



Accepted for publication in Analytical Methods

ARTICLE

Inexpensive Simple Extraction of Trace PAHs from Water using PS-DVB Monolithic Beads

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/C8AY01562G

www.rsc.org/

A new simple and sensitive analytical technique based on polystyrene-divinyl benzene (PS-DVB) monolithic bead extraction followed by gas chromatography–mass spectroscopic detection (GC-MS) was developed for the determination of polycyclic aromatic hydrocarbons (PAHs) in water. The PS-DVB monolithic bead was fabricated and used as the adsorbent. The experimental parameters controlling the performance of the bead extraction were optimized. Calibration curves showed excellent linear fits, with $r^2 > 0.995$ for all PAHs in the 2–30,000 ng mL⁻¹ range. The limits of detection (LODs) ranged from 0.01 to 0.47 ng mL⁻¹. Recoveries of the PAHs in environmental water samples spiked at a concentration of 500 ng mL⁻¹ were 72–109%, while they were 69–114% for water spiked at 20 ng mL⁻¹. Both intraday and interday repeatabilities were high, with RSDs for 16 PAHs spiked standard solutions being less than 10%. The present study indicated that the proposed method is well suited for the quantification of PAHs in environmental and drinking water samples.

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are an important group of environmental contaminants, with 16 of them listed as priority pollutants by the US Environmental Protection Agency (EPA).¹ PAHs originate from natural sources, such as volcanoes and forest fires; and anthropogenic activities,² such as industrial production, transportation, combustion, waste incineration, oil spills, and agriculture. PAHs are also used as ingredients in industrial products, such as creosote, lubricants, pharmaceuticals, petroleum-based fuels, polymers, and solvents. Combustion products that include PAHs are released by motor vehicles,³ fossil-fueled power plants and refineries,⁴ or by agricultural activities such as burning of brushwood, straw, and heathland. PAH can also enter soils by the release of lubricant and fuels from agricultural equipment. The release of PAHs as particulates or vapour phase can contaminate the atmosphere, sludge sediment, soil, and water – and eventually end up in surface and ground water as well as the ocean.² The potential for long-distance transport of PAHs has resulted in these contaminants being found far away from human sources of entry, as illustrated by the presence of anthropogenically-derived PAHs in remote mountain lakes.⁵

Environmental PAHs can accumulate in human tissues, e.g. liver, spleen, adrenal glands, ovaries and fat, via inhalation, ingestion, and direct contact. This accumulation has been associated with decreased immune function, cataracts, kidney and liver damage, breathing problems, asthma-like symptoms, and lung function abnormalities. Exposure to PAHs has also been associated with increases in lung, breast, skin, and esophageal cancers.⁶ The US EPA currently classifies the following PAHs as possible human carcinogens: benz(*a*)anthracene, benzo(*a*)pyrene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, chrysene, dibenz(*a,h*)anthracene and indeno (1,2,3-*cd*)pyrene.¹ Because of their potential toxicity, the EPA has established water quality criteria for PAHs in water, for example the maximum contaminant level in drinking water for benzo(*a*)pyrene is 0.2 ng mL⁻¹.⁷ The European Community Council Directive 98/83/EC suggested a water standard for human consumption with the maximum concentration of benzo(*a*)pyrene at 0.010 ng mL⁻¹ and the sum of four PAHs, namely benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*ghi*) perylene and indeno (1,2,3-*cd*)pyrene, not to exceed 0.1 ng mL⁻¹.⁸ The World Health Organization (WHO) issued a guideline value for benzo(*a*)pyrene of 0.7 ng mL⁻¹ in drinking water.⁹

As PAHs contaminants are present in the environment at trace concentration levels, an essential step in the assay inevitably involves extraction and preconcentration. A classical method of PAHs determination in water matrix employs a large volume of organic liquid as a solvent for extraction.^{10–12} This method has been downsized to the micro-level, namely dispersive liquid-liquid microextraction (DLLME), where a fine suspension of organic solvent is utilized for extraction and has the advantage of a high enrichment factor.¹³ Hollow fibers are also employed in microextraction (SBME) for analysis of PAHs at sub ng L⁻¹ levels.¹⁴

