C, as well as repetitive extractions. Extraction time can be further reduced to *ca.* 70 min per sample if a high-pressure pump is used for the delivery of the modifiers during dynamic extraction. Except for naphthalene, the SFE results for the 16 PAHs obtained from several certified reference materials and sediments samples were comparable to certified or Soxhlet values in terms of both precision and accuracy. The SFE recoveries of naphthalene as well as methylnaphthalenes which were coextracted alongside other PAHs and methyl-PAHs, ranged from 150 to 125% of their respective Soxhlet values due to higher evaporative losses in the Soxhlet procedure.

INTRODUCTION

Polycyclic or polynuclear aromatic hydrocarbons (PAHs/PNAs) are ubiquitous environmental pollutants that are present in large numbers and varying quantities in air, water, and sediment samples. PAHs are formed naturally by many routes such as forest fires and volcanic activities, however, the recent build-up of the aromatic hydrocarbons in densely populated areas is likely related to the incomplete combustion of coal and other fossil fuels. While the occurrence of alkyl- and nitro-substituted as well as other heteroatom-containing PAHs are often reported, the most abundant and routinely monitored PAHs are the 16 listed in Method 610 [1] by the United States Environmental Protection Agency (US EPA). These compounds are also included in the Priority Substances List under the Canada Environmental Protection Act (CEPA). Many of these hydrocarbons as well as

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* Corresponding author.

their derivatives and metabolites are suspected mutagens and carcinogens. Due to the low solubilities and persistence of the PAHs, they are readily adsorbed and accumulated in sediments at levels from μg/g to ng/g in many sites of the Great Lakes Basin [2].

Numerous analytical methods have been reported for the final analysis of PAHs. Flame ionization, photoionization, electron capture and other detectors have been used with capillary column gas chromatography [3,4]. In the case of high-performance liquid chromatography (HPLC), ultraviolet, fluorescence and photodiode array detectors are generally used in conjunction with reversed-phase columns [5,6]. Mass spectrometry interfaced to either GC or HPLC is also a popular choice for many workers because of its selectivity and sensitivity for PAHs [7]. In contrast, extraction of sediment samples in many cases is accomplished by the Soxhlet technique using various mixtures of organic solvents [8]. This mode of sample preparation, while exhaustive in terms of recovery, requires a lengthy extraction time from 8 to 48 h, consumes large amounts of solvent, and generates a large amount of coextractives which necessitate two to three subsequent column cleanup steps before final analysis. The cleanup procedures further aggregate the time and solvent problem.

More recently, applications of supercritical fluid extraction (SFE) for the determination of PAHs from soil and sediments have been demonstrated [9–11]. The new extraction technique practically eliminates the use of solvents and produces extracts suitable for analysis with selective detectors such as the mass spectrometer without cleanup. The early work with supercritical carbon dioxide at room temperature produced quantitative recovery for five PAHs in an urban dust standard reference material (SRM 1649) distributed by the National Institute of Science and Technology, however, the extraction time was still a lengthy four hours [9]. Subsequent work with a shorter extraction time produced incomplete recovery, particularly for those PAHs with a molecular mass of 252 or higher [12]. While raising the extraction temperature from 50 to 200°C greatly increased the recoveries of PAHs by using pure carbon dioxide

