Microchim Acta (2012) 178:187–193
DOI 10.1007/s00604-012-0813-6

ORIGINAL PAPER

Pressurized fluid extraction of polycyclic aromatic hydrocarbons using silanized extraction vessels

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Received: 12 January 2012 / Accepted: 18 March 2012 / Published online: 17 May 2012

Abstract We have investigated the extraction efficiency of a pressurized fluid extraction system using an Ottawa sand matrix, soils and a certified reference material (HS-6) spiked with the 16 polycyclic aromatic hydrocarbon (PAHs) associated with method EPA 8100. Acceptable recoveries were achieved for all PAHs using a nominal sand concentration of 2.0 μg.g^{-1}. However, similar experiments that were conducted at a concentration of 0.20 μg.g^{-1} afforded poor recoveries and poor reproducibility for the six-ring PAHs indeno(1,2,3-cd) pyrene, dibenz(a)anthracene, and benzo(ghi)perylene. These were not adequately addressed by the use of indeno(1,2,3-cd) pyrene-d12 and benzo(g,h,i)perylene-d12 surrogates. Silanization of vessels using dichlorodimethylsilane adequately passivates the system but is only required for the high surface area retention frits. Replicate analyses at concentrations of 200 and 20 ng.g^{-1} demonstrated that detection limits in the low ppb range (ng.g^{-1}) are achieved for Ottawa sand, dry soil and soil with moisture contents up to a mass fraction of 30 %. Such performance is consistent with the analytical requirements of the Canadian Sediment Quality Guidelines. Improved analyte recoveries were also observed for the certified reference material HS-6 which were further improved by increasing extraction temperatures from 100 to 150 °C.

Keywords Polycyclic aromatic hydrocarbons · Pressurized fluid extraction · Silanization · Sediment

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Introduction

The sources, environmental transport, toxicity, degradation and remediation of polycyclic aromatic hydrocarbons (PAHs) are all extensively studied. Numerous natural and anthropogenic sources have been identified, and the carcinogenic and mutagenic properties of specific PAHs have been established [1]. Although many structurally diverse PAHs have been synthesised [2], environmental assessment often focuses on small groups of PAHs based on toxicity and occurrence. These PAHs are mainly drawn from a core of 16 compounds [3]. The number of regulated PAHs, as well as their maximum acceptable concentrations (MACs) varies as a function of country, matrix and environmental application and human exposure route. For example Canadian environmental guidelines identify 13 PAHs in sediment at MACs of 0.00587–0.111 μg.g^{-1} and 2 PAHs in soil with MACs between 0.1 μg.g^{-1} and 22 μg.g^{-1} [4, 5]. Thus, the requirement to provide sediment and soil detection limits for PAH analyses in the part per million to part per billion range is not unusual.

The extraction of PAHs from soils, sediments and solid wastes can be accomplished by a number of methods. Soxhlet, pressurized fluid, ultrasonic, microwave and supercritical fluid extraction are all recognised by the US Environmental Protection Agency (EPA) for the analysis of semivolatiles, including PAHs [6], whilst an EPA method for micro-scale extraction makes use of a simple shaking procedure [7]. Pressurized fluid extraction (PFE) facilitates the use of common laboratory solvents at elevated temperatures by the application of pressure, typically 10–15 MPa. Improved extraction kinetics are complemented by the automation of analysis and a reduction in solvent consumption relative to Soxhlet. The closed systems retain semivolatiles and operate over a wider range of total extracted mass than supercritical fluids. PFE has been commercialised by three vendors and modifications to commercial systems can be accomplished for research purposes [8, 9]. Whilst some workers accommodate small sizes or achieve in situ clean-up by changes in the type and amount of extraction vessel packing, others have constructed dedicated systems [10–13]. The development of PFE instrumentation and the application of PFE continue to be active areas of research [14–16]. Manufacturers' application notes specifically identify the acceptable performance of commercial instrumentation with respect to PAH extraction [17–20]. However, these studies have been conducted in the part per million range (μg.g^{-1}) and, although replicate analyses have been conducted, data analyses are not consistent with the requirements associated with accreditation to the ISO 17025 standard. The present work describes validation analyses conducted in the part per billion concentration range (ng.g^{-1}) for one commercial PFE system that resulted in low and inconsistent recoveries for some PAHs, and discusses methods of system passivation to facilitate the analysis of soils, sediments and solid wastes in the environmentally and legislatively relevant part per billion (ng.g^{-1}) concentration range.