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Solid phase extraction (SPE) is one of the most popular methods for PAH analysis in water.^{10, 15, 16} It is also the standard method employed by many organizations.^{17, 18} Several sorbent materials have been utilized for PAH extraction, such as C18,¹⁹ PS-DVB,²⁰ fluorocarbon polymer,²¹ multi-wall carbon nanotubes.²² SPE using C18 material for PAH analysis is achieved with either sonication during elution,²³ with a three-phase solvent elution,²⁴ or with some modification of the sorbent.²⁵ Employing a miniaturized apparatus, solid phase microextraction (SPME) has gained more attention for PAH determination in water, and uses modified silica fibers,²⁶ or a polymer housed in an optical fiber²⁷. A stir bar sorptive extraction (SBSE) usually employs a stir bar coated with liquid PDMS.^{28, 29} This method does not require sample preparation, but have the drawback of sample carry-over effect.

Monolithic substances provide high surface area, pore sizes and volume, and consist of a single rod of porous material with macropores and micropores. Both silica-based and polymer-based monolith are used for extraction and chromatography - owing to their high permeability, ease of fabrication and functionalization.³⁰ Silica-based monolith is widely applicable for a wide range of organic analytes and matrices; it has been utilized as adsorbent in various configurations, such as cartridge, disk, capillary,³¹ pipette tip and syringe.³² PS-DVB polymeric material possesses similar hydrophobicity, but is more robust and its monolithic form in a needle has been utilized for extraction.³³ Although C18-silica monolith is commercially available, no PS-DVB monolith is currently marketed for extraction. In this work we investigated the use of polystyrene-divinylbenzene polymer monolithic beads for pre-concentration of PAHs from a water matrix. The polymeric monolithic material is easily fabricated, is robust and any fabrication residues are easily removed.

2 Materials and Methods

2.1 Chemicals and Materials

For optimisation of the extraction process with monolithic beads, the following seven PAHs were used: Standard-grade naphthalene (99.7%) from Loba Chemie (Mumbai, India); anthracene (97%) and pyrene (98%) from Aldrich (St. Louis, Mo, USA); fluorene (95%) from TCI (Tokyo, Japan); chrysene, and both benzo(*b*)fluoranthene and benzo(*a*)pyrene from Supelco (Bellefonte, USA). 1,4-Diphenyl benzene (98.5%) from Fluka (St. Louis, Mo, USA) was used as an internal standard (IS). For method validation, 1,000 ng μL^{-1} of a mixed PAHs standard in toluene - containing naphthalene (NaP; 99.6%), acenaphthylene (AcPy; 99.0%), acenaphthene (AcP; 99.5%), fluorine (Flu; 99.0%), phenanthrene (Phe; 98.0%), anthracene (Ant; 99.0%), fluoranthene (FL; 99.0%), pyrene (Pyr; 99.0%), benz(*a*)anthracene (BaA; 98.7%), chrysene (Chr; 99.5%), benzo(*b*)fluoranthene (BbFL; 99.9%), benzo(*k*)fluoranthene (BkFL; 99.1%), benzo(*z*)pyrene (BaP; 99.1%), indeno(1,2,3-*c,d*)pyrene (InP; 98.9%), dibenz(*a,h*)anthracene (DBA; 99.4%), and benzo(*g,h,l*)perylene (BghiP; 99.3%) was purchased from Dr. Ehrenstorfer (Augsburg, Germany). Anthracene-*d*10 (99 at.% D) from CDN isotopes Inc. (Quebec, Canada) was used as the internal standard (IS) for PAH quantitation. All PAH standard stock solutions

were prepared in anhydrous toluene from RCI Labscan (Bangkok, Thailand).

For synthesis of the PS-DVB monolithic beads, styrene (99.0%) from Merck (Darmstadt, Germany), divinylbenzene (80.0%) from Aldrich (St. Louis, Mo, USA), dibenzoyl peroxide (75.0%) and decanol (99.0%) from Acros Organics (New Jersey, USA), tetrahydrofuran (THF) (99.99%) from Fisher Scientific (Leicestershire, UK) were employed in the formulation. HPLC-grade dichloromethane from RCI Labscan (Bangkok, Thailand) was used as an extraction solvent for PAHs in water. Deionised water with 18 M Ω cm resistivity was produced by a double-deionised water system (Maxima, Elga, Bucks, England). Except where specified otherwise, chemicals were of analytical grade.

