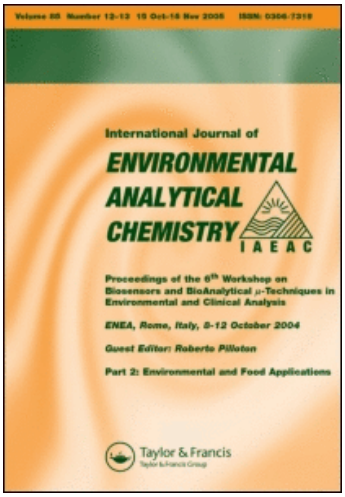

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THE EXTRACTION OF POLYCYCLIC AROMATIC HYDROCARBONS FROM ATMOSPHERIC PARTICULATE MATTER SAMPLES BY ACCELERATED SOLVENT EXTRACTION (ASE)

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The Accelerated solvent extraction (ASE) of PAHs (23 2- to 6-ring species) spiked onto glass fibre filters (GFFs) was studied as a function of variable extraction solvents, pressure, temperature and extraction times. Acceptable recoveries (85% ± 15%) were obtained for certain combinations of conditions and a tentative method (1500 psi, 150°C, 70:30 hexane:acetone mixture, 7 min heat-up time, 5 min static extraction time, 60% flush volume, 2 static cycles) was selected for further testing. However, this method did not prove as effective as the traditional Soxhlet method of extraction when these parameters were used to extract native PAHs from ambient atmospheric particulate matter collected on a GFF by Integrated Atmospheric Deposition Network (IADN) sampling protocols. The extraction recovery study for spiked GFFs was repeated using slightly different extraction conditions: 2000 psi, 100°C, 70:30 hexane:acetone, 5 min heat-up time, 5 min static extraction time, 150% flush volume, 3 static cycles. When this method was applied to the extraction of native PAHs from ambient atmospheric particulate matter collected on GFFs, the results showed equivalent or better recoveries to that of the Soxhlet method. The total time of extraction was 25 min requiring only 30 mL of solvent. This ASE method is presently used to quantitatively determine PAHs in IADN particle-phase samples.

Keywords: Ambient air samples; Glass fibre filters; Polycyclic aromatic hydrocarbons; Accelerated solvent extraction

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INTRODUCTION

In recent years, awareness has grown concerning the levels of toxic substances present in the air, water and soil of the Great Lakes Basin. In 1987, the Integrated Atmospheric Deposition Network (IADN) was mandated by the Great Lakes Water Quality Agreement Annex 15 to monitor the deposition of such substances into the Great Lakes. Today there are five "master" stations [1] at which air and precipitation samples are collected regularly. Air samples from the Canadian sites are analyzed by the Meteorological Service of Canada (MSC) (formerly the Atmospheric Environment Service) for a range of organic trace pollutants including polychlorinated biphenyls (PCBs), organochlorine pesticides (OCs) and PAHs.

Polycyclic aromatic hydrocarbons (PAHs) are one of the groups of compounds targeted by IADN as they are suspected human carcinogens [2]. PAHs are formed as products of incomplete combustion of fossil fuels and other organic matter. Major sources include emissions from wood and coal burning, automobiles, power plants, tobacco smoke and municipal waste incineration. In the atmosphere, PAHs have been found in both the vapour-phase and particle-phase, with the degree of vapour/particle partitioning dependent upon species vapour pressure and particle surface area [3,4]. In the Great Lakes atmosphere, toxicologically significant, higher molecular weight PAHs such as benzo[a]pyrene are found predominantly on particles [1].

Typical air sampling methods used at Canadian IADN sites involve a sampling train containing a glass fiber filter (GFF) and polyurethane foam (PUF) plug, through which approximately 350 m^3 of ambient air are drawn by a pump over a 24 h period. Particle-phase organic pollutants are effectively collected on the GFF, while vapour-phase species are retained on the PUF.

Historically, the MSC has subjected the exposed GFF and PUF separately to Soxhlet extraction using large volumes of high purity solvents, typically 300 mL of dichloromethane (DCM) and 475 mL hexane, respectively. The extraction requires 24 h in duration to achieve acceptable recoveries, following which the extract must be dried with sodium sulphate, filtered and reduced in volume before moving to a sample clean-up step. The use of high volumes of DCM is currently of some concern, due to evidence of carcinogenicity [5]. Furthermore, significant expense is involved in procuring and safely disposing of the large volumes of organic solvents required. Overall, the Soxhlet extraction method can

be considered to be relatively inefficient in terms of time, labour and material costs. A clear need has existed for the development of an automated extraction method with the potential to reduce the time of extraction, manual input and volume of solvent required. Accelerated Solvent Extraction (ASE) appears to meet these criteria and was selected for further study at MSC.

ASE makes use of low volumes of solvent heated to high temperatures under pressure to extract organic compounds. By pressurizing the solvent, it can be raised well above its boiling point and remain in the liquid state. The high temperature enhances analyte solubility and accelerates desorption from the matrix. Previous studies have shown ASE to be capable of yielding recoveries comparable to traditional techniques for a number of environmental organic pollutants and matrices: organophosphorus pesticides and herbicides from clay, loam and sand[6]; polychlorinated biphenyls (PCBs) from oyster tissue and sewage sludge[7]; atrazine and alachlor from soil[8]; PAHs from spiked silica and urban dust[7], coal fly ash[9], marine particulate matter[10], spiked soil[11], true soil[12], urban dust and diesel particulate[13]. The effects of ASE operating variables (temperature, pressure, solvent composition) on recoveries of PAHs from highly contaminated soil have been studied[14]. There are no published reports detailing the extraction of PAHs from GFF air samples using ASE.

This paper examines the extraction efficiency of airborne particle-phase PAHs (collected on a GFF sampling medium) using both the conventional Soxhlet method and ASE. A number of experimental factors – temperature, pressure, solvent composition, extraction time and cycles – have been evaluated to define the optimum operational conditions for the ASE system. As mentioned previously, most published evaluations to date of ASE efficiency for organic pollutants in environmental media have dealt with matrices spiked with a known amount of the target species. A similar approach has been followed in this study, with the use of GFFs spiked with PAHs. This provides an informative, but not completely accurate, indication of the effectiveness of ASE as applied to the extraction of native PAHs from the airborne particles. This general problem has been studied previously[15], where it was clearly shown that extraction rates from solid matrices may vary significantly for spiked and native compounds. For completeness, actual environmental samples need to be examined: in this work, airborne particulate-phase samples have been extracted by traditional Soxhlet method and ASE to provide a realistic comparison.

EXPERIMENTAL

Solvents

Solvents used were all high-purity distilled-in-glass grade: acetone, acetonitrile (ACN), dicholoromethane (DCM), toluene, water, 2-propanol (all Omnisolv, EM Science): hexane (non-UV, Caledon Laboratories) and iso-octane (2,2,4-trimethylpentane-195, Caledon Laboratories).

Glassware preparation

Glassware was washed with detergent (Contrad) in hot tap water, rinsed with cold tap water and then deionised water (prepared by sequential Millipore RiOs 16+Milli-Q gradient systems), rinsed with acetone and oven dried overnight at 350°C. Any glassware items used for measuring volumes; pipettes, graduated centrifuge tubes and graduated cylinders, were baked at only 125°C to prevent distortion. Prior to use, all glassware was rinsed three times with the appropriate solvent.

