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Analysis of 23 polynuclear aromatic hydrocarbons from natural water at the sub-ng/l level using solid-phase disk extraction and mass-selective detection

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Abstract

An Empore disk extraction method for the analysis of 23 polynuclear aromatic hydrocarbons (PAHs) in natural waters at ng/l levels is described. Experimental variables investigated include determination of solvent type, extraction number, preconditioning requirements, breakthrough and the use of an in-line drying agent. The stability of PAHs stored extracted on Empore disks compared to samples left unextracted is demonstrated. Disks stored at −19°C for 60 days had higher recoveries than samples left in sampling bottles unextracted at 4°C. In general, less decomposition of the target analytes occurred when extracted and stored on the disks. The accuracy of the method was evaluated through the use of certified reference material analyzed as blind samples. The Empore disk extraction method achieved equivalent or better detection limits, used significantly less amounts of solvent, and was faster to use than traditional liquid–liquid methods. Method detection limits for the 23 PAHs ranged from 9 to 56 ng/l.

Keywords: Extraction methods; Water analysis; Environmental analysis; Polynuclear aromatic hydrocarbons

1. Introduction

The National Laboratory for Environmental Testing (NLET) is responsible for measuring the levels of a wide variety of organic and inorganic contaminants found in natural waters throughout Canada. These measurements are used in support of Environment Canada programs focused on the evaluation and maintenance of aquatic ecosystems. As such, the analytical methods used within NLET must be sufficiently versatile to produce scientifically rigorous data from water samples containing widely differing matrix components. As with other laboratories, NLET is also mandated to develop and use methods that produce a minimum amount of waste from the use of excess volumes and types of solvents, particularly chlorinated organic solvents [1]. In general, this has required converting traditional liquid–liquid based extraction methodologies into solid-phase based sample preparation methods.

To incorporate a new method into NLET, a number of requirements must be met. The method must achieve equivalent or better accuracy, precision, recovery and detection limits compared to standard methods; provide a savings of time and money; be easy to use; be rugged enough to handle a wide variety of waters; and be amenable to high production output. The method must also be capable

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of measuring contaminants at low levels from small sample volumes. For example, because of shipping and field sampling restrictions, sample volumes have generally been restricted to 1 l. This limited sample size has placed a practical restriction on the level at which contaminants can be detected.

As polynuclear aromatic hydrocarbons (PAHs) in water are the second most frequently analyzed class of compounds by NLET, it was decided to convert the currently used 1-l liquid–liquid based methodology into a solid-phase based analytical method. A number of papers have recently described solid-phase sample preparation techniques using reversed-phase disks with octadecylsilica (C_{18}) enmeshed in PTFE as the solid phase [2–9].

This paper describes the development, verification and performance characteristics of an Empore disk-based solid-phase analytical method for the analysis of 23 PAHs in natural water at the ng/l level. The 23 PAHs chosen were selected for analysis based on our past monitoring requirements and regulatory concerns. Seven deuterated analogues were used as surrogates and internal standards in order to monitor recoveries and chromatographic integrity. The new method was shown to provide equivalent or superior performance to traditional liquid–liquid methods, to eliminate the use of chlorinated solvents, to reduce the total volume of solvents used, and reduce sample extraction and work-up time. An additional benefit, which has yet to be exploited, is that of field extraction and shipping of samples stored on the Empore disk. Initial storage stability will be presented to indicate the feasibility of this approach.

2. Experimental

2.1. Chemicals

2,2,4-Trimethylpentane (isooctane), dichloromethane, hexane, cyclohexane, ethyl acetate and acetone were all analytical grade and purchased from BDH (Toronto, Canada). Reagent grade acetone and light petroleum ether were used for glassware cleaning and were purchased from Caledon Labs. (Georgetown, Canada). All solvents were used as received. Sodium sulphate (Na_2SO_4) was purchased from Fisher Scientific (North Kingstown, RI, USA) dried in the muffle furnace at 600°C, crushed to a fine powder and stored in a desiccator before use. Silanized glass wool was purchased from Chromatographic Specialties (Brockville, Canada). Empore filter aid 400 high-density glass beads from 3M were purchased from Varian Assoc. (Georgetown, Canada). Reversed-phase disks (Empore) with octadecylsilica (C_{18}) enmeshed in PTFE were purchased from Varian Assoc. Individual native and deuterated PAH stock standards were purchased from Ultra Scientific (North Kingstown, RI, USA) and Cambridge Isotope Labs. (Andover, MA, USA), respectively, and were used for the preparation of all calibration, surrogate and spiking solutions. Calibration standards were prepared in isooctane and surrogate spiking solutions in methanol. PAH certified reference material in methanol was purchased from the Quality Assurance Branch of the National Water Research Institute (Burlington, Canada).

2.2. Instrumentation

Gas chromatographic (GC) analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph interfaced with a Hewlett-Packard 5791A mass-selective detector. The following conditions were used in the analyses: the column was a 60 m RTX 5 capillary column purchased from Rose Scientific (Edmonton, Canada) with a 0.25 mm inner diameter and a 0.25 μm film thickness. Ultra-high-purity (99.999%) helium was used as the carrier gas with the head pressure set at 10 p.s.i. (1 p.s.i.= 6894.76 Pa). The injector was set at 255°C with the initial oven temperature set at 80°C for 2 min. The oven temperature was then increased at 5°C/min to 200°C then at 3°C/min to a temperature of 260°C. This temperature was held for 15 min then increased at 3°C/min to 324°C and held for 10 min.

Low-resolution electron impact positive ion mass spectrometry was performed in the selected ion monitoring mode (SIM) using chromatographic windows for the specific ions. Table 1 describes the time windows and selected ions used for detecting and quantifying specific polynuclear aromatic hydrocarbons.

2.3. Water samples

Hamilton Harbour (HH), located at the west end of Lake Ontario, is mostly surrounded by land