2.2 PS-DVB Monolithic Bead Preparation

The formulation of PS-DVB monolith beads was adapted from the method of Premstaller³⁴ and was initially optimized to achieve a high extraction yield of PAHs. The optimized liquid mixture contained 10.0 mg dibenzoyl peroxide, 200 μL styrene, 200 μL divinyl benzene, 400 μL decanol and 80 μL THF. It was vigorously shaken to achieve homogeneity, and then poured into a 1.30 mm i.d. polypropylene tube, which was later tightly sealed with a stopper, and placed in an oven at 70 °C for 24 h. This resulted in the formation of a hemispheric bead-shaped monolith with a diameter of 0.9-1.0 cm. The polypropylene tube was discarded and the monolithic bead was washed with acetone multiple times under sonication until complete removal of any possible residues, and finally dried at 45°C for 6 h.

The synthesised PS-DVB beads were morphologically examined using a Quanta 450 scanning electron microscope (FEI, Hillsboro, OR, USA) and the surface area and pore volume of the polymer monolith were characterised by nitrogen absorption using a 3Flex surface characterization analyzer (Micromeritics, Norcross, Georgia, USA).

2.3 Sample Collection and Preparation

Water samples were collected from localities in Samutprakarn, Roi-Et, and Bangkok, Thailand. After collection, all samples were kept in amber glass bottles and stored at 4°C.

A monolithic bead was put into a narrow-neck glass bottle containing 100 mL of a water sample, and covered with aluminium foil. The water was stirred at 900 rpm under ambient temperature for 2 h. After extraction, the bead was transferred to a vial and eluted with 2 mL dichloromethane under sonication for 10 min. The eluent was preconcentrated and reconstituted to 1.00 mL with toluene. One microliter of the liquid extract was then used for GC analysis.

2.4 GC Analysis

PAHs in the liquid extract were quantified using a QP2020 gas chromatograph coupled to a mass spectrometer (GC-MS) (Shimadzu, Kyoto, Japan). The separation was carried out on a 0.25 mm i.d. x 30 m x 0.25 μm ZB-5HT capillary column (Phenomenex, Torrance, CA, USA) with He carrier gas flow of 1.0 mL min^{-1} . A 1- μL

extract was applied in a splitless mode with an injector temperature of 280 °C. The oven temperatures were as follows: initially at 60 °C, ramped to 170 °C at 10 °C min⁻¹ held for 2 min, ramped to 210 °C at 7 °C min⁻¹, ramped to 240 °C at 10 °C min⁻¹, ramped to 248 °C at 2 °C min⁻¹ held for 3 min, ramped to 290 °C at 3 °C min⁻¹, and held at this temperature for 3 min.

3 Results and Discussion

Since PAHs are present in water at trace levels and have high hydrophobicity and low water solubility, a widely-used analytical method for preconcentration of the analytes involves solid phase extraction (SPE) employing non-polar materials, such as C18-silica or PS-DVB.^{19, 20, 35} An initial experiment was carried out and tested on the C18-silica monolith synthesised by a sol-gel process utilising tetramethoxysilane precursors. The one-step synthesis reaction resulted in a monolithic skeleton with shrinkage, resulting in a small gap between the monolith and the wall, which facilitated removal of the monolithic solid from the container. The C18-silica monolith was unsuitable for adsorbing PAHs from water because the monolith cracked and abraded away during stirring. Polystyrene co-divinylbenzene (PS-DVB) monolith was then considered as an alternative, owing to its ruggedness. The PS-DVB material exhibits high hydrophobic adsorption, with more retentive power than the C18-silica, and comparatively high stability over the wide pH 2-12 range.³⁶

For synthesis of the monomer, the formulation's cross-linking, macroporogenic, and micro porogenic agents were varied and optimised, resulting in a monolithic adsorbent that was robust and had high PAH adsorption. As can be seen from the SEM image in Figure 1, the fabricated PS-DVB bead had a globule-like monolithic structure with an average surface area and pore volume of 72.6 m² g⁻¹ and 0.24 cm³ g⁻¹, respectively.