Standards

Table I shows the PAH target list measured by MSC for IADN and also details typical information for PAH standard mixtures used in this study. PAHs were obtained in pure (> 99%), solid form from a number of commercial suppliers. A C-32 microbalance (Cahn) was used to accurately weigh milligram quantities of each PAH for preparation of individual stock solutions in toluene with concentrations covering the range from 100 to 2800 μg/mL (see Table I) dependent upon the PAH and ultimate calibration range. Substock mixtures of PAHs in ACN were prepared from the 23 stock solutions and then used to prepare seven "working" standards in ACN for multi-level calibration of the HPLC analysis system. A mixture of the PAHs was also prepared in DCM (matrix spiking standard) at a concentration level within the HPLC calibration range; this was then used for the conduct of matrix spike recovery evaluations for both the Soxhlet and ASE methods. A response-check standard was prepared in ACN and was used to monitor system response, retention time stability and determine instrument detection limits (IDL). All standards were stored in amber glassware at 4°C then brought to room temperature and sonicated for 5 min prior to use.

TABLE I Meteorological Service of Canada PAH target list for IADN: The table shows details for stock solutions, matrix spiking standard, response check standard, HPLC calibration range and optimum excitation and emission fluorescence detection wavelengths. Acenaphthylene does not fluoresce, hence the wavelength shown is that used with the UV detector

PAH	*Supplier code*	*Stock solution in toluene* (μg/mL)	*Matrix spiking (DCM)* (pg/μL)	*Response check standard (ACN)* (pg/μL)	*HPLC calibration standards* (pg/μL)	λ_{Ex} (nm)	λ_{Em} (nm)
Naphthalene	US[1]	1623.8	81.2	64.9	16.2–324.8	220	342
Acenaphthylene	CS[2]	1854.7	185.5	148.4	37.1–741.9	227	N/A
Acenaphthene	SIG[3]	757.5	3.8	3.0	0.8–15.1	228	343
Fluorene	US	2756.7	68.9	55.1	13.8–275.7	256	332
Phenanthrene	CS	411.2	10.3	8.2	2.1–41.1	249	366
Anthracene	US	2064.1	5.2	4.1	1.0–20.6	250	390
Fluoranthene	US	426.6	21.3	17.1	4.3–85.3	233	453
Pyrene	ANA[4]	331.2	4.1	3.3	0.8–16.6	237	386
Triphenylene	CS	346.1	34.6	27.7	6.9–138.5	254	365
Benzo[ghi]-fluoranthene	BCR[5]	1055.2	26.4	21.1	5.3–105.5	232	435
Benz[a]anthracene	CS	404.8	20.2	16.2	4.1–81.0	287	399
Chrysene	CS	828.2	20.7	16.6	4.1–82.8	265	370
Retene	SUP[6]	465.4	46.5	37.2	9.3–186.2	263	370
Benzo[e]pyrene	US	1179.8	59.0	47.2	11.8–236.0	235	387
Benzo[b]fluoranthene	CS	365.7	9.1	7.3	1.8–36.6	233	442
Dibenz[a,c]anthracene	US	515.5	12.9	10.3	2.6–51.6	284	389
Benzo[k]fluoranthene	CS	367.5	11.0	8.8	2.2–44.1	303	421
Benzo[a]pyrene	SUP	1051.4	10.5	8.4	2.1–42.1	295	414
Benzo[ghi]perylene	ALD[7]	102.5	10.3	8.2	2.1–41.0	295	417
Dibenz[a,h]anthracene	US	611.8	30.6	24.5	6.1–122.4	294	414
Indeno[1,2,3-cd]pyrene	US	363.6	27.3	21.8	5.5–109.1	248	480
Anthanthrene	BCR	372.6	7.4	6.0	1.5–29.8	230	440
Coronene	ALD	815.9	40.8	32.6	8.2–163.2	300	439

[1]Ultra Scientific, North Kingstown, RI
[2]Chem Service, Westchester, PA
[3]Sigma Chemical Company, St. Louis, MO
[4]Analabs, North Haven, CT
[5]Community Bureau of Reference, Brussels, Belgium
[6]Supelco Canada, Oakville, ON
[7]Aldrich Chemical Company, Milwaukee, WI

Collection and preparation of air samples

Air samples were taken at the Point Petre IADN site[1], using a General Metal Works Model PS-1 sampler to collect air volumes of approximately 350 m^3 over a 24-h period. The sampling head employed a 10.2 cm diameter GFF (Type A/E Microfibre, Gelman Sciences) for particle collection, followed by a cylindrical 7.5 cm × 6.2 cm PUF plug (polyether type, Levitt Safety) to retain the vapour phase. After sampling, the GFF and PUF were removed from the sampling head: the GFF was folded, placed in clean aluminum foil and stored at − 10°C in a freezer until extraction.

Selected archived GFF samples were utilized to conduct the comparison of ASE with the standard Soxhlet method. Using acetone-rinsed stainless steel scissors, the GFFs were cut into two portions of equal area with one portion being extracted by ASE and other by Soxhlet.

Soxhlet extraction procedures

Soxhlet extraction of the GFFs was conducted on a heated extraction rack (Precision Scientific) capable of accommodating up to six 250 mL Soxhlet units. The GFF samples were routinely extracted for 24 h using 300 mL of DCM, with approximately three siphoning cycles per hour. (NOTE: For some of the extractions discussed later, a 73:30 v/v mixture of hexane: acetone was used for comparison with solvent conditions selected for ASE use.) To evaluate recovery efficiency, each set of Soxhlet extractions included one GFF spike consisting of 1 mL of the PAH matrix spiking standard applied directly, with a graduated pipette, onto a whole, twice-folded GFF placed at the bottom of the extraction chamber. Soxhlet (solvent) blanks were incorporated regularly as a quality control sample to test for system contamination. Soxhlet extraction often incorporates small amounts of water from condensation of ambient vapour inside the extractor: as a precaution, the resulting extracts were then dried using anhydrous granular sodium sulphate [12–60 mesh, J.T. Baker, Ultra-Resi-Analyzed: pre-extracted (acetone, 24 h) and baked 350°C overnight)] and passed through a glass-fibre filter [934-AH, Whatman: pre-extracted (acetone, 24 h)/baked (350°C overnight)]. The dried extract was concentrated down to 500 μL in ACN using Zymark Turbovap 500, closed-cell concentrator procedures. The final volume was then accurately adjusted to 1000 μL of ACN using calibrated 5 mL graduated, tapered centrifuge tubes (LaSalle), then transferred to a 2 mL amber glass screw-cap vial and stored at −10°C until clean-up.

ASE procedures

Instrumentation

A Dionex ASE 200 accelerated solvent extractor was used for this study. A good description of the functional components and operating principles of this system has been previously presented by Richter *et al.* [7], to which the reader is referred for more details. The unit in question was capable of extracting up to 24 samples and provided precise control of several

important variables to optimize the extraction. The extraction temperature could be set from 40–200°C and the pressure from 500–3000 psi. Solvent delivery from four different solvent reservoirs was possible with accurate mixing of these solvents being software controlled, the plastic-coated reservoirs were replaced by all-glass flask (Kontes) to allow thorough cleaning and baking. Other important variables controlled by the system software included: pre-heat (0–99 min), heat-up time (automatically set by system depending on selected extraction temperature), static extraction (1–99 min) time, flush volume (10 to 150% of the cell volume) and the number of static cycles (up to 5).