Table 1
Analytical performance characteristics

Nr.	PAH compounds	Conc. (ng/l)	t_R (min)	Ions (m/z)	Slope	Intercept	r^2	Linear range (pg)	MDL[a] (ng/l)	Within-run precision	
										Mean (ng/l)	S.D.
1	Indene	150	12.9	115	0.935	−0.18	0.901	33–5000	9	63	3.79
2	Tetrahydronaphthalene	150	16.1	104	0.667	0.0433	0.994	17–5000	15	77	3.00
3	Naphthalene	150	16.9	128	1.52	0.00731	0.999	17–5000	28	90	3.06
4	2-Methylnaphthalene	150	20.1	142	0.953	−0.0281	0.998	17–5000	17	101	4.58
5	1-Methylnaphthalene	150	20.6	142	0.954	−0.028	0.998	17–5000	14	87	5.51
6	β-Chloronaphthalene	150	22.5	162	1.02	−0.0447	0.998	17–5000	12	111	3.79
7	Acenaphthylene	150	24.5	152	1.5	−0.0902	0.998	17–5000	13	87	6.56
8	Acenaphthene	150	25.4	154	0.893	−0.029	0.999	17–5000	15	91	4.04
9	Fluorene	150	28.0	166	0.989	−0.0717	0.999	17–5000	13	106	1.53
10	Phenanthrene	150	33.4	178	1.4	−0.118	0.999	17–5000	18	120	3.21
11	Anthracene	150	33.6	178	1.37	−0.135	0.999	17–5000	12	139	3.06
12	Fluoranthene	150	40.9	202	1.62	−0.103	0.999	17–5000	13	120	4.36
13	Pyrene	150	42.5	202	1.71	−0.0987	0.999	17–5000	11	128	5.57
14	Benzo[*a*]anthracene	150	52.1	228	1.58	−0.209	0.998	17–5000	9	138	7.94
15	Chrysene	150	52.5	228	1.45	−0.309	0.904	17–5000	7	132	8.33
16	Benzo[*b*]fluoranthene	150	65.1	252	0.0125	−0.00125	0.995	17–5000	21	134	11.15
17	Benzo[*k*]fluoranthene	150	65.4	252	0.0119	−0.00167	0.998	17–5000	16	125	4.58
18	Benzo[*e*]pyrene	150	68.4	252	1.28	−0.106	0.999	17–5000	19	110	10.02
19	Benzo[*a*]pyrene	150	68.6	252	1.34	−0.188	0.997	17–5000	36	116	8.62
20	Perylene	150	68.9	252	1.25	−0.166	0.997	17–5000	14	246	31.21
21	Indeno[123*c*,*d*]pyrene	300	79.8	276	1.04	−0.273	0.995	34–10000	29	281	28.05
22	Dibenzo[*a*,*h*]anthracene	300	80.0	278	0.643	−0.268	0.993	34–10000	56	213	32.02
23	Benzo[*g*,*h*,*i*]perylene	300	81.8	276	0.903	−0.213	0.992	34–10000	28	369	45.61
Surrogates											
24	[$^2H_8$]Naphthalene	500	16.8	136	0.999	0.145	0.813	250–500–750	38	271	12.66
25	[$^2H_{10}$]Fluorene	500	27.9	176	0.578	0.0654	0.898	250–500–750	42	342	2.52
26	[$^2H_{10}$]Pyrene	500	42.4	212	0.978	0.12	0.895	250–500–750	35	368	15.52
27	[$^2H_{12}$]Benzo[*a*]pyrene	500	68.6	264	0.831	−0.0809	0.926	250–500–750	48	393	26.16

[a] MDL=method detection limits.

sources. The harbour is connected to Lake Ontario by a shipping channel. The southwest end of the harbour is heavily industrialized with the majority of the land occupied by large steel making installations. The northwest side is bounded by a natural swamp fed by waters from the farming community and runoff from large botanical gardens.

Grindstone Creek (GCr), is located at the northwest side of Hamilton Harbour. The Creek receives runoff from a large botanical garden, area farming and residential sites.

Fort Erie (FE) and Niagara on the Lake (NR) sites are located at opposite ends of the Niagara River. The Niagara River flows between Lake Ontario and Lake Erie. The sites were set up by Environment Canada, the United States Environmental Protection Agency (US EPA), the Ontario Ministry of Environment and Energy, and the New York State Department of Environmental Conservation to monitor the chemical inputs to the Niagara River from the eastern basin of Lake Erie and chemical outputs from the river into Lake Ontario.

Groundwater (GW) site is located in a small farming community in southern Ontario, Canada. The sample water was delivered from a 10-m well with no filtration system. Possible influences include farming activities, septic beds and three area golf courses.

Laboratory water (LW) was delivered from a Millipore, Milli-Q water system available at the Canada Centre for Inland Waters (CCIW). Lake Ontario is the source water and is received at CCIW after treatment by the City of Burlington water treatment facility.

Most water samples were collected in April 1994 and analyzed by solid-phase methods and liquid–liquid techniques within two weeks. The Hamilton Harbour site and laboratory water were used on occasion to provide same-day sample analysis throughout the study period.

3. Method development

3.1. Initial development

The 23 PAHs were selected for analysis based upon historical and regulatory requirements and ranged from indene to benzo[*g,h,i*]perylene (Table 1). Analyses of standard PAH solutions in isooctane by GC–MS using the above conditions, demonstrated that adequate resolution and sensitivity could be achieved for all analytes of interest with instrumental response being linear over the range of 17 to 10 000 pg (Table 1). The spiking levels for the development of the analytical method were set at 150 to 300 ng/l. Native compounds were added to water at least 24 h prior to extraction while labelled surrogates ($[^2H_8]$naphthalene, $[^2H_{10}]$fluorene, $[^2H_{10}]$pyrene and $[^2H_{12}]$benzo[*a*]pyrene) were added immediately prior to extraction to give 500 ng/l concentrations. $[^2H_{12}]$Chrysene, $[^2H_8]$acenaphthylene and $[^2H_{10}]$fluoranthene were used as internal standards and were added to the final extracts immediately prior to analysis to provide a 500 ng/l spike. $[^2H_{12}]$Chrysene was used to calculate relative response factors while $[^2H_8]$-acenaphthylene and $[^2H_{10}]$fluoranthene served as chromatographic markers.

Previous work on the use of Empore disks provided a starting point for method development [10]. Other papers have described the need for filtering turbid and particulate laden water samples either prior to the Empore disk extraction or in-line with extraction [2]. As this has been well described, initial modification of the method included the use of high-density glass beads (Filter-aid) as a filtering device in-line with the Empore disk extraction (Fig. 1). An

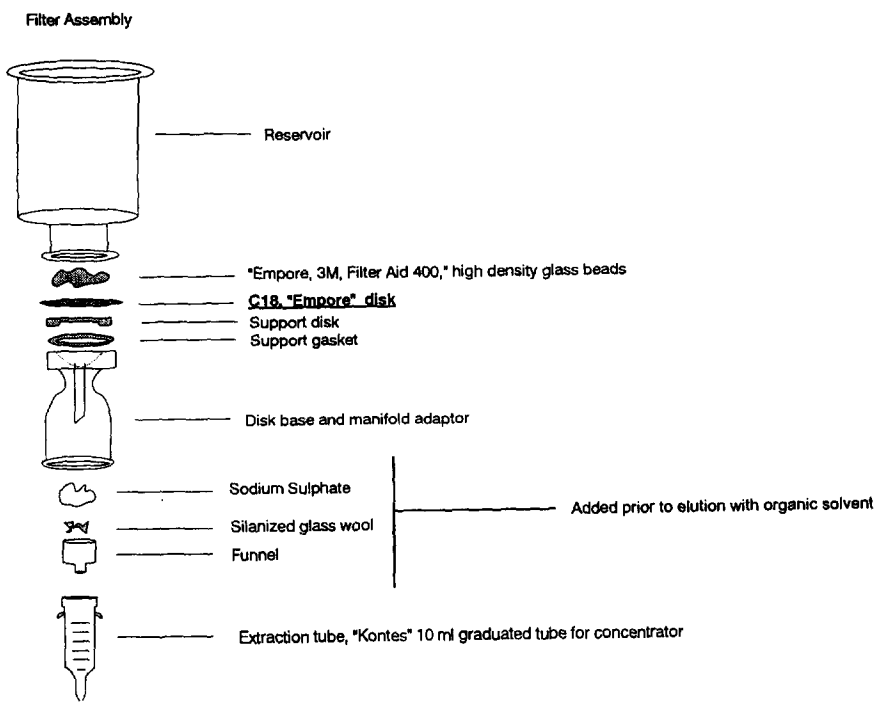

Fig. 1. Empore disk extraction apparatus and in-line drying funnel and high-density glass bead prefilter. Clamp, manifold and vacuum pump not shown.

amount of 12 g of Filter-aid is placed over the Empore disks and remains in place throughout the analytical sequence, including extraction and elution steps. Filter-aid was selected because it was expected that the amount of Filter-aid could be adjusted based upon the turbidity of the water. Another immediate modification was the use of three, instead of two 5-ml eluting volumes and the addition of labelled surrogates to water samples prior to extraction to monitor spiked recoveries.