Experimental

Reagents

Hexane (Certified A.C.S.), dichloromethane (DCM) (Optima), hydrochloric acid (trace metal grade), acetone (pesticide grade), and toluene (HPLC grade) were purchased from ThermoFisher Scientific (Whitby, Canada, www.thermofisher.com). Ottawa sand, glass wool, silica (0.3 mm mesh) and filter papers (Whatman, 41) were similarly sourced. Diatomaceous earth was obtained from Applied Separations (Allentown, PA, USA, www.appliedseparations.com). The certified reference material (CRM), HS-6 was obtained from National Research Canada (Ottawa, CA, www.nrc-cnrc.gc.ca). Double deionized water (17.8 MΩ) was prepared using an E-pure™ Water Purification System (Barnstead International, Dubuque, IA, www.barnstead.com). A commercial soil was characterised by particle size as being predominantly 'sandy loam'. Eight replicate analyses of this soil afforded PAH concentrations of the 16 PAHs studied below the detection limits of the present studies, and in practice produced negligible responses by extraction/GC-MS analysis. Soil was dried at 110 °C for 4 h and stored in air tight containers. Soils of defined gross moisture content were then prepared by the combination of dried soil and distilled deionized water on a weight: weight basis. PAH calibration and control standards solutions containing the 16 PAHs associated with US EPA 610 (Table 1) were obtained from Supelco (Bellefonte, PA, www.supelco.com). Control spikes were obtained as individual PAH solids from the same vendor. Deuterated PAHs were also supplied by Supelco, with the exception of indeno(1,2,3-cd)pyrene-d12 and benzo(g,h,i)perylene-d12 (Cambridge Isotope Laboratories, Andover, MA, www.isotope.com). Solutions were prepared by serial dilution in DCM to afford calibration standards containing analytes at concentrations of 80, 200, 400 and 800 μg.mL^{-1} and d-PAHs at a concentration of 400 μg.mL^{-1}.

Table 1 Validation Data Obtained from Nominal 0.020 μg.g^{-1} Samples

Compound in Elution Order	Replicate Sample Analyte Concentration/(μg.g^{-1})							Mean	Std. Dev.	MDL[a]	CCME ISQG [4]
	1	2	3	4	5	6	7	/(μg.g^{-1})	/%	/(μg.g^{-1})	/(μg.g^{-1})
Naphthalene	0.025	0.020	0.018	0.018	0.022	0.021	0.020	0.021	12	0.0095	0.0346
Acenapthylene	0.021	0.021	0.019	0.019	0.022	0.019	0.019	0.020	6	0.0050	0.00587
Acenapthene	0.021	0.019	0.002	0.021	0.019	0.019	0.019	0.020	5	0.0037	0.00671
Fluorene	0.020	0.018	0.018	0.018	0.020	0.016	0.018	0.018	8	0.0054	0.0212
Phenanthrene	0.022	0.020	0.022	0.020	0.021	0.017	0.017	0.020	11	0.0082	0.0419
Anthracene	0.022	0.020	0.021	0.018	0.016	0.021	0.018	0.019	11	0.0083	0.0469
Fluoranthene	0.022	0.021	0.021	0.019	0.022	0.018	0.018	0.020	9	0.0069	0.111
Pyrene	0.024	0.022	0.021	0.021	0.024	0.018	0.019	0.022	11	0.0089	0.053
Benz(a)anthracene	0.019	0.019	0.021	0.024	0.019	0.019	0.022	0.020	10	0.0077	0.0317
Chrysene	0.016	0.022	0.019	0.020	0.019	0.018	0.002	0.019	10	0.0072	0.0571
Benzo(b)fluoranthene	0.019	0.019	0.021	0.022	0.020	0.020	0.022	0.020	6	0.0049	-[b]
Benzo(k)fluoranthene	0.017	0.016	0.021	0.018	0.018	0.018	0.019	0.018	9	0.0061	-[b]
Benzo(a)pyrene	0.022	0.022	0.026	0.023	0.026	0.027	0.024	0.024	8	0.0080	0.0319
Indeno(1,2,3-cd)pyrene	0.019	0.019	0.021	0.020	0.021	0.019	0.019	0.020	5	0.0037	-[b]
Dibenz(a,h)anthracene	0.018	0.018	0.021	0.019	0.020	0.019	0.020	0.019	6	0.0043	0.00622
Benzo(g,h,i)perylene	0.018	0.018	0.019	0.018	0.019	0.018	0.019	0.018	3	0.0021	-[b]