[13], improved results for the heavier PAHs were obtained by extraction with supercritical carbon dioxide pre-modified with a polar solvent such as methanol [14]. In contrast, quantitative recovery of PAHs was achieved by the use of supercritical nitrous oxide modified with methanol [11]. Presumably due to its higher dipole moment, Freon-22 (chlorodifluoromethane) has recently been shown to yield higher extraction efficiency than non-modified nitrous oxide and carbon dioxide [15]. Though Freon-22 has a lower ozone-depletion potential and is used as an interim substitute for Freon-11, a common refrigerant, it was estimated that the former had a third to a quarter of the global warming effect as the latter [16]. At a time when government agencies are legislating on the drastic reduction of the use of many chlorofluorocarbons (CFCs) in industrial applications and domestic products, the advocacy of a freon as a SFE solvent is a step backward in environmental protection. Notwithstanding the higher extraction efficiency, Freon-22 is only suitable for research purposes since it is less commonly available, more expensive and poses a greater health risk in the working environment than carbon dioxide. For routine applications, there is still a need to investigate how the efficiency of supercritical carbon dioxide can be improved for the extraction of native PAHs in sediment samples. In this work, we shall discuss the factors affecting the extraction recovery of the 16 PAHs from naturally contaminated sediments using supercritical carbon dioxide. Procedures to further shorten the extraction time by the use of a high-pressure pump to deliver mixtures of modifiers during the extraction will also be introduced.

EXPERIMENTAL

Reagents and chemicals

PAHs and methyl PAHs were obtained from Aldrich (Milwaukee, WI, USA) and Ultra Scientific (North Kingstown, RI, USA). Deuterated PAHs were obtained from Aldrich and MSD Isotopes (Pointe Claire, Canada).

Individual stock solutions of PAH, methyl PAH, and deuterated PAH internal standards at 1000 or 500 μg/ml were prepared in toluene.

Mixtures of the 16 PAHs in US EPA Method 610 [1] at 2 and 0.5 μg/ml, as well as the ten methyl PAHs (see Results and Discussion and Table III) at 500 and 100 ng/ml were prepared in isooctane. Another mixture of six deuterated PAHs was also prepared in isooctane at the following concentrations: [$^2H_8$]naphthalene, 100 μg/ml; [$^2H_{10}$]phenanthrene, 100 μg/ml; [$^2H_{10}$]pyrene, 100 μg/ml; [$^2H_{12}$]chrysene, 50 μg/ml; [$^2H_{12}$]benzo[*a*]pyrene, 50 μg/ml; and [$^2H_{12}$]benzo[*ghi*]-perylene, 30 μg/ml. Appropriate amounts of the native and deuterated PAH solutions were mixed and used as calibration standards for GC–MS analysis.

SFE-grade carbon dioxide without a helium head pressure was obtained from Praxair Canada (Mississauga, Canada) and Air Products (Nepean, Canada).

Sediment samples

The samples used in this work are either certified reference materials (CRM) (EC-1 and HS-3) or lake or harbour sediments naturally contaminated with PAHs. EC-1, developed and distributed by Environment Canada, is a lake sediment derived from Hamilton Bay, a heavily industrialized location in western Lake Ontario. The certified PAH concentrations in this material were obtained by over 75 in-house Soxhlet extractions followed by GC–flame ionization detection (FID), GC–MS, or HPLC–ultraviolet/fluorescence detection [17]. These values were further confirmed by an interlaboratory study involving 15 laboratories across Canada. HS-3 is a marine sediment CRM purchased from the National Science and Engineering Research Council of Canada. The other two samples also used in this work were obtained from Vancouver Harbour (VAN-4) and Detroit River (DET-1). All samples were freeze-dried, crushed, ground and sieved before extraction.

SFE of sediment samples

All extractions were done by either the Hewlett-Packard 7680A or 7680T SFE module, both controlled by an IBM compatible personal computer and a dedicated SFE software. The latter extractor is an upgraded model of the