As one of the primary goals of this project was to reduce or remove the use of chlorinated solvents, solvent selection for each of the steps had to be considered. Using the previously published methods as a starting point, six solvent mixtures were initially evaluated. These were selected to provide a range of differing polarities and included: cyclohexane–acetone (3:2); methylene chloride–acetone (3:2); hexane–acetone (3:2); methylene chloride–cyclohexane–acetone (1:1:1); ethylacetate–acetone (3:2); and methylene chloride–cyclohexane (1:1). All analyses were conducted in triplicate using 1-l laboratory distilled water spiked with between 150 and 300 ng/l with the PAH analytes of interest. The PAHs were added to individual 1-l volumes of water, stirred and left overnight. The samples were extracted following the method outlined in Table 2 incorporating the modifications described above. Of the six solvent choices, hexane–acetone (3:2) and methylene chloride–cyclohexane (1:1) provided the highest overall recoveries (Table 3).

From the previous experiments, it was observed that from 0.1 to 1.0 ml of water remained in the extracts. Large amounts of water, if not removed, can cause recovery and chromatographic difficulties [6]. Because of limitations in the volume of the collection vessel and the concern over relatively large volumes of water affecting the efficiency of the method, an in-line drying method was developed for the removal and reduction of water carried over from the solid phase with the eluting solvents. The system consists of approximately 8 g of sodium sulphate which had been dried at 600°C and added to the funnel placed below the Empore disk. The funnels are placed in-line after the disks have been air-dried and prior to elution with organic solvent (Fig. 1). Triplicate measurements were again conducted using methylene chloride–hexane (3:2); hexane–acetone

Table 2
Empore disk extraction sequence

Place disks in beaker to soak in high-grade acetone (1 h)
Put disks and (12 g) glass beads in apparatus and add 5 ml of eluting solvent (cyclohexane) to reservoir (with vacuum off) allow to soak 3 min.
Pull in eluting solvent leaving vacuum on 20–30 s to dry disk.
Add 10 ml methanol to reservoir with vacuum off (pull in enough methanol to ensure disk is wet and soak 3 min).
Add 10 ml deionized (Milli-Q) water. Pull water through disks with vacuum, turning vacuum off to ensure that disks remain wet.
Invert 1-l water samples, to which appropriate surrogates have been added, over the Empore disk apparatus.
Turn on vacuum and pull samples through at 20–25 p.s.i. Before turning on vacuum, ensure Filter-aid glass beads have settled.
While sample running add glass wool to drying funnels, rinse with cyclohexane and add 8 g Na_2SO_4 to drying funnels.
Remove sample bottles after the samples have passed through the disk. Maintain vacuum for at least 5 min after samples have been eluted.
Put test tubes and drying funnels (filled with 8 g Na_2SO_4) in apparatus. With vacuum off wet disks with 2 ml acetone and let soak (approx. 2–5 min)
Add 5 ml eluting solvent (c-hex) to 1-l bottles and wash. Empty eluting solvent from the sample bottle to disks, pull in, allow to soak 3 min.
Turn on vacuum slowly to pull solvent through, leaving disk wet.
With vacuum off, add 5 ml of c-hex to reservoir and allow to soak 3 min. Turn on vacuum slowly to pull eluting solvent through but leave layer on top. Repeat one more time.
Carefully remove extract and concentrate to 1 ml under nitrogen, solvent exchange with isooctane.

Table 3
Influence of eluting solvent on analyte recovery

Compounds	Hexane–acetone (3:2)		Cyclohexane–acetone (3:2)		Methylene chloride–cyclohexane–acetone (1:1:1)		Methylene chloride–acetone (3:2)		Methylene chloride–cyclohexane (1:1)		Ethylacetate–acetone (3:2)	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Indene	28.3	7.4	28.3	7.4	17.9	14.8	44.0	13.9	61.7	2.5	33.3	13.7
Tetrahydronaphthalene	58.7	10.6	58.6	10.6	34.6	34.0	126.7	56.0	100.3	11.6	79.3	5.5
Naphthalene	74.3	11.1	74.3	11.1	42.7	44.7	78.7	11.4	147.3	16.5	97.0	6.0
2-Methylnaphthalene	112.3	11.1	112.3	11.1	Contamination		176.3	26.7	Contamination		Contamination	
1-Methylnaphthalene	84.0	10.5	84.0	10.5	47.3	51.9	72.0	9.5	178.3	13.2	88.0	4.4
β-Chloronaphthalene	56.0	11.0	56.0	11.0	33.5	31.8	73.0	12.5	99.7	8.1	87.7	4.9
Acenaphthylene	56.7	10.0	56.7	10.0	33.3	33.0	71.7	9.7	101.3	7.6	82.0	2.6
Acenaphthene	50.7	6.0	50.7	6.0	28.3	31.6	80.3	12.7	106.7	8.0	85.3	2.1
Fluorene	64.7	12.0	64.7	12.0	38.3	37.2	75.7	11.7	115.3	6.1	86.3	5.5
Phenanthrene	67.3	17.5	67.3	17.5	42.4	35.3	81.7	11.9	148.7	7.2	95.7	4.2
Anthracene	67.3	13.6	67.3	13.6	40.5	38.0	80.7	11.9	102.7	6.4	89.7	4.9
Fluoranthene	71.0	14.0	71.0	14.0	42.5	40.3	79.7	10.1	102.3	4.9	87.3	2.5
Pyrene	70.7	13.5	70.7	13.5	42.1	40.4	79.7	10.2	101.3	6.1	86.0	2.6
Benzo[*a*]anthracene	74.0	12.5	74.0	12.5	43.2	43.5	78.3	7.6	91.0	4.6	86.3	3.1
Chrysene	74.0	12.5	74.0	12.5	43.2	43.5	78.3	7.6	91.0	4.6	86.3	3.1
Benzo[*b*]fluoranthene	69.7	9.5	69.7	9.5	39.6	42.6	82.3	9.1	78.0	2.6	80.0	1.0
Benzo[*k*]fluoranthene	72.3	10.0	72.3	10.0	41.2	44.1	72.6	9.7	78.0	2.6	80.0	1.0
Benzo[*e*]pyrene	72.3	11.9	72.3	11.9	42.1	42.7	70.0	10.4	75.0	3.0	76.3	3.1
Benzo[*a*]pyrene	66.7	9.3	66.7	9.3	38.0	40.6	63.7	7.1	70.7	2.1	63.3	3.5
Perylene	66.7	9.5	66.7	9.5	38.1	40.5	63.0	6.1	70.7	1.5	63.7	2.1
Indeno[123*c*,*d*]pyrene	73.7	11.9	73.7	11.9	42.8	43.7	70.0	9.6	71.0	6.9	80.3	1.5
Dibenzo[*a*,*h*]anthracene	73.0	2.8	73.0	2.8	37.9	49.6	38.7	4.9	70.0	7.1	41.0	2.8
Benzo[*g*,*h*,*i*]perylene	71.3	9.9	71.3	9.9	40.6	43.5	70.3	6.7	76.7	3.5	80.7	1.2

Mean % recovery ± standard deviation with $n=3$.