Operational description

The ASE extraction cells used for this study had a capacity of 11 mL. Prior to use, the cells were disassembled and the body and end caps (including frits and seals) were soaked and sonicated in acetone, allowed to dry, then baked at 125°C. The cell body and one end cap were assembled, following which acetone-rinsed stainless steel forceps were used to load a GFF sample (folded three times to form an inverted cone) into the cell. The top cap was then installed on the cell, both caps were finger-tightened and the cell loaded into the sample carousel. A prerinsed, 40 mL screw-cap collection vial (Dionex Canada) was loaded onto the bottom tray. A Teflon®-faced silicone septum (Pierce Tuf-Bond™) was used with the cap as the vial septa supplied by Dionex were not used following some observations of susceptibility to coring and contamination by silicone oil. Ultra-high purity (UHP) nitrogen (Praxair) purge gas was used to displace any remaining solvent from the cell and into the collection vial.

Recovery studies: Optimization of extraction conditions

To determine the optimum ASE conditions for the 23 targeted PAHs, a series of extractions were conducted using matrix GFF spikes as the test samples. A clean, previously baked (350°C, 24 h) Gelman GFF was folded and loaded into the cell as described previously to form an "inverted cone", following which a volumetric pipette used to distribute 0.5 mL or 1 mL of the PAH matrix spiking standard evenly over the surface of the GFF. The cell was then immediately sealed by the addition of the top cap.

Following extraction of the cell in the ASE system, the extract (~ 34 mL) was concentrated down to 500 μL in ACN using Zymark Turbovap nitrogen blowdown procedures. The volume was accurately adjusted to a final

volume of 1000 μL of ACN using calibrated 5 mL graduated, tapered centrifuge tubes (LaSalle), then transferred to a 2 mL amber glass screw-cap vial and stored at −10°C until clean-up.

The above process was repeated using different operating conditions for the ASE to evaluate the dependency of extraction efficiency upon these parameters.

Clean-up procedures

The automated Waters Millilab 1A Workstation (Waters Canada) was used to perform sample cleanup by solid phase extraction. A Waters SepPak Plus® silica column was conditioned with 10 mL of DCM (previously degassed by sparging with UHP helium), loaded with the sample (~ 1 mL), then eluted using 6 mL of DCM. The eluent was concentrated and exchanged into ACN using procedures identical to those described previously for the ASE extracts, with the final volume (1000 μL) of the sample being transferred to a 2 mL amber glass autosampler screw-cap vial to await subsequent analysis by HPLC.

Analysis of prepared extracts for PAHs by HPLC

Instrumental analysis was performed with an HP1090 LC system equipped with a variable volume injector (2 μL injection volume used), and a six-port injection valve (Rheodyne). A filter screen (2 μm) module, (Chromatographic Specialties) was present in the sample loop to prevent contamination of the analytical system. Water (pump A) and acetonitrile (pump B) were pumped through the system at a flow rate of 1.5 mL/min in proportions dictated by a reverse-phase gradient program (Table II). The solvents were sparged on hour prior to, and throughout the analysis by UHP helium via a charcoal purifying trap.

In order to separate the twenty-three PAHs, a 150 mm × 46 mm Vydac 202TP5415 C_{18} reverse-phase column (Vydac) was used. A guard column (3.0 cm Aquapore RP-18DS, Brownlee) in a separate housing was included ahead of the analytical column. The oven temperature was set to 30°C and was maintained to within ±0.1°C using a VWR 1160 refrigerated water bath which pumped water at 10°C through the cooling coil of the oven compartment.

Detection of twenty-two of the twenty-three PAHs was achieved using a Hewlett Packard 1046A programmable fluorescence detector (FLD). The fluorescence detector was time programmed (Table III) such that individual PAHs would be detected at, or close to, the optimum wavelengths as they were eluted. Acenaphthylene has negligible fluorescence response, and

TABLE II Liquid chromatograph solvent gradient timetable. The initial conditions consisted of 55.0% water and 45.0% acetonitrile. The flow rate was 1.5 mL/min

Time (min)	*Pump A (water)*	*Pump B (acetonitrile)*
5.00	55.0	45.0
12.50	40.0	60.0
22.50	30.0	70.0
26.00	20.0	80.0
30.50	0.0	100.0
38.50	0.0	100.0
39.00	55.0	45.0
40.00	55.0	45.0

TABLE III Fluorescence detector timetable

Time (min)	*Excitation* (nm)	*Emission* (nm)	*PMT gain*	*PAH being monitored*
1.00	224	342		Naphthalene, Acenaphthene
1.00			12	
9.90	256	332		Fluorene
11.00	249	366		Phenanthrene
12.50	250	390		Anthracene
13.80	233	453		Fluoranthene
15.00	237	386		Pyrene
16.70	254	365		Triphenylene
18.30	232	435		Benzo[ghi]fluoranthene
19.70	287	399		Benz[a]anthracene
21.10	265	370		Chrysene, Retene
23.80	235	387		Benzo[e]pyrene
25.20	233	442		Benzo[b]fluoranthene
26.70	284	395		Dibenz[a,c]anthracene
27.75	295	414		Benzo[k]fluoranthene Benzo[a]pyrene Benzo[ghi]perylene Dibenz[a,h]anthracene
31.80	248	480		Indeno[1,2,3-cd]pyrene
33.00	230	440		Anthanthrene
34.60	300	439		Coronene
33.00	Zero order	Zero order	1	

was therefore detected using a Hewlett Packard 1050A variable wavelength detector (standard flow cell, 10 mm path length and a wavelength of 227 nm). The variable wavelength detector was incorporated downstream of the FLD. The detector outputs (analog) were acquired via a Hewlett Packard 35900C A/D Multichannel interface to a PC using the HP 3365 ChemStation software. The fluorescence detector possesses a response range of 0–100 F units (dimensionless) with a corresponding analog output of 0–1 V (1000 mV). The data acquisition results in 250 response units (counts) on the y-axis of the chromatogram (for example see Fig. 4), per 1 mV of input signal. Therefore, 2 500 displayed counts on the y-axis is equivalent to a response of 1 F (fluorescence) or 10 mV analog output.

RESULTS AND DISCUSSION

For the purpose of conciseness, detailed data and results are presented here only for selected PAHs on the target list. Five representative species have been chosen: phenanthrene, one of the more volatile PAHs found predominantly in the vapour-phase of ambient atmospheric samples; fluoranthene, pyrene, benzo[k]fluoranthene and benzo[a]pyrene, four PAHs found mainly in the particle-phase.

A primary goal in these investigations was to develop an ASE method delivering performance comparable to, or better than, the established Soxhlet method. To provide the reader with some basis for comparison, Table IV shows some representative data for all the target PAHs obtained from Soxhlet-extracted (DCM) GFF matrix spikes (1.0 mL of the PAH matrix spiking standard): these 8 spikes were conducted over the period 971111 to 980311, in parallel with the extraction of a full-year (1997) of exposed air sampling filters from Point Petre.

Initial ASE method optimization using GFF spikes

As a starting point for method optimization, DCM was used as the solvent for ASE to provide a direct comparison with typical results from the established Soxhlet extraction method. Based upon ASE default values, the initial operating parameters were as follows: 100°C, 1500 psi. 5 min heat-up time, 5 min static extraction time, 60% flush volume and 60 s purge.