7680A with an eight-position thimble-holder for automated sequential extraction of up to eight samples. Before the extraction, two layers of Whatman GFC filter paper cut to the diameter of the thimble were placed just above the cap at the bottom of the thimble. Then 200 mg of Celite and 1 g of freeze-dried or air-dried sample were weighed into the thimble. In the absence of a modifier pump, the modifier was spiked onto the sediment and the mixture was mixed on a vortex mixer for 1 min. The sample was typically extracted with CO_2 at 36 MPa and a flow-rate of 2 ml/min for 25 min (5 min static and 20 min dynamic) and at various temperatures. For quantitative recovery of nearly all PAHs, three consecutive extractions of the same sample at 120°C in the presence of 500 μl of a 1:1 mixture of methanol and dichloromethane (DCM) were performed. During the dynamic extraction, the PAHs were collected by an octadecylsilane (ODS) trap maintained at 15°C. At the end of the extraction, the trap was heated to 40°C before the PAHs were eluted from the trap with two 1.5-ml rinses of a 1:3 (v/v) mixture of isooctane and DCM. The extracts were combined and the solvent was exchanged into pure isooctane for GC–MS analysis. Using this procedure, each extraction cycle required *ca.* 50 min.

The modifier pump

A Hewlett-Packard 1050 quaternary LC pump was used for the delivery of up to four different modifiers to be mixed with the supercritical carbon dioxide. The outlet tubing from the modifier pump was interfaced to the check valve weldment downstream of the 7680T SFE pulse damper through a 1/16 in. (0.16 cm) stainless-steel tubing with Swagelok and Valco fittings. The pump and the SFE apparatus were both controlled by the same 80386-based personal computer running a pre-release SFE control software (version A.00.00) under the Microsoft Windows 3.1 environment. Before the operation of the modifier pump, the solvent modifiers were first degassed and the channels being used were primed at 5 ml/min. The software switches the pump on and off at the prescribed time as well as controls the percentages (up to a total of 20%)

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of the modifiers to be blended with the extraction fluid.

For the SFE of PAHs from sediments using the modifier pump, 500 μl of water was spiked to a 1-g sample and it was thoroughly mixed prior to extraction. A three-step extraction outlined below was used for all sediments. The sample was first extracted with pure carbon dioxide at 34 MPa for 7 min (2 min static and 5 min dynamic) at 120°C and a flow-rate of 4 ml/min. The extract was rinsed off the ODS trap by 1.5 ml of a 1:3 mixture of isooctane and DCM. (Note: if PAHs are analyzed by HPLC methods, the rinse solvent should be replaced by a 1:1 mixture of tetrahydrofuran and acetonitrile.) Without depressurization of the thimble, the extraction was continued at the same temperature and pressure with CO_2 mixed with 1% methanol and 4% DCM at a flow-rate of 2 ml/min for 31 min (1 min static and 30 min dynamic), followed by the final step with pure CO_2 again for 2.5 min at 4 ml/min. At the end of the extraction, the trap was rinsed again with 1.5 and then 1.2 ml of the same solvent mixture, before and after thimble depressurization. The combined extract was also solvent exchanged into isooctane prior to analysis. The entire extraction cycle took ca. 70 min.

GC–MS analysis of PAHs

The SFE extracts for each sample were combined and solvent exchanged into a suitable volume (typically between 1 and 10 ml) of isooctane. A 1-ml aliquot of this extract was removed and mixed with 20 μl of the six deuterated internal standard solutions. The extract was then analyzed by capillary column GC–MS using a Hewlett-Packard Model 5890 Series II gas chromatograph equipped with a Model 5971 Mass Selective Detector. A 30 m × 0.25 mm I.D. DB-5 column and the following temperature programs were used: initial oven temperature 70°C, initial hold and valve time 1.0 min, oven temperature programming rates 30°C/min (from 70 to 120°C) and 4°C/min (from 120 to 280°C). Carrier gas (helium) head pressure was 35 kPa. Splitless injections (1 μl) were made by a Model 7673 autosampler. Data were acquired in selected ion monitoring mode for the molecular ions of the PAHs and methyl PAHs as listed in Tables