(3:2) and methylene chloride–cyclohexane (1:1) as the eluting solvents. The methylene chloride–cyclohexane (1:1) mixture was again shown to provide the highest overall recoveries (Table 4). The in-line drying also delivered a higher recovery and smaller standard deviation than when no in-line drying was performed; in some cases, small amounts of water remained in the system, usually 0.1 ml or less. Although the in-line drying was unable to remove all of the water, the volume of water remaining after the extraction step was significantly lower than with no in-line drying. No measurable level of PAHs remained in the water layer as determined from extraction and analysis of the remaining water layer. An additional difficulty was the observation that increasing amounts of Filter-aid increased the amount of water carried over in the system. This would indicate that the Filter-aid acts as a water reservoir which makes the amount of water, at least in part, a function of the amount of Filter-aid used.

To determine if the mixture of cyclohexane–dichloromethane gave the highest recovery or if an individual solvent could give equivalent results, recoveries using cyclohexane–methylene chloride 1:1, methylene chloride and cyclohexane were determined. Fig. 2 shows that cyclohexane alone provided the highest recoveries for the low- and mid-range PAHs (indene to acenaphthene) while cyclohexane–methylene chloride 1:1 delivered the highest recoveries for the high-range PAHs (fluorene to benzo[*g*,*h*,*i*]perlene). There was an average of 5% difference in recoveries at the high range which was small enough to allow the selection of cyclohexane to be made as the eluting solvent based upon the requirement to reduce or remove the use of chlorinated solvents from the process.

Table 4
Influence of eluting solvent with in-line drying

Compounds	Methylene chloride–hexane (1:1)		Hexane–acetone (3:2)		Methylene chloride–cyclohexane (1:1)	
	Mean	S.D.	Mean	S.D.	Mean	S.D.
Indene	3.3	5.8	15.7	18.4	11.0	10.1
Tetrahydronaphthalene	100.7	43.5	65.7	17.6	85.7	24.7
Naphthalene	79.3	14.0	70.3	13.3	77.3	4.2
2-Methylnaphthalene	131.0	16.7	116.7	20.5	122.0	3.0
1-Methylnaphthalene	81.3	13.5	70.5	19.1	77.0	1.7
β-Chloronaphthalene	82.0	14.5	69.3	13.2	77.3	2.3
Acenaphthylene	82.7	10.0	74.7	12.3	67.0	5.6
Acenaphthene	90.7	14.6	81.3	13.9	82.7	2.1
Fluorene	83.0	13.0	73.3	12.5	79.0	0.0
Phenanthrene	79.0	7.2	78.0	11.3	71.7	2.3
Anthracene	83.0	12.0	74.7	11.9	79.3	2.9
Fluoranthene	86.7	10.7	76.3	11.6	80.7	3.1
Pyrene	85.3	10.3	76.0	11.4	79.7	3.1
Benzo[*a*]anthracene	70.7	8.1	85.7	12.0	91.7	7.2
Chrysene	71.3	7.6	71.7	6.5	76.0	5.6
Benzo[*b*]fluoranthene	68.3	7.4	50.3	6.5	78.3	17.0
Benzo[*k*]fluoranthene	54.3	17.7	72.7	7.6	74.7	19.3
Benzo[*e*]pyrene	64.3	6.0	53.0	11.3	69.7	4.7
Benzo[*a*]pyrene	59.0	4.2	59.0	4.6	61.0	10.1
Perylene	48.0	11.8	49.3	12.9	58.3	5.9
Indeno[123*c*,*d*]pyrene	131.0	3.6	45[a]	25.0	34.3	3.5
Dibenzo[*a*,*h*]anthracene	51[a]	29.0	45.5	2.1	31.7	22.0
Benzo[*g*,*h*,*i*]perylene	45.7	5.5	40.0	4.2	56.7	4.5

Mean % recovery ± standard deviation with $n=3$.
[a] Contamination.

Surrogate recoveries ranged from 40 to 91%.

3.2. Empore disk extraction pre-soak

Three different pre-soak methods were examined for use in this method. In the first, 2 ml of analytical grade acetone were used to soak the disks for between 3 and 5 min prior to the addition of the eluting solvent. In the second, no pre-soak was used and in the third, 1 ml analytical grade acetone with a soak time of between 3 and 5 min, eluted with 5 ml cyclohexane and repeating for a total of three cycles. Of the three methods, the 2 ml acetone with a 3–5 min soak delivered the best recovery (Fig. 3).

3.3. Extraction number

The modified method calls for the use of three 5-ml extractions using cyclohexane. The three extractions were determined to be optimum based upon the analysis of the individual 5-ml fractions. In general, between 20 and 50% of the PAHs are recovered from the first extraction with an equal to slightly lower amount recovered from the second extraction. The third extraction recovers generally less than 10% of the material while a fourth extraction could recover only trace amounts of selected target PAHs.

3.4. Breakthrough

To determine the amount of PAH target compounds which passed through the Empore disks, extracted water was collected and re-extracted using new Empore disks. This process was repeated two additional times. In general, between 0 and 10% of the total PAH material remained in the water after the initial Empore disk extraction, with between 0

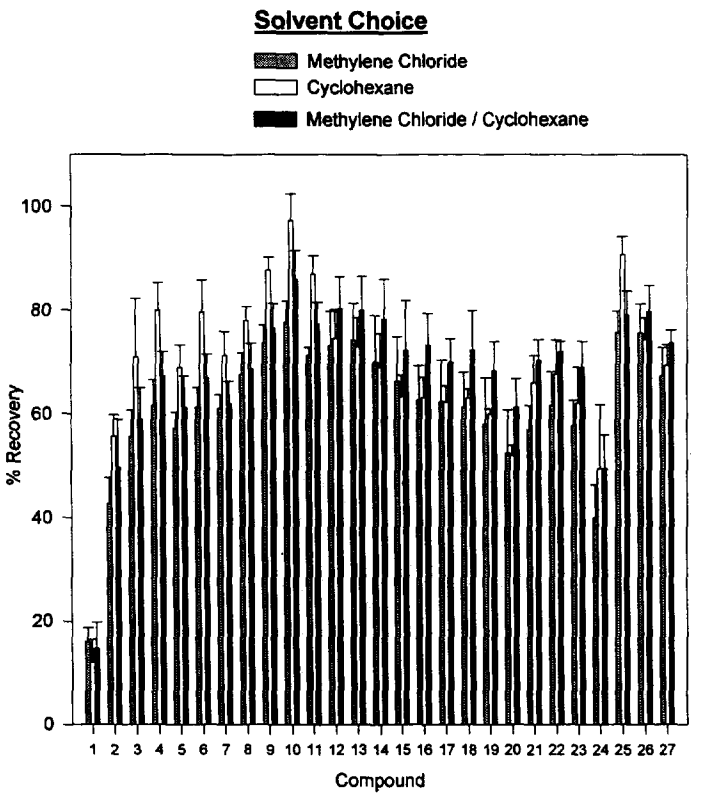

Fig. 2. Mean % PAH recovery±standard deviation based on extraction with different solvents. See Table 1 for compound names.

and 5% remaining after the second extraction. Depending upon the analyte, this represented between 5 and 20% of the total amount of PAHs spiked into the 1-l water samples.