[a] Based on twice the Student's t-weighed standard deviation at 95 % confidence; [b] ISQG not derived

Silanization and extraction

The PFE sample container used consists of a simple cylindrical stainless steel vessel (33 mL), which is mechanically sealed by the application of Telfon-lined upper and lower closures. Sample is retained by a sintered stainless steel frit, which is held in place by a locking nut. In the present work these vessels, frits and retaining nuts were passivated by soaking in a solution of 15 % dichlorodimethylsilane (Aldrich, www.sigmaaldrich.com) in toluene for 16 h. The components were then transferred to beakers and sonicated in toluene for 10 min. Post sonication, the components were allowed to dry in a flow of dry air before reassembly. Components were stored in sealed containers prior to use. An Applied Separations (Allentown, PA) '*fast PSE*' unit, capable of six simultaneous extractions, was used for PFE. Extraction vessels were packed from bottom to top with; Ottawa sand (1 g), silica (1 g), diatomaceous earth (*ca.* 5 g) sample (10 g), and then successive layers of diatomaceous earth, Ottawa sand and glass wool until the void volume was filled. For developmental work, the sample portion comprised of 10 g of Ottawa sand spiked with 50 μL of the 40 μg.mL^{-1} solid spike standard and 100 μL of the 40 μg.mL^{-1} d-PAH surrogate standard, to afford nominal matrix concentrations of 200 ng.mL^{-1} and 400 ng.mL^{-1}, respectively. Experiments conducted with moisture-bearing soil replaced the upper Ottawa sand layer with diatomaceous earth. Vessels were extracted with 50:50 DCM:hexane in one static cycle of 5 min with solvent rinsing and nitrogen gas flush times of 1 min each. Temperature and pressure were maintained at 100 °C and 10 MPa, respectively. Sample extracts of *ca.* 30 mL volume were collected in 60 mL vials, containing 1 g of diatomaceous earth to remove residual moisture. Extracts were cooled to ambient temperature and weighed prior to direct transferal to GC vials for analysis. Modifications to this procedure included; (i) increase in collection vial diatomaceous earth to 3 g for experiments with moisture-bearing soil, (ii) extract concentration to < 2 mL for nominal spikes of 0.020 μg.g^{-1}, and (iii) increased extraction temperature to 150 °C for CRM extraction.