I and III. As outlined in US EPA Method 625 [1], response factors for the native PAHs were calculated by using an appropriate deuterated internal standard as described below: (1) [$^2H_8$]naphthalene (m/z 136) for naphthalene, all methyl naphthalenes, acenaphthene, and acenaphthylene; (2) [$^2H_{10}$]phenanthrene (m/z 188) for fluorene, phenanthrene, and anthracene, and their methyl derivatives; (3) [$^2H_{10}$]pyrene (m/z 212) for fluoranthene and pyrene; (4) [$^2H_{12}$]chrysene (m/z 240) for benzo[a]anthracene and chrysene; (5) [$^2H_{12}$]benzo[a]pyrene (m/z 264) for benzo[b]- and benzo[k]fluoranthenes, as well as benzo[a]pyrene; and (6) [$^2H_{12}$]benzo[ghi]perylene (m/z 288) for indeno[1,2,3-cd]pyrene, dibenzo[ah]anthracene and benzo[ghi]perylene.

RESULTS AND DISCUSSION

Effect of modifiers on the SFE of PAHs

There are many examples of incorporating modifiers to increase the recovery of organic compounds under SFE conditions [14,18–20]. In many cases, these modifiers are either water, acids or polar organic solvents. The purpose is either to modify the sample matrix so that the organics are freed for extraction or to increase the solubility of the organics in the supercritical fluid, particularly the non-polar carbon dioxide. The SFE recovery of PAHs can also be benefited by the use of modifiers. Fig. 1 depicts the results for seven PAHs in EC-1 obtained by spiking 500 or 750 μl of the modifier directly onto 1 g of EC-1 prior to extraction at 80°C with 36 MPa of CO_2. These seven compounds, ranging from naphthalene to indeno[1,2,3-cd]pyrene, cover the entire mass range for the PAHs in Method 610 and thus their results are truly representative for the whole group of PAHs. As shown in Fig. 1, relatively small amounts of PAHs of mass 252 and above could be recovered by pure carbon dioxide. The presence of 500 μl of either water, methanol, and DCM as modifiers improves the recovery of all PAHs, although the modifiers had the least effect on the recovery of phenanthrene and the largest on indeno[1,2,3-cd]pyrene. Among various modifiers, the difference in recovery is small for all PAHs between methanol
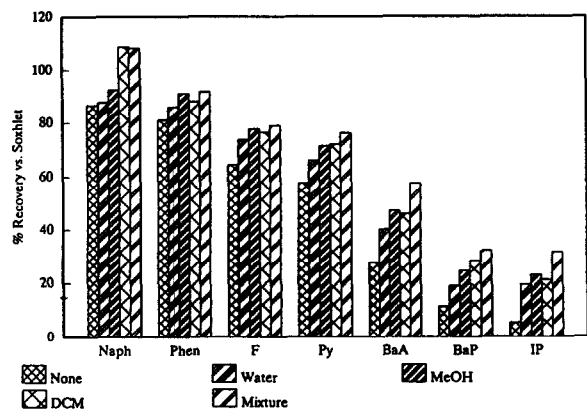
Fig. 1. Effect of modifiers on the SFE recovery of selected PAHs in the certified reference material EC-1. For every PAH, the SFE result (mean of three extractions) is expressed as a percentage of its Soxhlet or certified value. Each extraction was carried out with a 1-g sample at 80°C and CO_2 of 36 MPa. Prior to extraction, each sample was spiked with 500 μl of water, methanol or DCM, or in the case of the mixture, 250 μl each of the above three solvents. Naph = naphthalene, Phen = phenanthrene, F = fluoranthene, Py = pyrene, BaA = benzo[a]anthracene, BaP = benzo[a]pyrene, IP = indeno[1,2,3-cd]pyrene.
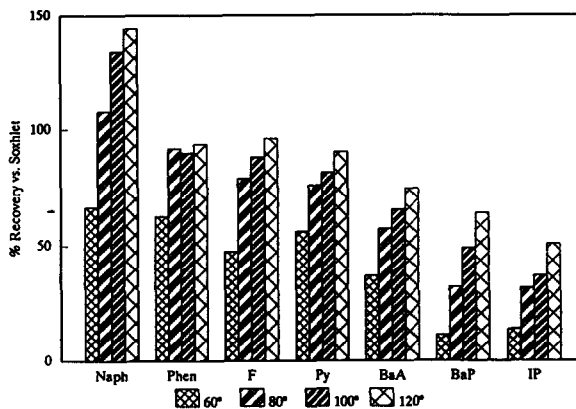
Fig. 2. Effect of extraction temperature (in °C) on the SFE recovery of selected PAHs in EC-1. For every PAH, the SFE result (mean of three extractions) is expressed as a percentage of the Soxhlet or certified value. Each extraction was carried out with a 1-g sample in the presence of 250 μl each of water, methanol and DCM and CO_2 of 36 MPa. For abbreviations see Fig. 1.