TABLE IV Mean GFF matrix spike recoveries of ASE and Soxhlet extractions. ASE extractions were conducted using ASE Method 2. Soxhlet extractions were conducted using DCM. N/C denotes not calibrated

Compound	*ASE Extraction (March 1, 1999–April 8, 1999, n = 5)*		*Soxhlet Extraction (November 11, 1997–March 11, 1998, n = 8)*	
	Mean% Recovery	*Standard Deviation*	*Mean% Recovery*	*Standard Deviation*
Naphthalene	N/C	N/C	N/C	N/C
Acenaphthene	82.8	15.9	70.3	13.3
Fluorene	89.2	11.9	72.3	13.7
Phenanthrene	93.9	14.6	94.1	16.8
Anthracene	84.8	16.7	74.7	9.3
Fluoranthene	90.1	8.6	84.1	12.8
Pyrene	90.2	11.4	92.2	11.4
Triphenylene	108.1	9.6	94.2	12.3
Benzo[ghi]fluoranthene	92.6	9.0	95.0	15.8
Benz[a]anthracene	96.6	11.1	92.6	11.5
Chrysene	98.7	7.1	97.9	11.9
Retene	78.6	9.9	87.7	12.3
Benzo[e]pyrene	98.7	14.0	109.7	20.7
Benzo[b]fluoranthene	101.9	13.0	101.5	14.1
Dibenz[a,c]anthracene	92.0	21.9	97.6	11.6
Benzo[k]fluoranthene	108.6	10.2	96.9	11.6
Benzo[a]pyrene	95.6	15.4	97.1	12.4
Benzo[ghi]perylene	106.5	10.8	106.6	12.8
Dibenz[a,h]anthracene	104.8	16.3	97.9	9.5
Indeno[1,2,3-cd]pyrene	98.9	15.6	106.3	13.4
Anthanthrene	N/C	N/C	49.8	27.5
Coronene	N/C	N/C	N/C	N/C
Acenaphthylene	92.0	20.5	71.1	15.3

Temperature

In theory, the solubility of analytes in a given solvent increases as the temperature of the solvent rises. Increased temperatures can weaken analyte–matrix interactions caused by van der Waals forces and hydrogen bonding. Thermal energies can overcome these interactions by decreasing the activation energy required for the desorption process[16]. Thermal energies easily overcome the low energy barrier associated with weakly adsorbed species. For strongly adsorbed analytes, the activation energy must be reduced by selective interaction of the solvent molecules with the analyte–matrix complex in order to break the bond. Increased temperatures lower the viscosity of the solvents allowing for better matrix penetration and faster diffusion rates of the analytes from the matrix into the solvent.

Figure 1 shows recoveries for the five representative PAHs from GFF matrix spikes conducted at 50°C, 100°C and 150°C: for this series of runs,

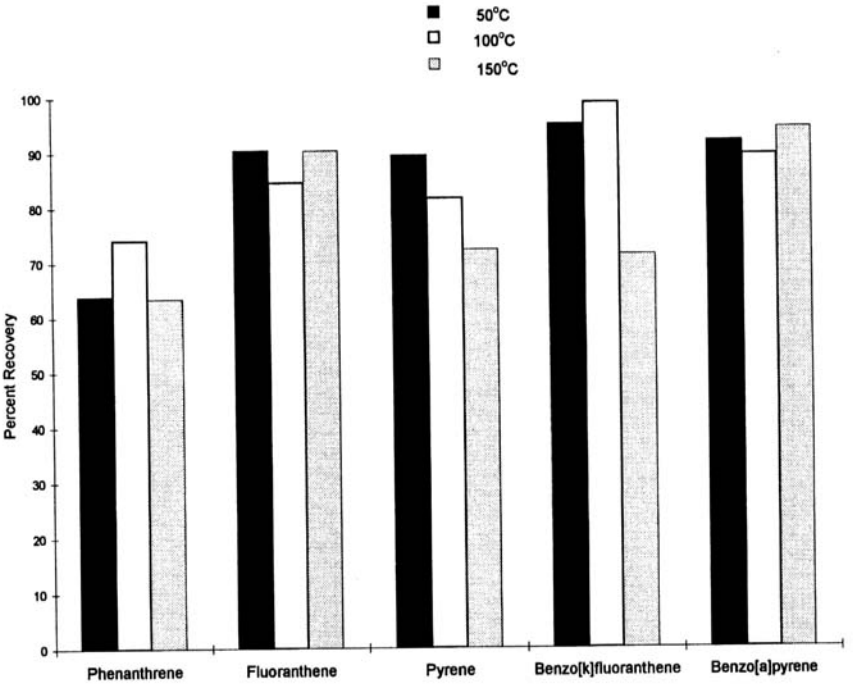

FIGURE 1 Percent recoveries of 5 PAHs from spiked GFF samples (0.5 mL matrix spiking standard) extracted by ASE at 50°C, 100°C and 150°C (DCM, 1500 psi, 5 min heat-up time, 7 min heat-up time at 150°C, 5 min static extraction, 60% flush volume, 60 s purge). Data shown are the composite of analytical results from two sequential extractions at each temperature.

0.5 mL of the PAH matrix spiking standard was used. Also, the numbers shown are the combined recoveries from two sequential extractions conducted to evaluate the efficiency of a single step: for all these runs, a significant portion of the total recovery was found in the second extraction. This limited data set implies that the effect of temperature may be species-dependent: for pyrene and benzo[k]fluoranthene, the recovery decreased significantly from 50°C to 150°C, whereas for fluoranthene and benzo[a]pyrene the different temperatures exerted little influence. For the subsequent optimizations, 100°C was retained as the operating temperature.

Pressure

The application of high-pressure to the extraction solvent allows for a temperature above the boiling point to be used in the extraction. Furthermore, the use of high pressure is believed to facilitate the extraction of analytes

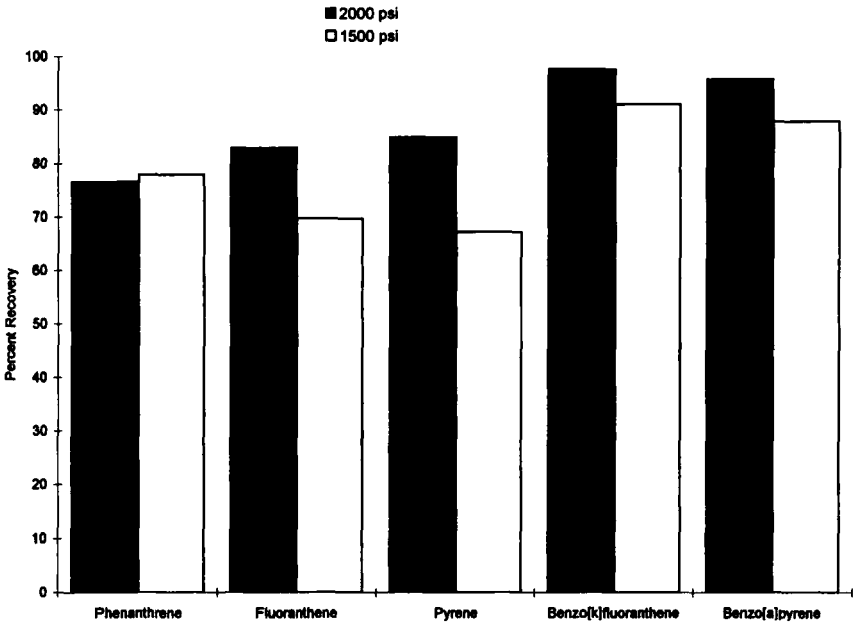

FIGURE 2 Percent recoveries of 5 PAHs from spiked GFF samples (0.5 mL matrix spiking standard) extracted by ASE at 1500 psi and 2000 psi (DCM, 100°C, 5 min heat-up time, 5 min static extraction, 60% flush volume, 60 s purge). Data shown for 1500 psi are the composite of analytical results from two sequential extractions. Data shown for 2000 psi are derived from 2 static cycles.

that have been absorbed into the sample matrix[7]. Figure 2 shows recoveries for the five PAH species obtained from extractions of GFF matrix spikes (0.5 mL of the PAH matrix spiking standard) using DCM at 1500 psi and 2000 psi. It should be noted that the runs at the two pressures are not entirely equivalent: at 1500 psi, the spiked sample was subjected to two sequential extractions, with each eluent being analyzed separately and the data being combined to calculate an overall recovery; at 2000 psi, the spiked sample experienced two static cycles. Given these slight differences in procedure and the precision of the analysis, there appears to be no significant advantage in the use of pressure above 1500 psi: to minimize strain on the ASE 200 pumping system, the pressure was maintained at 1500 psi for subsequent tests.