3.5. Optimized method

The optimized method is outlined in Table 2 and includes the use of cyclohexane as the eluting solvent, an acetone pre-elution soak, an in-line drying step, the use of three extraction volumes and labelled surrogates to monitor recovery and chromatographic response.

The method detection limit was determined in laboratory water (LW) according to the method prescribed by the United States Environmental Protection Agency [11]. These values ranged from 9 to 56 ng/l and are shown in Table 1. The within-run precision based on laboratory water, was determined from triplicate measurements on the same day and is also given in Table 1.

3.6. Accuracy

The accuracy of the method was determined from the analysis of a certified reference material (CRM) and is reported as the percent error. Accuracy was determined using triplicate samples containing certified concentrations of specific PAHs. This material was received in the laboratory as a blind set of samples, that is, the analyst had no prior knowledge of the concentrations or types of PAHs present. This material is used by the Canadian Association of Environmental Analytical Laboratories (CAEAL) in their performance evaluation program and was obtained from the Quality Assurance Branch of the National Water Research Institute. Table 5 provides the results of this study. The blind samples contained

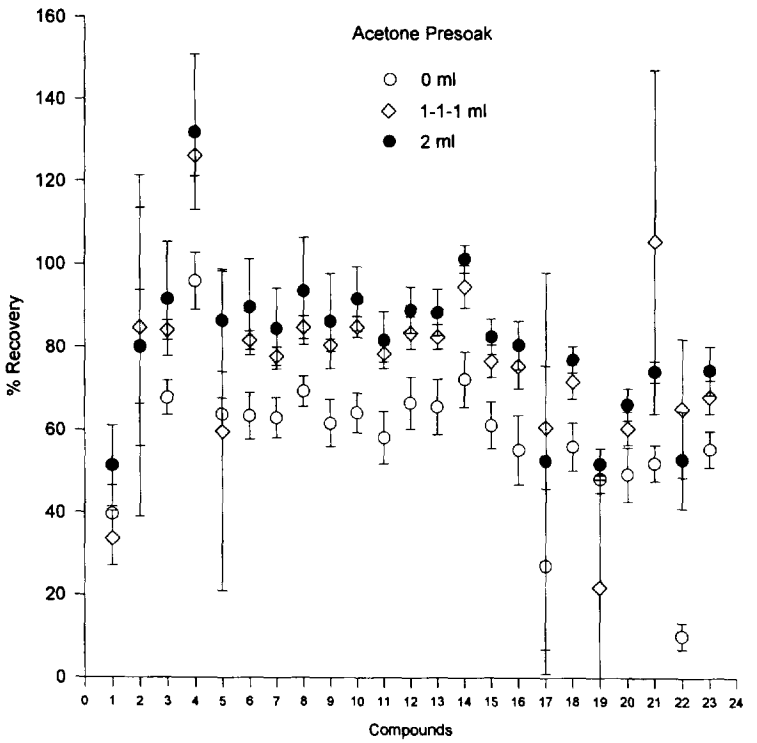

Fig. 3. Mean % PAH recovery±standard deviation from different acetone pre-soak conditions.

only 7 of the 23 PAHs analyzed in this method. In general, the accuracy of the method was between 1.4 and 44%. With the exception of benzo[*b*]fluoranthene, the results were of sufficient quality to meet the CAEAL performance criteria for the analysis of these sets of PAHs. That is, the results would fall within those normally obtained from round robin studies using multiple laboratories. The poor performance of the benzo[*b*]fluoranthene represents a problem with chromatographic resolution rather than poor extraction recoveries, as the benzo[*k*]fluoranthene closely elutes with the benzo[*b*]fluoranthene isomer. This problem has been well described [11] and in many cases individual benzo[*b*] and benzo[*k*] isomers are reported as a total rather than as specific isomers. Careful reevaluation of the analytical data for these isomers supported this finding, as the accuracy for the benzo[*b*]fluoranthene was shown to be 8.6%.

Table 5
Accuracy determinations from blind samples

Compounds	Accuracy as % error
Fluoranthene	4.7
Pyrene	10.8
Benzo[*b*]fluoranthene	44.1
Benzo[*k*]fluoranthene	14.8
Benzo[*a*]pyrene	4.2
Indeno[123*c*,*d*]pyrene	27.2
Benzo[*g*,*h*,*i*]perylene	1.4
Surrogates	*% Recovery*
[$^2H_8$]Naphthalene	49.5
[$^2H_{10}$]Fluorene	85.1
[$^2H_{10}$]Pyrene	88.9
[$^2H_{12}$]Benzo[*a*]pyrene	95.3

The determination of accuracy based upon blind samples is an essential component in method development. The use of blind samples of known concentrations allows problems in the method to be demonstrated prior to routine use. In this case, it was

demonstrated that the extraction and sample work-up steps of the method were in control while the quantitation step required further modification.

4. Method performance

4.1. Matrix effects

The optimized Empore disk extraction method was used for the analyses of both spiked and unspiked 1-l samples from five separate locations. Additional samples were collected for storage stability studies as well as for the determination of turbidity, hardness, pH, dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC). The locations, described above, were HH, GW, FE, NR and GCr. Enough water was collected from each location to perform spiked and unspiked studies in triplicate. Spiked samples were at the 150 to 300 ng/l levels. Samples were also collected for spiked and unspiked studies using traditional liquid–liquid methodology, with the samples being submitted to the routine laboratory for analysis. Unfortunately, laboratory contamination precluded the use of the liquid–liquid results in this study. However, historical values from the National Laboratory indicate that the Empore disk methodology achieved significantly better method detection limits, accuracy and precision than the liquid–liquid procedure employed by the laboratory.

Table 6 shows the percent recoveries and background amounts present in the different waters. Table 7 provides water quality parameters as well as the analysis time required for each of the different water types. The amount of time required to prepare each sample set was recorded as the time required for extraction to the time when samples were ready for analysis. In general, the low- to mid-range PAHs were found most often (naphthalene through pyrene) with higher numbers and concentrations of PAHs present in GCr, FE and HH locations. Naphthalene was the most commonly found PAH followed by acenaphthene. Samples with the highest turbidity and DOC measurements took the longest to elute through the disks. No significant difference could be observed in the spiked recoveries based upon turbidity, although the GCr location (highest turbidity) appeared to have slightly lower recoveries overall.