and DCM, although they were both more efficient than water. While the mechanism was not clearly understood, 750 μl of a 1:1:1 mixture of the three modifiers definitely gave the highest results for all PAHs, particularly for those PAHs of molecular mass 228 and higher. Apparently, the higher (750 vs. 500 μl) modifier volume in the case of the mixture was not responsible for the improved PAH recovery since experiments with either 500 or 1000 μl of the single modifier produced very similar results.

Effect of extraction temperature on the SFE of PAHs

Earlier we have examined the recovery of PAHs after they were spiked to sediment samples and found that quantitative recoveries of PAHs could be obtained at an extraction temperature of 80°C or lower and an extraction time of about 30 min with either methanol or DCM as a modifier. With real world samples such as EC-1, however, it is obvious from Fig. 1 that we were not able to get full recovery of all PAHs even with the most efficient modifier at 80°C. A study of the recovery of the seven PAHs in EC-1 at 60, 80, 100 and 120°C (Fig. 2) clearly indi-

cated that a higher extraction temperature provided a better recovery for *all* PAHs, although going from 80 to 120°C the relative percentage improvement for naphthalene (mass 128), phenanthrene (mass 178), fluoranthene and pyrene (mass 202) was obviously smaller than the higher-molecular-mass PAHs. Thus for the benefit of better extraction efficiency of the heavier PAHs, all subsequent extractions were done at a temperature of 120°C. A closer examination of the results in Fig. 2 also indicated that the SFE recovery for naphthalene at 100 and 120°C were both significantly (30 to 40%) higher than the Soxhlet result. Since the SFE extract required minimal evaporation and no cleanup, the lower naphthalene result is more likely due to higher evaporative loss of the volatile hydrocarbon in the concentration steps for the Soxhlet extract before and after the column cleanup rather than a reflection of the extraction efficiency of the two techniques.

Effect of consecutive SFE on the same sample

As shown in Fig. 2, the recovery of naphthalene, phenanthrene, fluoranthene and pyrene was close to their Soxhlet values (90% or above) after a single extraction at 120°C in the presence of modifiers. However, recovery for the heavier PAHs under the same conditions was still less

than quantitative. In our work, the modifier was spiked directly onto the sample prior to extraction. This method to introduce the modifier is simple and very flexible during method development stages since each extraction can be done with a different modifier, if required. However, it has the drawback that the modifier is quickly consumed in the early part of the dynamic extraction. Since it is not replenished during the extraction, the latter part of the dynamic extraction is virtually done with non-modified carbon dioxide only. This problem can be easily solved by using supercritical fluids premixed with a fixed amount of modifier of choice, yet the latter are more expensive and under some storage conditions, the modifier can separate from the supercritical fluid, resulting in an extractant other than the one labelled and producing unexpected results. A premixed fluid is also not flexible enough for method research purposes since the extractant is confined to a single, predetermined composition. Another way to overcome the problem of incomplete recovery is to perform more than one extraction and spike additional modifier to the sample again before extraction. As shown in Fig. 3, the second and even the third extractions are clearly beneficial to the recovery, percentagewise, of PAHs such as benzo[a]pyrene and indeno[1,2,3-cd]pyrene.
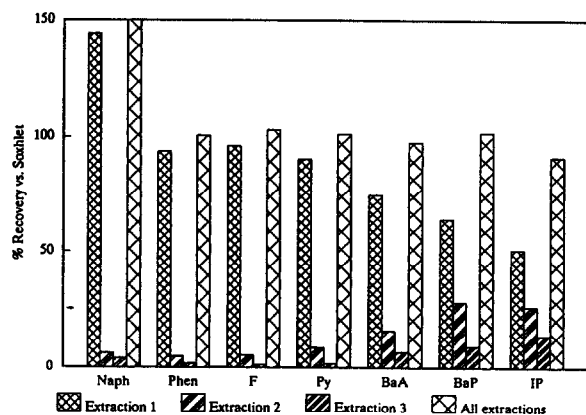