In general, the bead contained trace components that originated from the fabrication of the PS-DVB monoliths. These trace residual components showed as interference peaks overlapping with some PAH peaks in the GC chromatogram, and could be removed from the monolith by sonication with solvent(s) prior to use. Several organic solvents were examined, e.g. pure acetonitrile; acetonitrile followed by hexane; or pure acetone. It was found that a complete elimination of those interferences was achieved by multiple sonications with acetone until disappearance of the objectionable THF odour.

3.1 Optimisation of monolithic bead extraction

Parameters that potentially affected the efficiency of extraction included extraction time, stirring rate, salt addition, extraction temperature, and the number of monolithic extraction beads. To optimise these parameters, seven PAH standards (Nap, Flu, Ant, Pyr, Chr, Bbfl, and BaP) were chosen to cover the range of their physicochemical properties. Extraction efficiencies for the use of monolithic bead under different parameter values were compared by using the peak area ratio of each individual PAH to the internal standard.

In general, slight improvements in extraction efficiency were observed after increasing the extraction time from 1.0 to 2.0 h

(Figure 2). Extraction efficiencies generally did not increase when the extraction time was extended to 3 h. Responses were slightly different for naphthalene; we expect that its higher volatility (in comparison to the other PAHs) makes it more likely to evaporate during long extraction times. The period of 2 h extraction was chosen in this work.

Stirring supports an interaction between the analytes and the surface of monolith. Varying the stirring rate revealed that increasing the rate from 700 to 900 rpm improved the extraction efficiency, except for naphthalene (Figure 3). Stirring rates exceeding 900 rpm resulted in a lower extraction efficiency. This is likely to be due to vigorous agitation promoting the evaporation of nonpolar PAHs from the highly polar water matrix. The rate of 900 rpm was therefore selected as the optimal stirring rate.

Salt addition into an aqueous sample not only offers the salting-out effect, but prevents adsorption of analytes on the wall of container, thus it is likely to increase the extraction efficiency especially for compounds with intermediate polarity and volatility.³⁷ An experiment comparing salt addition was then carried out with either no addition of NaCl, or the addition of 5 and 10% NaCl. Increasing the salt concentration reduced the signals for all analytes (Figure 4). It is likely that many factors can contribute to a decrease in adsorption efficiency, e.g. a change in physical configuration of the chemical functionality of the surface coating;³⁸ lowering of PAH solubility in water, especially for the heavy PAHs; and an increase in viscosity by the NaCl. Liquid suspensions occurred in the aqueous sample containing 10% NaCl (but not at 0 and 5% NaCl) indicating that the standard PAHs in toluene spiked into the water sample formed a suspension at the high salt concentration. This reduces the amount of PAH that can be adsorbed onto the PS-DVB monolith bead. In addition, the increase in salt concentration raised the viscosity of the aqueous solution, thus reducing the flow of water through the macropores of the polymer monolith and thereby reducing the extraction yield. As it is clearly not advantageous, salt addition was therefore not used in the remainder of this study.

Although PAHs are non-polar volatile compounds, increasing temperature of the aqueous sample did not have a significant effect on the extraction yield of analytes. Figure 5 clearly showed that maximum PAHs signals were generally obtained when the extraction was done at ambient temperature (32 °C). Raising the temperature to 50 and 80 °C generally decreased the signal (with again a different pattern for naphthalene). This effect could be a result of evaporation of the analytes at the elevated temperatures during stirring. The temperature of 0 °C not only gave low yield of analytes, but was difficult to control. All subsequent extractions of water samples were therefore conducted at 32 °C temperature.

Enhancing the surface area for adsorption of analytes was expected to achieve higher efficiencies. This was tested by adding more than one adsorbent bead at the start of the extraction process. The result in Figure 6, however revealed that a single PS-DVB monolithic bead was sufficient for the extraction of the analytes. The extraction using two beads gave a reduced PAH extraction efficiency. Moreover, the efficiencies when using two beads were not significantly different from those with three beads. This implies that a single bead provided enough surface area for the absorption of trace PAHs - hence only one bead was subsequently used in the measurements.