Surrogates in both spiked and unspiked waters showed recovery values within 25% with the exception of [$^2H_{12}$]benzo[*a*]pyrene from the GCr sample which showed 44% difference. The mean and standard deviation (in parentheses) for the surrogate recoveries over all water types was: [$^2H_8$]naphthalene 66(10), [$^2H_{10}$]fluorene 98(9.6), [$^2H_{10}$]pyrene 82(6.9), and [$^2H_{12}$]benzo[*a*]pyrene 66(14.7). The mean, first and second standard deviations were used to establish lower and upper control limits for initial method performance. As can be seen, the low and high molecular masses gave the poorest recoveries while the mid-weight surrogates gave the highest recoveries. This behaviour mimics that of native compounds observed in spiked studies.

4.2. Storage stability

Triplicate sets of 1-l samples from NR and FE locations were spiked at the 150 to 300 ng/l level and placed in a refrigerator at 4°C. Spiked sets from all locations were extracted using the Empore disk methodology, the disks were then dried and placed in the freezer at −19°C. These samples were stored for a period of 60 days. After the 60 days, the 1-l samples from NR and FE were extracted using the Empore disk methodology while the stored disks were extracted following the methodology and beginning at the cyclohexane stage. Table 8 and Table 9 show the percent recoveries of the samples stored both in water and on the disks as compared to freshly prepared and extracted water samples. The recoveries of the samples on the disks were better or equivalent to those stored in water; however, all sets showed lower recoveries than samples extracted and analyzed shortly after collection and spiking. This would imply that samples could be extracted in the field and the disks sent back to the laboratory for analysis with a minimum of sample loss. Behaviour of the surrogates are difficult to compare as, following the method, they are added immediately prior to extraction. This would explain why surrogate recoveries for samples stored in bottles (FE and NR) are somewhat higher than those stored on the Empore disks. In all samples, the higher molecular mass PAH compounds had much lower recovery after storage than the mid-range PAHs. Nutrients and

Table 6
Spiked recoveries %) and unspiked (ng/l) background levels of PAHs from five locations

Compound	Spike level (ng/l)	GCr				FE				HB				GW				NR			
		Spiked		Unspiked		Spiked		Unspiked		Spiked		Unspiked		Spiked		Unspiked		Spiked		Unspiked	
		Mean %	S.D.	Mean (ng/l)	S.D.	Mean %	S.D.	Mean (ng/l)	S.D.	Mean %	S.D.	Mean (ng/l)	S.D.	Mean %	S.D.	Mean (ng/l)	S.D.	Mean %	S.D.	Mean (ng/l)	S.D.
Indene	150	26.4	3.3	0.0	0.0	46.8	2.6	0.0	0.0	42.1	2.6	12.3	10.7	31.4	2.9	0.0	0.0	31.0	3.3	0.0	0.0
Tetrahydronaphthalene	150	60.9	5.9	10.4	9.0	72.2	4.8	0.0	0.0	51.8	2.1	0.0	0.0	63.2	4.5	0.0	0.0	56.8	3.2	0.0	0.1
Naphthalene	150	58.9	9.8	27.1	14.5	91.1	3.9	12.7	0.6	60.9	2.1	9.7	4.2	79.7	2.8	13.0	0.6	70.9	4.1	12.4	1.1
2-Methylnaphthalene	150	57.8	8.5	4.9	4.3	100.5	8.9	4.2	2.8	69.9	3.4	0.0	0.0	82.3	2.7	0.0	0.0	83.2	6.8	0.0	0.0
1-Methylnaphthalene	150	58.9	9.3	3.3	2.9	84.3	5.4	2.2	1.5	58.9	3.7	1.5	1.4	71.2	2.7	0.0	0.0	68.0	4.8	0.0	0.0
β-Chloronaphthalene	150	52.5	9.2	0.0	0.0	101.9	10.5	0.0	0.0	78.1	2.8	0.6	0.1	81.8	2.3	0.0	0.0	88.0	8.5	0.0	0.0
Acenaphthylene	150	60.6	10.4	0.0	0.0	82.6	6.0	0.0	0.0	59.0	4.1	0.0	0.0	70.9	1.3	0.0	0.0	68.6	4.3	1.2	1.1
Acenaphthene	150	63.5	11.2	8.4	0.4	85.2	6.6	7.4	1.3	61.3	2.8	11.0	3.8	73.8	0.4	7.3	6.3	70.3	4.4	0.0	0.0
Fluorene	150	66.6	7.5	13.3	5.5	94.7	7.1	0.7	0.9	72.3	1.0	15.0	1.2	78.1	2.5	0.9	0.8	82.9	6.7	0.0	0.0
Phenanthrene	150	83.0	3.7	15.1	2.6	102.2	9.7	3.0	2.0	82.8	2.4	0.0	0.0	82.2	5.6	0.0	0.0	94.6	6.7	0.0	0.0
Anthracene	150	70.4	3.8	19.2	3.2	107.3	11.3	4.7	3.1	97.5	2.3	4.1	3.6	87.6	5.2	0.0	0.0	100.8	9.1	0.0	0.0
Fluoranthene	150	90.2	0.2	9.9	1.7	89.5	6.8	4.5	0.3	80.9	3.2	7.1	0.6	75.4	3.4	0.0	0.0	82.3	2.8	0.0	0.0
Pyrene	150	89.8	2.0	7.5	1.3	86.2	6.7	1.0	1.3	86.4	3.8	19.6	0.5	75.2	2.0	0.0	0.0	78.5	4.1	0.0	0.0
Benzo[*a*]anthracene	150	74.1	1.1	0.0	0.0	85.2	6.6	0.0	0.0	92.5	5.2	0.0	0.0	86.1	6.9	0.0	0.0	85.6	4.5	0.0	0.0
Chrysene	150	76.4	1.5	0.0	0.0	80.3	6.2	0.0	0.0	89.3	5.6	0.0	0.0	81.4	5.7	0.0	0.0	80.4	3.0	0.0	0.0
Benzo[*b*]fluoranthene	150	63.0	1.4	0.0	0.0	73.5	6.5	0.0	0.0	91.2	7.6	0.0	0.0	94.7	10.9	0.0	0.0	80.1	1.1	0.0	0.0
Benzo[*k*]fluoranthene	150	59.5	1.5	0.0	0.0	61.2	3.5	0.0	0.0	82.3	3.1	0.0	0.0	22.5	39.0	0.0	0.0	75.8	7.7	0.0	0.0
Benzo[*e*]pyrene	150	57.1	1.7	0.0	0.0	63.1	2.7	0.0	0.0	72.7	6.7	0.0	0.0	83.7	6.4	0.0	0.0	64.6	2.0	0.0	0.0
Benzo[*a*]pyrene	150	46.5	0.9	0.0	0.0	55.8	5.0	0.0	0.0	76.9	5.6	0.0	0.0	87.6	7.1	0.0	0.0	66.5	2.4	0.0	0.0
Perylene	150	46.4	2.0	0.0	0.0	50.5	2.7	0.0	0.0	66.8	7.2	0.0	0.0	84.1	6.5	0.0	0.0	61.2	2.7	0.0	0.0
Indeno[123*c*,*d*]pyrene	300	38.0	3.3	0.0	0.0	50.3	3.1	0.8	1.0	80.3	10.2	0.0	0.0	98.7	7.1	0.0	0.0	70.3	0.8	0.0	0.0
Dibenzo[*a*,*h*]anthracene	300	39.9	0.7	0.0	0.0	49.0	4.1	2.1	2.9	95.7	9.7	0.0	0.0	125.8	9.8	0.0	0.0	87.0	2.9	0.0	0.0
Benzo[*g*,*h*,*i*]perylene	300	36.9	1.3	0.0	0.0	44.6	1.9	0.0	0.0	68.6	10.2	0.0	0.0	81.6	4.0	0.0	0.0	54.6	3.0	0.0	0.0
Surrogates																					
[$^2H_8$]Naphthalene	500	51.4	9.8	382.5	81.1	76.2	4.1	310.6	44.3	55.1	2.6	343.1	34.5	65.9	3.0	325.8	28.8	59.6	3.6	416.3	34.7
[$^2H_{10}$]Fluorene	500	108.3	1.2	542.4	57.6	97.3	1.1	515.0	10.5	83.6	2.0	455.9	16.8	91.1	5.7	530.7	52.4	86.1	2.1	536.8	25.0
[$^2H_{10}$]Pyrene	500	89.7	4.6	456.4	61.2	85.7	5.9	412.3	24.3	73.5	3.1	400.7	17.5	75.0	2.1	381.1	40.9	75.7	3.8	452.6	32.3
[$^2H_{12}$]Benzo[*a*]pyrene	500	41.0	4.1	366.5	10.4	57.2	2.7	245.3	18.6	77.6	5.2	380.0	31.6	91.2	9.6	351.1	85.2	62.3	2.2	322.0	33.0