Fig. 3. Effect of consecutive SFE on the recovery of PAHs in EC-1. SFE was carried out on a 1-g sample at 120°C with CO_2 at 36 MPa. Aliquots of 250 μl each of water, methanol and DCM were added to the sample prior to the first extraction and 250 μl each of methanol and DCM were added to the sample prior to the second and third extractions. For abbreviations see Fig. 1.

The combined recovery of each of the seven PAHs in EC-1 after three extractions were all better than or equal to the Soxhlet results with the exception of indeno[1,2,3-cd]pyrene which was ca. 90% recovered.

Introduction of modifiers by means of a pump

Instead of spiking the modifier directly onto the sample prior to SFE, a better way to introduce the modifier is to mix it with the extraction fluid at a constant rate. This provides a continuous and uniform supply of modified carbon dioxide through the entire dynamic extraction period and thereby improves the recovery of all PAHs. Note that in the modifier pump method, the sediment was wetted to a 50% moisture content before SFE. To improve extraction and trapping efficiency, our extraction method consisted of three extraction and three rinse steps. In extraction step one, the more readily extractable aliphatic hydrocarbons and some of the lower molecular PAHs were first removed from the sediment by a short extraction with pure CO_2 and they were rinsed off the trap before the subsequent steps. The rest of the lighter PAHs and the bulk of the heavier PAHs were extracted in step two when modified CO_2 was introduced. In order to reduce the amount of solvents accumulated in the trap causing degraded adsorption efficiency, a 1:4 instead of a 1:1 mixture of methanol and DCM was used as modifiers. In this case, all of the DCM and some of the methanol were evaporated at the nozzle with a temperature set at 45°C during the depressurization of CO_2. The last step was a short extraction designed to remove any residual modifier in the CO_2 pump and lines before the extraction of the next sample. Using this procedure with the modifier pump, we obtained the same recovery for all PAHs in EC-1 as the Soxhlet or certified values (Table I). By eliminating the second and third extractions of the same sample as in the case without the pump, we were also able to fully automate the entire extraction sequence and reduce the sample extraction time by over 50% from 150 to 70 min. As indicated by the standard deviations for all PAHs in replicate determinations in Table I, the precision of the

TABLE I

PRECISION AND ACCURACY OF THE SFE METHOD USING THE MODIFIER PUMP FOR THE RECOVERY OF PAHs IN EC-1

Standard deviations given for SFE values were based on six replicate extractions.