Instrumentation

PAH analyses were carried out using 6890/5973Series GC-MS with autosampler (Agilent Technologies, Santa Clara, CA, www.agilent.com). Separations were carried out on an Agilent J&W DB-5 fused-silica capillary column (30 m×0.25 mm i.d., 0.25 μm film thickness). GC parameters were typical of those used for PAH analysis; injection volume (1 μL), injection temperature (275 °C), inlet pulse pressure (0.12 MPa 0.4 min), oven temperature (70 °C to 280 °C at 8 °C.min^{-1}). Helium carrier gas flow was 1 mL.min^{-1} and transfer line temperature was 280 °C. Quantitation was achieved using the parent ion of each PAH with at least one secondary ion for each analyte. Surrogate correction was performed based on elution order (Table 1) as follows; naphthalene (naphthalene-d8), acenapthylene to pyrene (mean of phenanthrene-d10 and anthracene-d10), benz(a)anthracene to benzo(g,h,i)perylene (benz(a)anthracene-d12). Scanning electron microscopy (SEM) was performed using an XL-30cp (FEI, Hillsbor, OR, www.fei.com). Energy dispersive X-ray (EDX) analysis was completed using a Genesis Spectrum SEM QuantZAF, Version 3.60 (EDAX, Mahwah, NJ, www.edax.com).

Results and discussion

Extraction from untreated vessels

Initial studies were conducted to determine the accuracy and precision of PAH extraction using untreated vessels and frits. Several studies were conducted using previously used and new vessels, frits and nuts using simulated PAH concentrations of 2.0 μg.g^{-1}. These experiments afforded acceptable recoveries and sample standard deviations for all analytes. These data are consistent with published application notes [17–19], which used similar PAH concentrations. For experiments conducted using a simulated PAH concentrations of 0.20 μg.g^{-1}, each experiment examined eight replicate extractions of PAHs (50 μL, 40 μg.mL^{-1}) and d-PAH spikes (100 μL, 40 μg.mL^{-1}) onto an Ottawa sand matrix (10 g). The mean analyte recoveries of the 16 PAHs are identified for two such experiments (Fig. 1). These data afforded combined means and relative sample standard deviations for the surrogate-corrected recoveries of the first 13 PAHs of 109±12 % and 113±14 %, respectively. In contrast, the three PAHs of highest molecular weight, indeno(1,2,3-cd)pyrene, dibenz(a)anthracene and benzo(ghi)perylene, each afforded low surrogate corrected recoveries. These recoveries were also inconsistent between the two experiments being 62±6 % and 28±6 %, 51±10 % and 38±8 %, and 58±8 % and 69±9 %, respectively. Moreover, the surrogate-corrected recovery of these analytes was weakened by the decrease in recovery of the surrogate itself that was observed with increasing molecular weight (Fig. 2). Indeno(1,2,3-cd)pyrene, dibenz(a)anthracene and benzo(ghi)perylene represent the only six ring structures in the PAH series analysed; the remaining analytes having 2–5 rings. Attempts to improve surrogate correction by the use of six ring surrogates, indeno(1,2,3-cd)pyrene-d12 and benzo(g,h,i)perylene-d12, did afford surrogate-corrected analyte recoveries closer to 100 %. However, absolute recoveries of analyte and surrogate were <30 %, and the use of low surrogate recoveries to correct low analyte concentrations was deemed unacceptable.

The poor recoveries and precisions observed for nominal Ottawa sand concentrations of 0.20 μg.g^{-1} relative experiments at a ten times greater concentration suggest the retention