3.2 Method validation

To test the effectiveness of extraction using PS-DVB monolithic adsorbent, the following method validation characteristics were measured: linearity, detection limit, recovery, and precision. The GC-MS calibration curves with the PAH concentrations between 2 to 30,000 ng mL⁻¹ were found to be linear with r-squared values exceeding 0.995 (Table 1). The extractions performed under the optimal conditions as described above resulted in detection limits for 16 PAHs in high-purity water spiked with low concentrations of standard PAHs and conducted with 10 replicates, were in a range of 0.01 to 0.47 ng mL⁻¹ (Table 1). Recoveries were quantified at two concentrations (500 ng mL⁻¹ and 2,500 ng mL⁻¹ of spiked PAH standard in high-purity water) with 3 replicates. Recoveries were very good in the ranges of 72-107% and 69-112% for spiking at 500 ng mL⁻¹ and 2500 ng mL⁻¹, respectively. Recovery for actual water samples was also measured and is presented in below. Repeatability of the method was assessed by determining the RSD of the intraday and interday repeated analyses for both the 500 and 2500 ng mL⁻¹ spiked concentration in the high-purity water. The RSDs ranged from 1.0 to 9.5% (Table 2). Using a two-tailed *t*-test at 95% confidence limit, no significant difference was found for variabilities between intraday and interday analyses.

3.3 Application to Actual Water Samples

The analysis result of water samples collected from different locations in Thailand and examined using the proposed method revealed that five out of ten water samples contained PAHs in a range of 14-200 ng mL⁻¹ in total (Table 3). The chromatogram of waste water extracted using the monolithic bead method is illustrated in Figure 7 (a), together with that of the same waste water spiked at 20 ng mL⁻¹ for each PAH (Figure 7(b)). Fifteen PAHs were detected at a very low concentration (0.06-26 ng mL⁻¹) in an industrial water sample from Samutprakarn, whereas no DBA was detected in this sample. Waste water samples from a market (Samutprakarn), a vehicle LPG-filling station (Saraburi), and drainage from a highway (Samutprakarn), contained some PAHs. No PAHs were detected in most of the drinking water samples, though Phe, Pyr, and BaA were detected at a very low concentration in tap water from Roi-et. No PAHs were detected in Bangkok tap water. Analyses of bottled water of a number of commercial water brands also did not detect any PAH contamination. To verify that the lack of detection was not a false negative, the various water samples were spiked with PAHs at the low concentration of 20 ng mL⁻¹, and recoveries were determined. These ranged from 69.0-114.5% (Table 4) and are consistent with the recoveries obtained for spiked pure water.

3.4 Comparison with other extraction methods

A comparison with some other extraction methods followed by gas chromatography-mass spectrometric detection of PAHs is shown in Table 5. It can be observed that the analytical performance is, in general terms, comparable with those of the other reported (micro)extraction approaches. The sample volume of 100 mL used in this work was in the medium range, and the recovery percentage

of the method was in the satisfactory range, compared to the other methods. Although the detection limits were higher than those of SBSE,³⁹ IL-SPME,⁴⁰ and SBME,¹⁴ it was comparable to those of some other techniques. To synthesise the monolithic adsorbent the expense is only about 10 US cents per bead. The technique of the present study then offers the important benefit of a single use of the low-cost monolithic bead, therefore avoiding any carry-over effect. The new synthesised bead can be directly combined with the other typical glassware and equipment used in a chemical laboratory, offering a simple PAHs analysis at trace levels.

Conclusions

The monolithic bead was fabricated and successfully utilized for extraction of the 16 PAHs on EPA's list of priority pollutants in water. A single monolithic bead was employed per extraction, at ambient temperature and without salt addition. Although this method's extraction time is 2 h, it is comparable to some other methods, results in good recoveries for most PAHs, and has low detection limits. In addition, a single-use bead prevents carry-over effects. The monolithic bead extraction was shown to be efficient for water sample analysis at low-ppb levels in actual water samples. Commercial production of the PS-DVB beads is therefore attractive and would yield a new and improved standard method for the determination of PAHs in water.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Office of the Higher Education Commission, Ministry of Education for the financial support to V. Chunhakorn and P. Ratchathamma. Prof. Paul L Klerks is also acknowledged for comments to the manuscript.