Solvent composition

Due to matrix effects, the composition of the extraction solvent used in ASE would be expected to significantly influence the extraction efficiency from

real environmental samples. For PAHs retained on atmospheric particles and sampled on GFF, the extraction solvent must have optimal polarity to penetrate the GFF and the particles in order to extract the compounds of interest. Using the initial operating parameters defined earlier, with temperature and pressure settings unchanged but with the number of static cycles set to two, recoveries from GFF matrix spikes (0.5 mL of PAH matrix spiking standard) were determined using a number of different solvents, either pure or in combination.

For the example PAHs, Fig. 3 shows that a 73 : 30 v/v mixture of hexane-acetone gave recoveries superior to those obtained with pure dichloromethane, pure acetone or pure hexane for all of the selected PAHs except pyrene. The PAH recoveries obtained using some of the other solvent compositions were not the result of inefficient extraction as none of the spike analytes remained in the cell. The losses appeared to be occurring *after* the sample analytes had left the cell, either by poor retention in the collection vial or in the subsequent processing. In particular the poor recoveries observed with ACN included in the extraction mixture could be the result of increased sample blowdown times caused by the lower volatility of this solvent: consequently, the sample extracts experienced greater exposure to

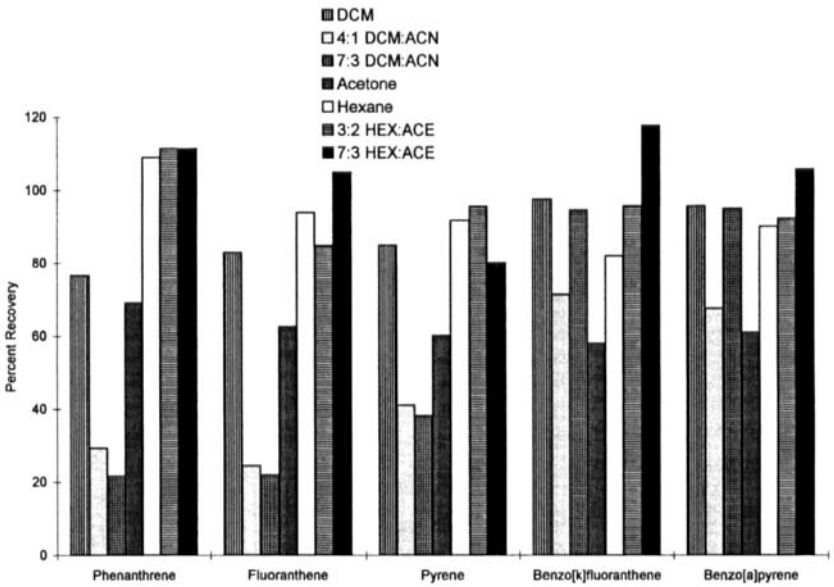

FIGURE 3 Percent recoveries of 5 PAHs from spiked GFF samples (0.5 mL matrix spiking standard) Extracted by ASE with different solvents/solvent mixtures (100°C, 1500 psi, 5 min heat-up time, 5 min static extraction, 2 static cycles, 60% flush volume, 60 s purge).

the heated (38°C) water-bath of the Zymark Turbovap 200 system, perhaps resulting in the enhanced losses, particularly for the most volatile species.

Comparison of Soxhlet and ASE extraction procedures for ambient air samples (GFF) using ASE Method 1

Based upon the investigations described above, a tentative method (ASE Method 1) was defined for further evaluation using real ambient air filiters as the test materials: 150°C, 1500 psi, 70:30 v/v mixture of hexane–acetone, 7 min heat-up, 5 min static time, 2 cycles, 60% flush volume, 60 s purge. Note that the temperature incorporated in the method was different to that (100°C) utilized in the optimization studies just described: this reflected a belief that efficient removal of the target analytes from actual atmospheric particles would require additional thermal energy. Prior to comparing the Soxhlet method of extraction with the ASE Method 1, 2 GFFs collected at Point Petre, Ontario in April 1989 and subsequently archived in a freezer, were cut into two portions of equal area. Each portion was extracted separately by Soxhlet using DCM, subjected to the silica clean-up procedure and analyzed by HPLC/FLD/UV. The results were within 10% of each other indicating that the distribution of the particles on the GFF was reasonably homogenous. A set of 10 GFF samples, collected at Point Petre over the period February to May 1989 and subsequently archive in a freezer, were similarly cut into portions of equal area and used to conduct the comparison of the Soxhlet (using 73:30 v/v hexane–acetone) and ASE Method 1 extractions.

A typical result from the Soxhlet/ASE comparison is shown chromatographically in Fig. 4, where the fluorescence detector outputs obtained after processing the Soxhlet (SOX) and ASE extracts for sample PPT098 (PPT890525P2SR) are compared. The fingerprint obtained was similar for both methods. Furthermore, the ASE extraction produced a positive bias for some of the PAHs (e.g. anthracene, fluoranthene), but seriously underperformed for certain of the higher molecular weight PAHs, particularly benzo[a]pyrene and benzo[ghi]perylene from real matrix samples as the concentrations were half of those obtained with the Soxhlet method. Note that acceptable recoveries (75–100%) were obtained for the ASE GFF spike that was carried out along with the extraction of these real samples for quality control purposes, emphasizing the importance of the matrix on extraction efficiency. It was concluded from these results that operating pressure was probably not high enough to penetrate the real sample matrix and