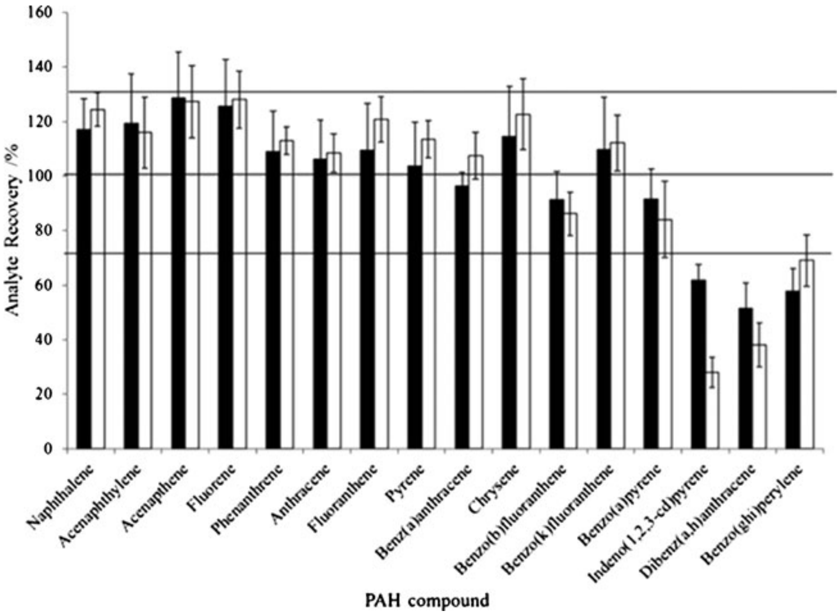

Fig. 1 Relative Mean and Standard Deviation for Replicate Analysis of 16 PAHs from Two Identical Experiments Using Untreated Components with a Nominal PAH Concentration of 0.20 µg.g^{-1}, Expt. 1 (*Black square*), Expt. 2 (*White square*)

of absolute analyte and surrogate masses within the PFE system, rather than relative ones. The retention of PAHs on glass, particularly those with extended ring structures, has been noted for other analytical methods [18]. Consideration was given in the present work to the use of elevated PAHs concentrations prior to analysis as a form of system passivation. However, the addition of PAHs at significantly greater concentrations than the ng.g^{-1} detection limits required is unattractive. Moreover, despite the low recoveries observed for indeno(1,2,3-cd)pyrene-d12 and benzo(g,h,i)perylene-d12, these surrogates were also periodically and unpredictably recovered at > 200 % from nominally identical extractions. Thus, it is evident that PAH binding and liberation, particularly for extended ring structures, can occur in an unpredictable manner. The potential role of solvents and consumables, such as diatomaceous earth, in PAH retention were eliminated by the preparation and analysis of spike solutions. Thus, attention focused on extraction vessels and associated instrumentation.

Component characterisation and silanization

EDX spectroscopy confirmed composition of vessels, frits and nuts as stainless steel. SEM of the frit identified an approximate particle size for the sintered material (Fig. 3). Vessel and nut surface areas were determined geometrically, whilst the frit surface area proved too small for BET surface area measurements. However, numerical estimates based on SEM suggested a frit surface area of 1000 cm^2, or more than ten times that of the extraction vessel, and more than one hundred times that of the locking nut. The interaction between frit surface and PAHs has not been investigated. However, the dispersive forces associated with extended ring structures may

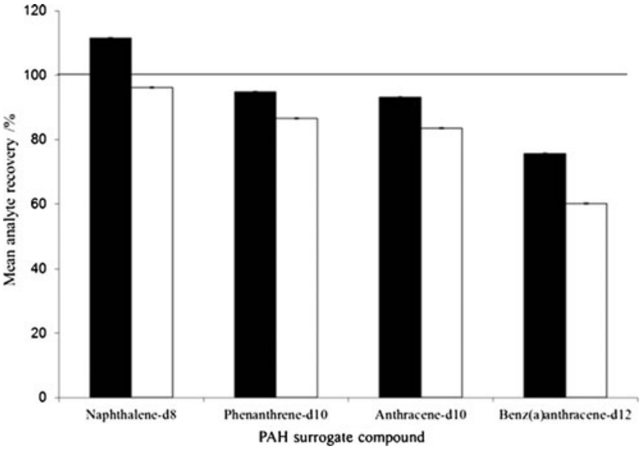

Fig. 2 Relative Surrogate Recovery and Standard Deviation for Replicate Analysis from Two Identical Extraction Experiments using Untreated Components, Expt. 1 (*Black square*), Expt. 2 (*White square*)