PAH	m/z	Certified value (μg/g)	SFE value (μg/g)	% of certified
Naphthalene	128	(27.9)[a]	41.3 ± 3.6	(148)
Acenaphthylene	152	(0.8)	0.9 ± 0.1	(112)
Acenaphthene	154	(0.2)	0.2 ± 0.01	(100)
Fluorene	166	(15.3)	15.6 ± 1.8	(102)
Phenanthrene	178	15.8 ± 1.2	16.1 ± 1.8	102
Anthracene	178	(1.3)	1.1 ± 0.2	(88)
Fluoranthene	202	23.2 ± 2.0	24.1 ± 2.1	104
Pyrene	202	16.7 ± 2.0	17.2 ± 1.9	103
Benzo[a]anthracene	228	8.7 ± 0.8	8.8 ± 1.0	101
Chrysene	228	(9.2)	7.9 ± 0.9	(86)
Benzo[b]fluoranthene	252	7.9 ± 0.9	8.5 ± 1.1	108
Benzo[k]fluoranthene	252	4.4 ± 0.5	4.1 ± 0.5	91
Benzo[a]pyrene	252	5.3 ± 0.7	5.1 ± 0.6	96
Indeno[1,2,3-cd]pyrene	276	5.7 ± 0.6	5.2 ± 0.6	91
Benzo[ghi]perylene	276	4.9 ± 0.7	4.3 ± 0.5	88
Dibenzo[ah]anthracene	278	(1.3)	1.1 ± 0.2	(85)

[a] Values in parentheses were obtained from or compared to Soxhlet extraction results which were not certified.

SFE procedure is virtually the same as the Soxhlet method.

Application of the SFE method to other types of sediments

So far, all the results were based on the work of a single CRM. In order to test the SFE method using the modifier pump for general applicability, it was further examined on several other different types of sediment, including a marine sediment CRM (HS-3) and sediment samples collected in Vancouver Harbour (VAN-4) and Detroit River (DET-1). For HS-3, 13 out of the 16 SFE results (Table II) were within one standard deviation from their certified values. Also in consistency with our findings, all of our PAH results for HS-3 were a few times higher than those obtained on the same CRM by other workers using pure carbon dioxide at 350 atm (1 atm = $1.01 \cdot 10^5$ Pa) and 60°C for 20 min [21]. No certified PAH concentrations were available for DET-1 and VAN-4, however, it is obvious from Table II that the SFE and Soxhlet values are very comparable in nearly all cases. The above

results suggested that our proposed SFE procedure is suitable for the extraction of PAHs in environmental samples.

SFE of methyl PAHs in sediments

Lower-molecular-mass PAHs are more readily metabolized in the environment to give methyl or alkyl derivatives. Methylated derivatives of naphthalene and a few other PAHs are commonly found in sediment samples. Our current SFE method can also be applied to the extraction of methyl PAHs which are metabolites of their parent compounds. Because of the availability of authentic standards, our work was only limited to the five methyl and dimethyl naphthalenes, three methyl and dimethyl anthracenes and one each of methylfluorene and methylphenanthrene as listed in Table III. Similar to the findings for naphthalene in EC-1 and other samples in Table II, the SFE recoveries for methyl and dimethyl naphthalenes in DET-1 and VAN-4 were ca. 150 and 125%, respectively of their Soxhlet values. Again, the lower results can be attributed to the evaporative losses of these semi-volatile com-

TABLE II

COMPARISON OF PAH RESULTS IN SEVERAL SEDIMENT OR SOIL SAMPLES USING THE SFE AND MODIFIER PUMP TECHNIQUE VS. CERTIFIED OR SOXHLET VALUES

All in-house SFE results were the mean of triplicate determinations.