Table 7
Water quality parameters and extraction time

Location	Time[a]		Turbidity (JTU)	pH	Hardness (mg/l)	DIC[b] (mg/l)	DOC[c] (mg/l)
	Run 1	Run 2					
Ground water	140	140	1.51	7.38	579	94.9	3.9
Fort Erie	140	140	2.26	7.93	115	21.1	2.7
Niagara River	140	120	2.55	7.94	116	21.2	2.7
Grindstone Creek	270	1951	7.95	7.96	249	41.4	7.6
Hamilton Bay	165	130	1.68	7.7	186	29.8	4.2

[a] In min, longest time in a triplicate run.
[b] Dissolved inorganic carbon.
[c] Dissolved organic carbon.

Table 8
Storage stability study of FE and NR waters

Compound	Spike (ng/l)	FE						NR					
		Extracted on day 1		Stored on Empore		Stored in bottle		Extracted on day 1		Stored on Empore		Stored in bottle	
		Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Indene	150	51	5.6	30	4.6	20	6.8	42	4.7	32	6.7	20	19.3
Tetrahydronaphthalene	150	78	9.4	52	8.5	31	4.4	76	4.6	66	13.8	36	31.0
Naphthalene	150	99	9.1	64	11.0	93	49.1	95	5.9	94	25.7	69	6.8
2-Methylnaphthalene	150	109	16.0	65	9.7	43	17.5	112	9.5	102	32.4	74	12.0
1-Methylnaphthalene	150	91	10.6	57	6.2	34	14.9	91	6.8	80	24.2	59	9.4
β-Chloronaphthalene	150	110	18.4	66	10.1	36	13.6	118	12.0	103	32.9	52	21.7
Acenaphthylene	150	89	11.4	54	6.2	38	7.6	92	6.1	71	21.9	46	39.8
Acenaphthene	150	92	12.3	61	7.0	49	4.9	94	6.2	81	23.5	65	12.0
Fluorene	150	102	13.4	64	10.6	53	7.0	111	9.3	86	27.5	73	13.7
Phenanthrene	150	111	17.5	76	15.2	49	20.1	127	9.3	121	34.1	78	15.5
Anthracene	150	116	20.0	63	13.8	34	12.8	135	12.6	93	32.3	70	12.9
Fluoranthene	150	97	13.4	64	17.1	60	11.7	111	4.0	96	23.9	73	17.1
Pyrene	150	93	12.8	59	15.9	57	9.8	106	5.6	88	22.4	68	19.1
Benzo[*a*]anthracene	150	92	13.5	53	16.9	27	9.7	115	6.2	87	28.3	34	12.9
Chrysene	150	87	13.4	52	15.6	39	10.8	108	4.1	76	24.8	46	13.9
Benzo[*b*]fluoranthene	150	80	13.7	43	12.3	22	9.5	108	2.1	85	31.2	33	11.8
Benzo[*k*]fluoranthene	150	66	7.8	38	9.9	22	8.8	102	10.4	84	56.5	35	9.5
Benzo[*E*]pyrene	150	68	7.3	37	9.5	26	8.9	87	2.7	59	20.2	38	10.8
Benzo[*a*]pyrene	150	61	10.4	31	8.2	7	6.2	89	3.4	55	22.9	19	6.8
Perylene	150	55	5.9	26	5.7	13	4.6	82	3.1	44	17.5	26	8.1
Indeno[123*c*,*d*]pyrene	300	54	6.5	24	4.3	17	7.4	94	1.5	41	19.8	34	10.4
Dibenzo[*a*,*h*]anthracene	300	53	7.9	18	5.6	21	8.6	117	3.4	35	15.5	39	12.9
Benzo[*g*,*h*,*i*]perylene	300	48	4.3	20	4.7	20	6.6	73	3.6	33	12.9	39	10.2
Surrogates													
[$^2H_8$]Naphthalene	500	82	8.8	44	6.2	67	4.4	60	5.2	63	19.7	75	17.4
[$^2H_{10}$]Fluorene	500	100	14.1	62	8.5	79	3.0	78	8.1	79	25.9	95	11.1
[$^2H_{10}$]Pyrene	500	93	11.6	56	15.2	76	5.3	76	5.1	75	23.1	90	16.1
[$^2H_{12}$]Benzo[*a*]pyrene	500	62	6.6	30	8.5	47	7.5	62	2.5	48	20.0	67	12.6

Mean % recovery ± standard deviation.