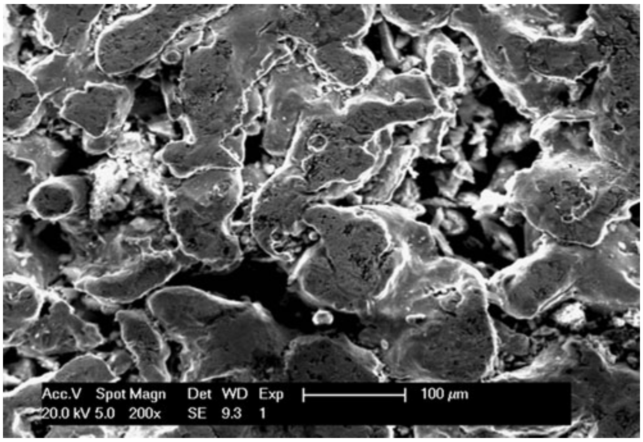

Fig. 3 SEM of Frit Surface

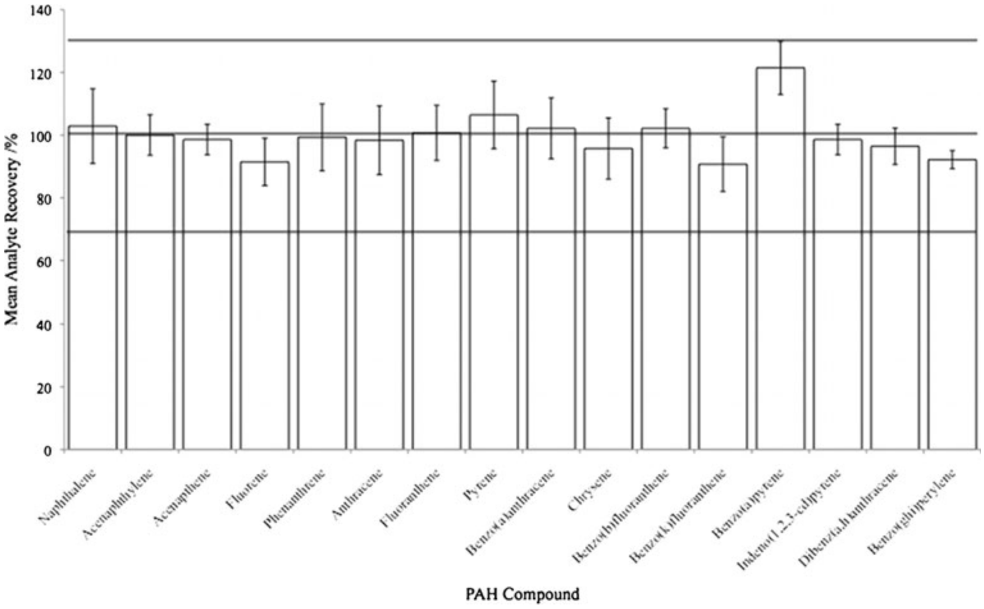

Fig. 4 Relative Recovery and Standard Deviation for Replicate Analyses Performed Using Silanized Frits and a Nominal PAH Concentration of 0.20 μg.g^{-1}

be sufficient to interact with the combined oxide, hydroxide and water moieties present on the stainless steel surfaces.

Although silanization using dichlorodimethylsilane is usually associated with the reaction of surface hydroxyl groups, the reagent was considered for the passivation of stainless steel vessel surfaces, frits and sealing nuts. Silanization significantly improved the combined average recoveries of the first 13 PAHs, 99±8 %. The relative precision for replicate analyses averaged 7 % for these PAHs. Recoveries of the remaining indeno(1,2,3-cd)pyrene, dibenz(a)anthracene and benzo(ghi)perylene were significantly enhanced, being 116±13 %, 82±15 % and 130±12 %, respectively. The role of vessel, frit and locking nut in the retention of PAHs was subsequently investigated and revealed that only frit silanization was essential to improved performance; this observation being consistent with the relative surface areas of the three components. Moreover, a cleaning procedure which involved the washing of vessels (water and laboratory detergent, followed by solvent rinsing and drying) and the ultrasonication frits and nuts in dichloromethane was sufficient to maintain performance over at least three consecutive extractions without PAH retention or blank contamination (Fig. 4).