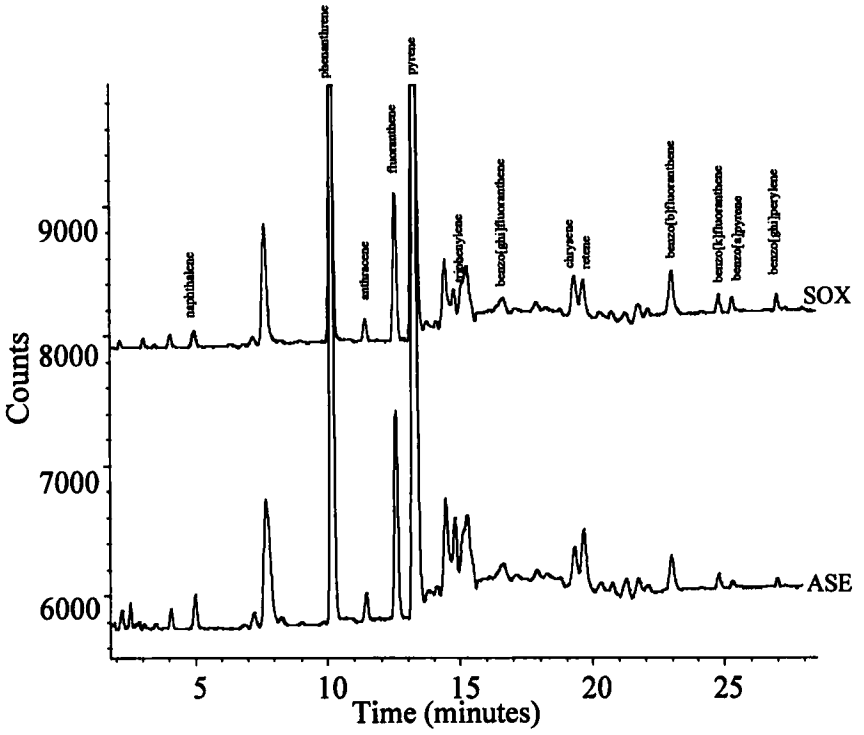

FIGURE 4 HPLC-FLD chromatograms obtained after processing of Soxhlet (SOX, 70:30 v/v hexane–acetone) and ASE (using ASE Method 1) extracts of split-GFF from Point Petre PPT 098 sample (PPT890525P2SR). See text for details of HPLC conditions. ASE Method 1 (150°C, 1500 psi, 70:30 v/v mixture of hexane–acetone, 7 min heat-up, 5 min static extraction, 2 cycles, 60% flush volume, 60 s purge). The two chromatograms were merged together and then displaced by 2000 counts to allow for a better comparison of the two chromatograms. 2500 counts is equivalent of 1 F (fluorescence) or 10 mV.

that two 5 min static extraction cycles with only 60% flush volume did not offer enough solvent/analyte interaction for the removal of particle-bound PAHs.

Further optimization of ASE – ASE Method 2

The results described in the preceding section demonstrated a need to revisit the optimization choices included in ASE Method 1 in the hope of improving the recoveries of the higher molecular PAHs from real samples.

Before proceeding to explore changes to the conditions for further extractions of real samples, a second round of tests was carried out to confirm the

effects of such changes upon GFF matrix spikes. These studies were performed using a pressure of 2000 psi, flush volume increased to the maximum value (150%), with the number of static cycles increased from 2 to 3 to increase the completeness of extraction of the PAHs. Variable purge times, static extraction time, temperatures and hexane : acetone solvents ratios were examined independently to fine-tune the extraction conditions.

Purge time

The purge time setting controls the length of time, in seconds, that the cell is purged with nitrogen at the end of the extraction for the removal of any trace solvent and analytes from the cell and into the collection vial. Although this was felt to be an unlikely controlling factor, the recoveries from GFF matrix spikes (1.0 mL of PAH matrix spiking standard) were determined using purge time settings of 40 and 120 s temperature set at 100°C and a solvent composition of 70 : 30 v/v hexane–acetone. Figure 5 shows that this parameter exerted minimal influence on the recoveries.

The purge time was retained at the default value (60 s).

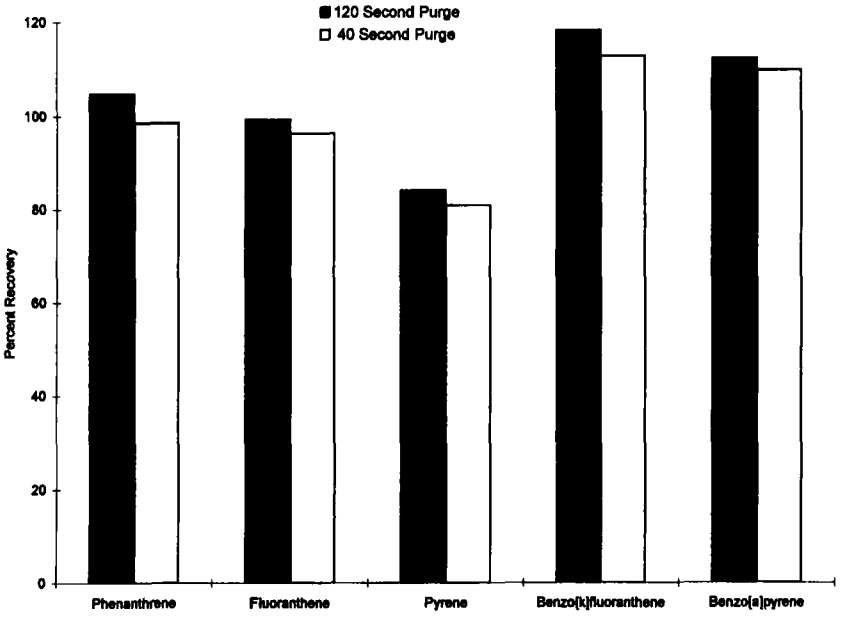

FIGURE 5 Percent recoveries of 5 PAHs from spiked GFF samples (1.0 mL matrix spiking standard) extracted by ASE with 40 s and 120 s purge times (2000 psi, 70 : 30 v/v hexane–acetone, 100°C, 5 min heat-up, 5 min static extraction, 3 cycles, 150% flush volume).

Static extraction time

The static extraction time controls the duration of sample exposure to the extracting medium. Recoveries from GFF matrix spikes (1.0 mL of PAH matrix spiking standard) were determined using static time settings of 5 min and 7 min, temperature set at 100°C and a solvent composition of 70 : 30 v/v hexane–acetone. Figure 6 shows that this parameter exerted minimal influence on the recoveries. The static time was set to 5 min in order to speed up the total extraction time.

Temperature

The effect of extraction temperature was revisited, with recoveries from GFF matrix spikes (1.0 mL of PAH matrix spiking standard) determined at 100°C and 150°C, using a solvent composition of 70 : 30 v/v hexane–acetone. Figure 7 shows recoveries to be slightly higher at 100°C, particularly for benzo[a]pyrene and benzo[k]fluoranthene. These results are somewhat different to those described earlier (see Fig. 1) when DCM was used as the extraction solvent at a lower pressure and very little dependence was seen for these species. In consequence, the use of a temperature higher

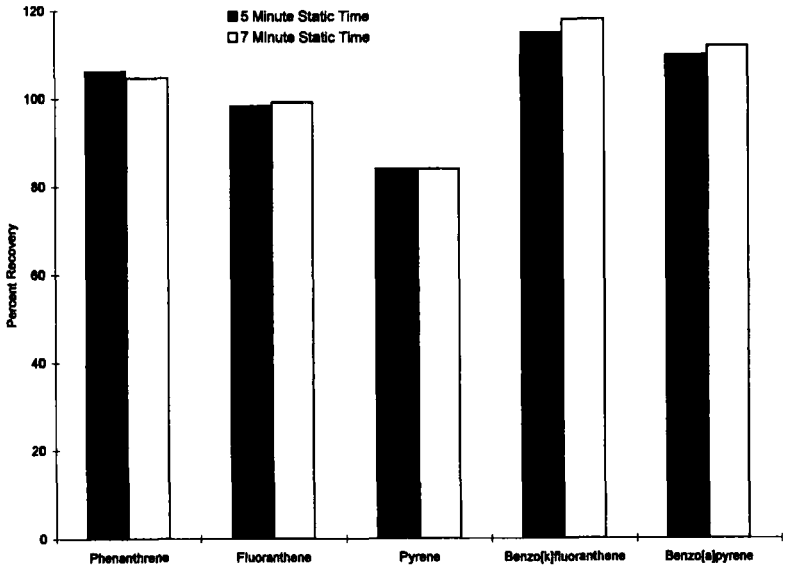

FIGURE 6 Percent recoveries of 5 PAHs from spiked GFF samples (1.0 mL matrix spiking standard) extracted by ASE with static times of 5 min nd 7 min (2000 psi, 70 : 30 v/v hexane–acetone, 100°C, 5 min heat-up, 3 cycles, 150% flush volume, 60 s purge time).