PAH	HS-3 (μg/g)		DET-1 (ng/g)		VAN-4 (μg/g)	
	Certified	SFE	Soxhlet	SFE	Soxhlet	SFE
Naphthalene	9.0 ± 0.7	7.4 ± 0.6	450	695 ± 73	7.1	11.6 ± 1.2
Acenaphthylene	0.3 ± 0.1	0.4 ± 0.1	139	144 ± 13	2.5	2.8 ± 0.3
Acenaphthene	4.5 ± 1.5	3.3 ± 0.3	65	58 ± 3	<0.1	<0.1
Fluorene	13.6 ± 3.1	10.4 ± 1.3	140	135 ± 11	4.8	5.1 ± 0.4
Phenanthrene	85 ± 20	86.2 ± 9.5	1044	1018 ± 88	25.4	25.8 ± 2.6
Anthracene	13.4 ± 0.5	12.1 ± 1.5	379	303 ± 46	4.5	4.3 ± 0.5
Fluoranthene	60 ± 9	54.0 ± 6.1	2345	2067 ± 157	20.7	20.5 ± 2.2
Pyrene	39 ± 9	32.7 ± 3.7	2189	2039 ± 176	30.9	29.4 ± 2.5
Benzo[a]anthracene	14.6 ± 2.0	12.1 ± 1.3	2116	2104 ± 235	12.4	12.4 ± 1.4
Chrysene	14.1 ± 2.0	12.0 ± 1.3	1754	1644 ± 149	10.7	9.4 ± 0.9
Benzo[b]fluoranthene	7.7 ± 1.2	8.4 ± 0.9	1080	1240 ± 117	4.0	4.2 ± 0.5
Benzo[k]fluoranthene	2.8 ± 2.0	3.2 ± 0.5	1142	1198 ± 158	2.1	2.1 ± 0.2
Benzo[a]pyrene	7.4 ± 3.6	6.6 ± 0.8	1296	1277 ± 135	9.3	8.5 ± 0.9
Indeno[1,2,3-cd]pyrene	5.0 ± 2.0	4.5 ± 0.6	1209	1113 ± 105	4.1	4.0 ± 0.5
Benzo[ghi]perylene	5.4 ± 1.3	4.4 ± 0.6	853	626 ± 71	4.2	3.9 ± 0.5
Dibenzo[ah]anthracene	1.3 ± 0.5	1.1 ± 0.3	304	288 ± 19	1.8	1.6 ± 0.2

pounds in the Soxhlet procedure. For the methyl derivatives of fluorene, phenanthrene and anthracene, the SFE results were only 5 to 10% higher than the Soxhlet results.

CONCLUSIONS

The 16 PAHs listed in the US EPA Method 610 can be recovered from naturally contami-

TABLE III

CONCENTRATIONS OF SOME METHYL PAHs IN DET-1 AND VAN-4 OBTAINED BY SFE AND SOXHLET EXTRACTION

All SFE results were the mean of triplicate determinations.

Methyl PAH	m/z	DET-1		VAN-4	
		Soxhlet (ng/g)	SFE % Soxhlet	Soxhlet (ng/g)	SFE % Soxhlet
2-Methylnaphthalene	142	56	150	1470	149
1-Methylnaphthalene	142	50	152	3760	147
2,6-Dimethylnaphthalene	156	42	131	2520	126
2,3-Dimethylnaphthalene	156	9	125	1540	120
1,2-Dimethylnaphthalene	156	N.D.	N.D.	746	125
1-Methylfluorene	180	36	109	1360	110
2-Methylanthracene	192	115	104	3210	105
1-Methylanthracene + 1-methylphenanthrene	192	221	107	4780	110
9,10-Dimethylanthracene	206	N.D.	N.D.	160	106

nated sediments including certified reference materials by SFE with carbon dioxide at rates similar to Soxhlet extraction. This was achieved by three consecutive extractions on the same sample at 120°C and a carbon dioxide pressure of 36 MPa in the presence of a mixture of water, methanol and DCM as modifiers. Yet, the same results were also obtained for less than half of the time if the modifiers were introduced by a pump during the dynamic extraction stage. Simultaneously, this SFE method using the modifier pump also provided quantitative recovery of several methyl PAHs in sediments. The elimination of cleanup steps and nearly all solvent evaporation, the substitution of carbon dioxide for the less desirable nitrous oxide or Freon-22, fast extraction times (*ca.* 70 min per sample) and Soxhlet-like recovery are the major advantages that make this technique a method of choice among other Soxhlet and SFE procedures developed for PAHs.

ACKNOWLEDGEMENT

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