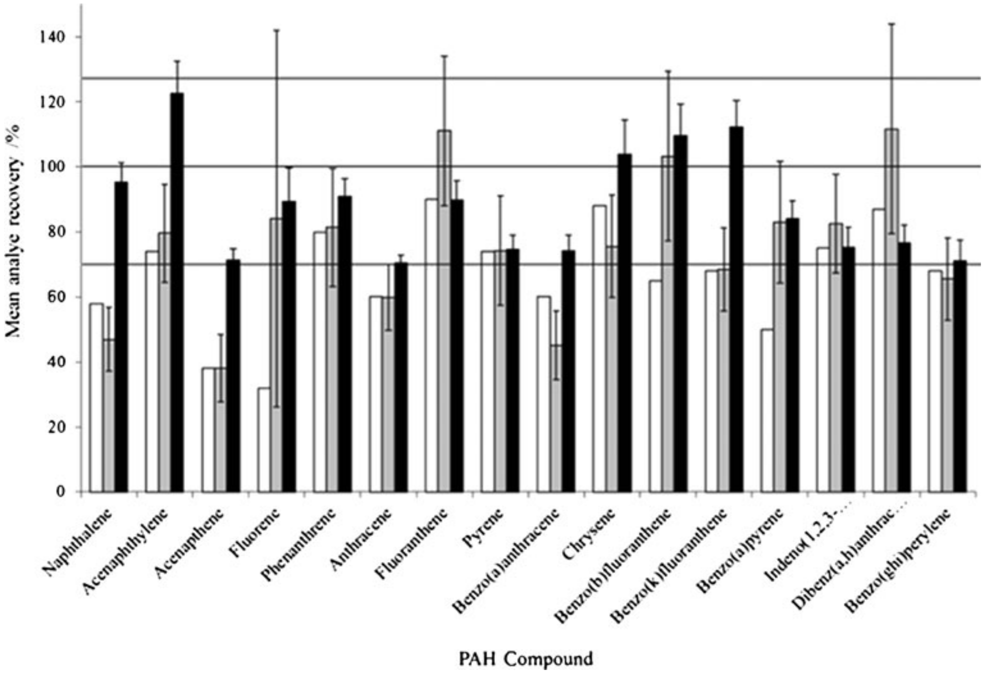

Fig. 5 Relative Recovery and Standard Deviation of Replicate Analyses of the CRM HS-6 Using Untreated Frits at an Extraction Temperature of 100 °C (*White square*), Silanized Frits at 100 °C (*Grey square*), and Silanized Frits at 150 °C (*Black square*)

Method validation

Method detection limit validations were conducted according to the requirements of the ISO standard 17025 in two series of experiments, using PAHs spikes onto Ottawa sand to afford nominal concentrations of 0.20 $\mu g.g^{-1}$ and 0.020 $\mu g.g^{-1}$, respectively. Seven replicate samples and one blank sample were prepared for each validation experiment. Silanization of frits was employed in each case. Method detection limits (MDLs) were expressed as twice the Student's t-weighted sample standard deviation at 95 % confidence. Using the higher spike concentrations, data demonstrated surrogate recoveries > 70 %, with surrogate-corrected analyte recoveries being 89–125 %, and MDLs of 0.032–0.049 $\mu g.g^{-1}$. Sample standard deviations were ≤ 6 %. Performance with respect to indeno(1,2,3-cd)pyrene, dibenz(a)anthracene and benzo(ghi) perylene was not statistically different from the PAH series as a whole. A second validation experiment was undertaken using a nominal concentration of 0.020 $\mu g.g^{-1}$ PAHs in order to investigate the possibility of achieving MDLs < 0.010 $\mu g.g^{-1}$ and validation consistent with the most stringent Canadian requirement for PAH solid analysis, the Canadian Sediment Quality Guideline Interim Sediment Quality Guideline (ISQG) [4]. Experiments were conducted in the same manner as previous extractions, but to afford adequate GC-MS signal to noise, extracts were concentrated to < 2 mL prior to analysis. In all cases MDLs were < 0.010 $\mu g.g^{-1}$, with all ISQG MDLs being met (Table 1).