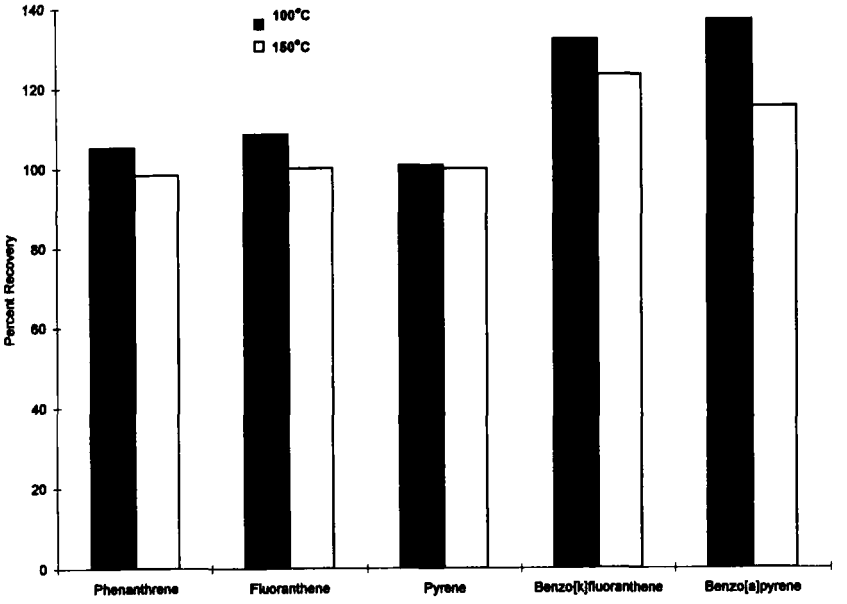

FIGURE 7 Percent recoveries of 5 PAHs from spiked GFF samples (1.0 mL matrix spiking standard) extracted by ASE at temperatures of 100°C and 150°C (2000 psi, 70:30 v/v hexane–acetone, 5 min heat-up, 7 min heat-up for 150°C, 5 min static extraction, 3 cycles, 150% flush volume, 60 s purge time).

than 100°C for the extraction of PAHs from real GFF matrix samples would probably be unadvisable. For all subsequent work, the temperature was maintained at 100°C.

Hexane : acetone ratio

The solvent composition was tested further to ensure that the 70:30 v/v hexane:acetone ratio was the optimum solvent mixture for extraction. Recoveries from GFF matrix spikes (1.0 mL of PAH matrix spiking standard) were determined for three different hexane:acetone ratios. Figure 8 shows that the 70:30 v/v hexane:acetone mixture proved significantly superior to the other solvent combinations. These findings are in general agreement with the earlier tests conducted (see Fig. 3).

ASE Method 2

Based upon the investigations described above, a modified method (ASE Method 2) was defined for further evaluation using real ambient air filters

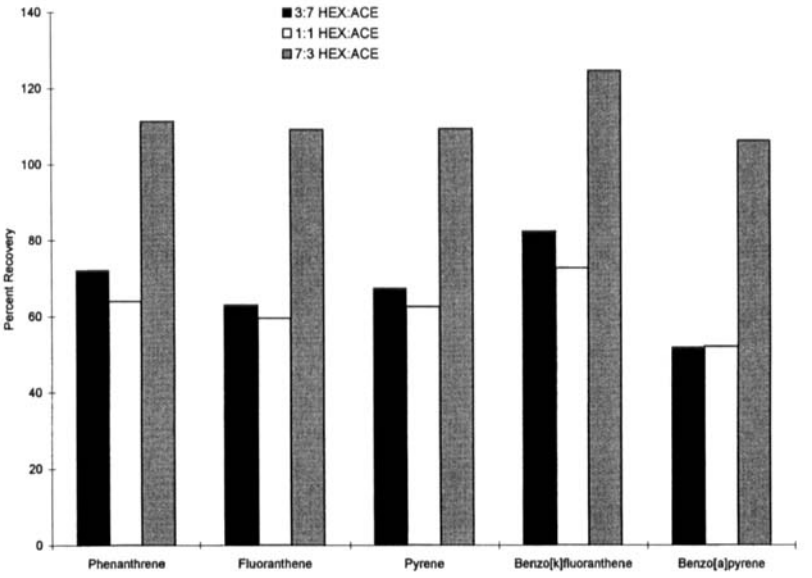

FIGURE 8 Percent recoveries of 5 PAHs from spiked GFF samples (1.0 mL matrix spiking standard) extracted by ASE with three different hexane : acetone v/v mixtures (2000 psi, 100°C, 5 min heat-up, 5 min static extraction, 3 cycles, 150% flush volume, 60 s purge time).

as the test materials: 100°C, 2000 psi, 70 : 30 v/v mixture of hexane–acetone, 5 min heat-up, 5 min static time, 3 cycles, 150% flush volume, 60 s purge. The total extraction time was ~ 25 min and utilized ~ 30 mL of solvent. Table IV shows performance data using this method for all the PAHs on the target list obtained from a series of 5 GFF matrix spikes (1.0 mL of PAH matrix spiking standard) conducted just after the completion of the optimization studies: the results show that the extraction efficiency using ASE Method 2 is comparable to that obtained by Soxhlet extraction when dealing with such matrix spikes.

Comparison of Soxhlet and ASE extraction procedures for ambient air samples (GFF) using ASE Method 2

A further set of 5 GFF samples, collected at Point Petre over the period March to September 1989 and subsequently archived in a freezer, were cut into two equal portions and used to conduct the comparison of the Soxhlet (this time using the regular IADN solvent, DCM) and ASE Method 2 extractions.

A typical result from this comparison is shown chromatographically in Fig. 9, where the fluorescence detector outputs obtained after processing the Soxhlet (SOX) and ASE extract for sample PPT059 (PPT890314P2SR) are compared: the agreement between the chromatographic responses is excellent. In particular, the low-bias seen previously for benzo[a]pyrene has been eliminated. Figure 10 shows ambient atmospheric concentrations (in pg/m^3) for the five representative PAHs in the five samples, as obtained with the Soxhlet method of extraction and the ASE Method 2: good agreement between the two extraction methods was observed for these species, even for a wide range of ambient concentrations and associated filter loadings.

Further evidence that the two extraction methods are capable of performing in equivalent fashion is provided by Fig. 11, which shows the ambient particle-phase concentration of benzo[a]pyrene in pg/m^3 in air samples collected at Point Petre, Ontario between 1997 and 1999. The seasonal