Table 9
Storage stability study of GCr, GW and HB waters

Compound	Spike (ng/l)	GCr				GW				HB			
		Extracted on day 1		Stored on Empore		Extracted on day 1		Stored on Empore		Extracted on day 1		Stored on Empore	
		Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Indene	150	47	16.4	47	7.5	31	2.9	29	2.2	42	2.6	46	5.6
Tetrahydronaphthalene	150	77	19.0	66	6.9	63	4.5	62	3.7	52	2.1	75	9.0
Naphthalene	150	93	34.6	94	13.4	80	2.8	70	5.0	61	2.1	136	21.5
2-Methylnaphthalene	150	75	13.1	85	10.3	82	2.7	77	9.4	70	3.4	69	9.5
1-Methylnaphthalene	150	73	10.4	78	9.3	71	2.7	73	7.9	59	3.7	91	12.8
β-Chloronaphthalene	150	68	9.1	87	10.3	82	2.3	80	12.5	78	2.8	55	7.4
Acenaphthylene	150	69	9.0	72	9.5	71	1.3	68	7.1	59	4.1	119	19.1
Acenaphthene	150	74	10.6	80	10.6	74	0.4	76	7.2	61	2.8	81	13.0
Fluorene	150	75	6.7	83	10.4	78	2.5	77	8.0	72	1.0	70	11.3
Phenanthrene	150	87	5.3	92	10.5	82	5.6	86	10.9	83	2.4	77	11.2
Anthracene	150	72	1.6	76	8.4	88	5.2	78	13.3	97	2.3	53	7.3
Fluoranthene	150	82	1.3	75	6.6	75	3.4	69	6.8	81	3.2	60	7.1
Pyrene	150	80	0.6	71	5.8	75	2.0	68	6.2	86	3.8	63	7.4
Benzo[*a*]anthracene	150	69	5.0	57	1.6	86	6.9	61	2.1	92	5.2	25	0.8
Chrysene	150	71	5.9	57	1.0	81	5.7	58	3.0	89	5.6	18	0.7
Benzo[*b*]fluoranthene	150	67	5.2	51	4.2	95	10.9	60	3.5	91	7.6	11	0.4
Benzo[*k*]fluoranthene	150	64	4.2	50	3.5	22	39.0	51	5.3	82	3.1	7	0.4
Benzo[*E*]pyrene	150	65	5.0	47	3.6	84	6.4	52	5.4	73	6.7	12	0.5
Benzo[*a*]pyrene	150	55	4.1	38	1.6	88	7.1	43	7.7	77	5.6	6	0.3
Perylene	150	56	5.0	39	1.7	84	6.5	43	5.8	67	7.2	6	0.4
Indeno[123*c*,*d*]pyrene	300	59	3.8	47	0.5	99	7.1	36	10.2	80	10.2	5	0.9
Dibenzo[*a*,*h*]anthracene	300	55	6.2	44	2.5	126	9.8	33	8.2	96	9.7	2	0.5
Benzo[*g*,*h*,*i*]perylene	300	60	4.9	44	1.8	82	4.0	36	10.1	69	10.2	6	1.1
Surrogates													
[$^2H_8$]Naphthalene	500	65	10.2	71	9.5	66	3.0	60	7.1	55	2.6	117	16.6
[$^2H_{10}$]Fluorene	500	76	7.0	81	10.5	77	3.3	80	8.1	69	0.5	60	9.9
[$^2H_{10}$]Pyrene	500	78	1.0	68	5.6	75	2.1	70	5.9	73	3.1	42	5.0
[$^2H_{12}$]Benzo[*a*]pyrene	500	54	4.7	37	0.4	91	9.6	47	6.6	78	5.2	4	0.2

Mean % recovery ± standard deviation.

other water quality parameters may play a significant role in the stability of PAHs on Empore disks.

4.3. Hamilton Harbour follow-up studies

As the amounts of PAHs can vary over time, based upon varying environmental conditions, the levels of PAHs within Hamilton Harbour were analyzed three separate times during the study. Table 10 shows these results and indicates that the low- to mid-range PAHs are the most commonly detected. The high levels of all PAHs detected in October are attributed to the fact that the samples were collected soon after a storm event which caused significant mixing within the harbour.

5. Conclusions

The use of Empore disks as an extraction medium for 23 polynuclear aromatic hydrocarbons from 1-l ambient water samples at the ng/l level was demonstrated. The method was shown to achieve equivalent or better method detection limits than traditional liquid–liquid based methods, reduce the amount of solvents required and eliminate the use of chlorinated solvents. Critical steps in the use of Empore disk technology include an adequate pre-soak period, a drying step after water extraction followed by a wetting step, and the use of multiple extractions to achieve adequate recovery of the target analytes. These conditions have been described as critical

Table 10
Hamilton Harbour follow-up studies

Compounds	April 1994		October 1994		November 1994	
	Mean (ng/l)	S.D.	Mean (ng/l)	S.D.	Mean (ng/l)	S.D.
Indene	12.3	10.7	7.8	0.3	6.6	5.9
Tetrahydronaphthalene	0.0	0.0	0.0	0.0	0.0	0.0
Naphthalene	9.7	4.2	61.5	6.7	11.9	1.1
2-Methylnaphthalene	0.0	0.0	26.8	1.9	0.0	0.0
1-Methylnaphthalene	1.5	1.4	16.5	1.7	0.0	0.0
β-Chloronaphthalene	0.6	0.1	0.6	0.6	0.0	0.0
Acenaphthylene	0.0	0.0	13.2	1.5	1.9	1.7
Acenaphthene	11.0	3.8	13.5	1.9	0.0	0.0
Fluorene	15.0	1.2	23.1	3.2	0.0	0.0
Phenanthrene	0.0	0.0	77.4	8.5	8.2	1.0
Anthracene	4.1	3.6	85.2	9.3	0.0	0.0
Fluoranthene	7.1	0.6	125.2	7.9	18.4	1.4
Pyrene	19.6	0.5	94.8	5.8	18.8	2.0
Benzo[*a*]anthracene	0.0	0.0	39.1	3.3	0.0	0.0
Chrysene	0.0	0.0	77.7	6.6	0.0	0.0
Benzo[*b*]fluoranthene	0.0	0.0	66.6	4.5	1.0	0.9
Benzo[*k*]fluoranthene	0.0	0.0	67.8	2.4	0.0	0.0
Benzo[*E*]pyrene	0.0	0.0	53.1	2.0	0.0	0.0
Benzo[*a*]pyrene	0.0	0.0	53.7	4.3	0.0	0.0
Perylene	0.0	0.0	52.1	4.3	0.0	0.0
Indeno[123*c*,*d*]pyrene	0.0	0.0	60.3	4.7	0.0	0.0
Dibenzo[*a*,*h*]anthracene	0.0	0.0	19.0	1.4	0.0	0.0
Benzo[*g*,*h*,*i*]perylene	0.0	0.0	58.7	3.4	0.0	0.0

Mean (ng/l) ± standard deviation with $n=3$

steps in the analysis of other analytes using a variety of solid-phase techniques [6,12–15]

A small amount of breakthrough was observed, generally being no greater than 10% of the individual components spiked into 1-l samples. It is assumed that the remaining material is either trapped onto the Empore disks in the case of the mid- and heavy-PAHs or volatilized during the disk drying or solvent concentration steps. An additional difficulty may arise from passing laboratory air across the disks during the drying step. Air contaminated with volatile PAHs could potentially contaminate the disks.

Storage stability studies showed the feasibility of extracting water samples in the field, as recoveries of PAHs stored on disks for 60 days was better or equivalent to those stored as whole water samples, although both types of storage had lower recoveries than samples analyzed 24 h after spiking. The use of this technique may therefore lend itself to field collections, eliminating the need to ship 1-l samples across country. This option is currently being investigated by NLET. It is unclear why some water types, for example, samples stored from HB had lower recoveries than other stored samples. Other water quality parameters, such as nutrient levels, may play a role in the loss of samples on the disks and will have to be investigated.

Turbidity of the water samples was shown to affect the amount of time necessary to extract samples. Although this effect was not quantified, it is believed that varying the amount of Filter-aid used in the method may improve extraction times for high-turbidity waters.

The method was shown to be useful for the analysis of PAHs at the nanogram level in 1-l ambient water samples. Studies are currently underway to evaluate the extraction of larger volumes of water using the Empore disk technology.

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