Although Ottawa sand provides an idealised matrix for development, obvious differences exist between this matrix and soil/sediment. In particular, the absence of water from the former and the possible significant water content of the latter are pertinent to a passivation method that is hydrolytically unstable. Thus, sandy loam soils containing mass fractions of 10 %, 20 %, 30 % and 40 % moisture were prepared and analysed using a nominal PAH spike of 0.20 $\mu g.g^{-1}$. In all cases detection limits < 0.050 $\mu g.g^{-1}$ were obtained. No deterioration in accuracy was observed, with the mean error for all 16 PAHs being 10 %, 7 %, 12 %, 12 % and 13 % for Ottawa sand and soils with 10 %, 20 %, 30 % and 40 % moisture, respectively. Similarly, all relative precisions (averaged for 16 PAHs) were < 10 % for all five experiments. However, at 40 % moisture content breakthrough of free water and soil particulates was observed in the extract, suggesting a practical moisture limit of 30 % water for soil/sediment extraction. Given the expected hydrolytic instability of the silanized functionalities, the performance of the system is notable. It may be postulated that since the primary frit/extract exposure occurs during extract discharge, hydrolysis conditions occur for a minimal period. The kinetic stability of dimethylsiloxane moieties, as a result of steric hindrance from reacting water, and the thermodynamic stability of dimethylsiloxane-surface bonds are unknown. Similar analyses, conducted using a dry soil matrix with a nominal PAH spike of $\mu g.g^{-1}$, also afforded accuracy, precision and detection limit data that did not differ significantly from that obtained using Ottawa sand.

Certified reference material analysis

The robustness of the proposed silanization and extraction method was challenged using the marine sediment CRM HS-6. Seven sediment samples and one blank were extracted using the same extraction procedure as previously described. PAH concentrations in the CRM range from 0.19 to 4.1 $\mu g.g^{-1}$. In order to produce a matrix with concentrations in the range associated with recovery problems (< 0.20 $\mu g.g^{-1}$), 1 g of the CRM was mixed with 9 g of Ottawa sand to produce a 10 g sample with a concentration range consistent with that requiring frit silanization for at least some PAHs. Studies were performed in the absence of frit silanization, after frit silanization, and using silanization at an elevated extraction temperature of 150 °C. Recovery, expressed as the average of all 16 PAHs, improved for each progressive method modification, being 69 %, 76 % and 88 % (Fig. 5). In addition to improved recovery, the combination of silanization and increased extraction temperature afforded precisions of each analyte of ≤ 10 %. These data are considered acceptable in terms of both recovery and uncertainty given that the two-sigma uncertainties associated with the CRM are 15–40 %.

Conclusions

The retention and irreproducible loss of higher molecular weight PAHs, using a commercial PFE system, are significant for soil and sediment extractions at concentrations in the part per billion ($\mu g.g^{-1}$) range. Such concentrations are relevant to analyses related to sediment quality guidelines. Acceptable passivation can be achieved by a simple silanization of the frits used with the extraction vessels. This silanization is sufficiently stable to facilitate the analysis of sediments with a water mass fraction of up to 30 %, and affords acceptable recovery for the CRM HS-6.

Acknowledgements The provision of pristine extraction vessels by Applied Separations Inc. is gratefully acknowledged.

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