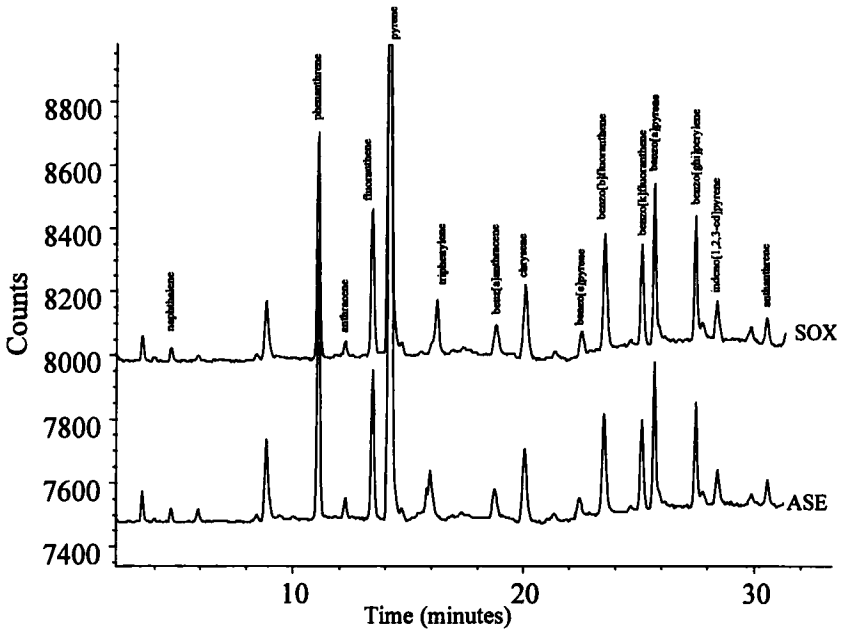

FIGURE 9 HPLC-FLD chromatograms obtained after processing of Soxhlet (SOX) and ASE (using ASE Method 2) extracts of split-GFF from Point Petre PPT 059 sample (100°C, 2000 psi, 70 : 30 v/v mixture of hexane–acetone, 5 min heat-up 5 min static time, 3 cycles, 150% flush volume, 60 s purge) The two chromatograms were merged together and then displaced by 500 counts to allow for a better comparison of the two chromatograms. 2500 counts is equivalent to 1 F (fluorescence) or 10 mV.

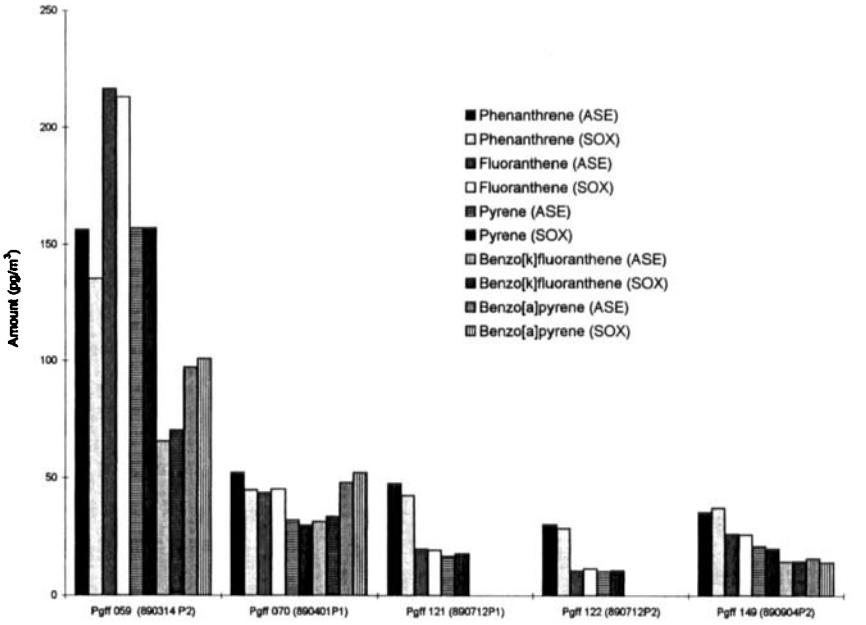

FIGURE 10 Ambient atmospheric particle-phase concentrations (in pg/m^3) for 5 PAHs from 5 GFF samples collected at Point Petre: GFF split into two equal portions, one part extracted by SOX (DCM), one part extracted by ASE (ASE Method 2).

variation of the PAHs is also illustrated in this figure, with the highest concentrations in the winter months when fossil-fuel consumption is at maximum and the lowest concentrations are present in the summer months when photochemical destruction of airborne organics would be expected to be highest. The samples collected between January 1997 and September 1998 were extracted with the Soxhlet method, whereas the samples collected between October 1998 and December 1999 were extracted with the ASE method: the point at which the methods were switched is indicated by the arrow in Fig. 11. There is no evidence for any step-change in the reported ambient particle-phase concentration of this PAH resulting from the change in extraction method. Similar findings (not shown) arise from the data for the other PAHs. It is worth nothing that the large "episode" in benzo[a]pyrene particle-phase concentration that occurs just after the changeover in extraction method is "real" and is mirrored by a substantial increase in many of the vapour-phase PAHs determined by Soxhlet extraction of the associated PUF cartridge i.e. it is not an artefact of the ASE method.

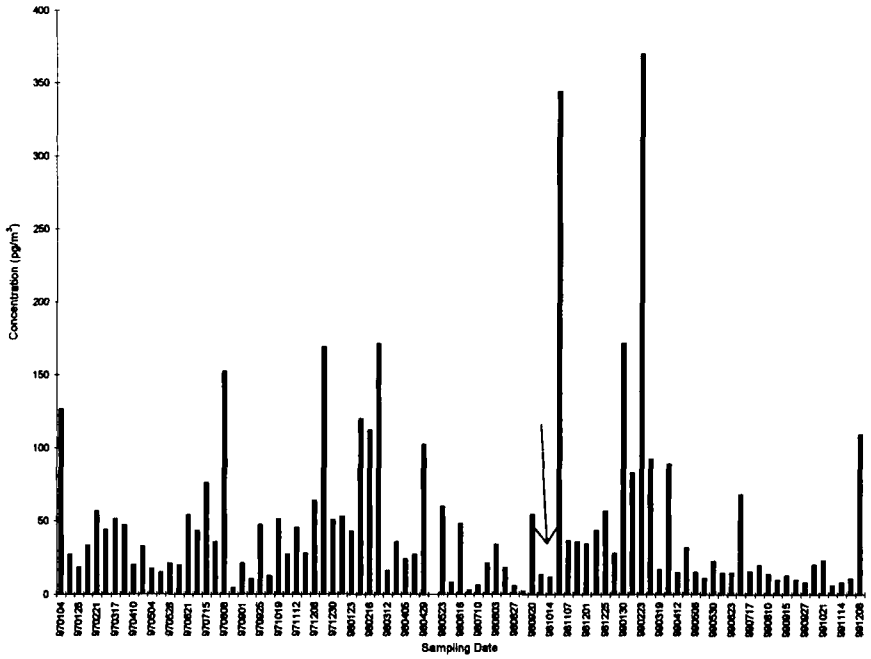

FIGURE 11 Ambient atmospheric particle-phase concentrations (in pg/m^3) of benzo[a] pyrene at Point Petre, Ontario between 1997–1999. Jan 1997 to Sept 1998 samples extracted by SOX (DCM), Oct 1998 to Dec by ASE (ASE Method 2).

CONCLUSIONS

This work has accomplished the optimization of ASE for the extraction of PAHs from ambient particulate matter collected on GFFs, providing performance equivalent to conventional Soxhlet extraction methods. Suprisingly, the favoured solvent used for Soxhlet extraction, DCM, was found to perform poorly when utilized in the ASE application: a 70 : 30 v/v hexane–acetone mixture was preferred. Care is required in the used of GFF matrix spikes to validate and optimize the ASE conditions, as this may provide an incomplete guide to method equivalency with the Soxhlet method of extraction when applied to the extraction of native PAHs from real atmospheric samples. For such samples, elevated pressures, combined with moderate temperature and repeated interaction with the solvent, served to increase the extraction efficiency. Using the developed method, operator time for extracting 12 samples has been reduced from three days to one and the solvent consumption reduced by a factor of 10.

Lastly, the ASE method has permitted the use of DCM for extraction of GFFs to be curtailed.

Acknowledgements

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