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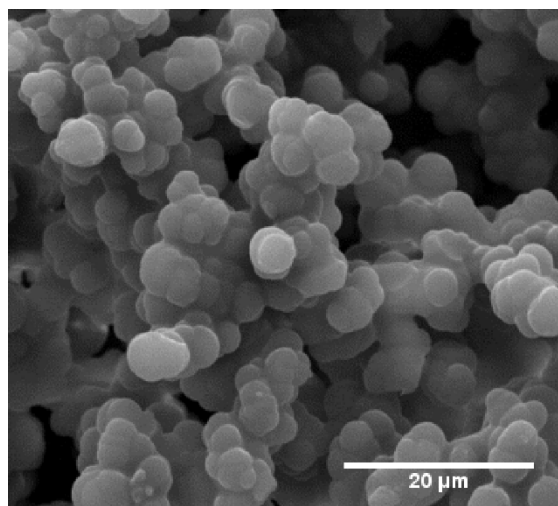


Figure 1 Scanning electron micrograph of synthesised PS-DVB monolithic bead.

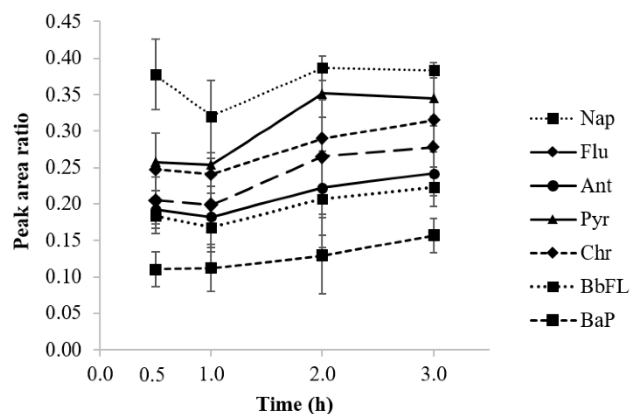


Figure 2 Effect of extraction time on the yield of selected analytes.

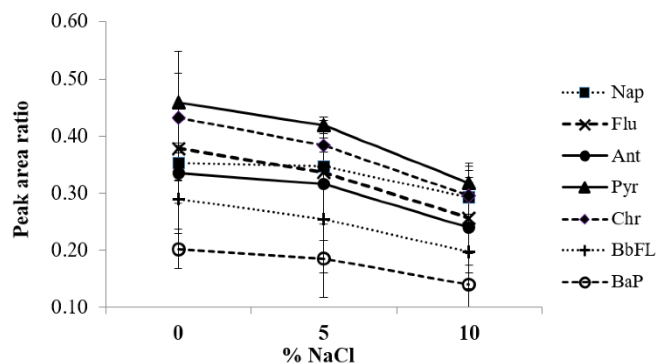


Figure 4 Effect of salt concentration in the aqueous sample on the extraction yield.

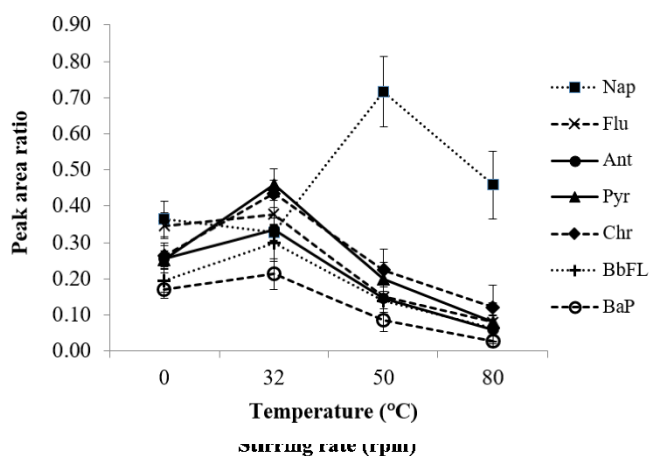


Figure 5 Effect of extraction temperature on the PAH extraction yield.

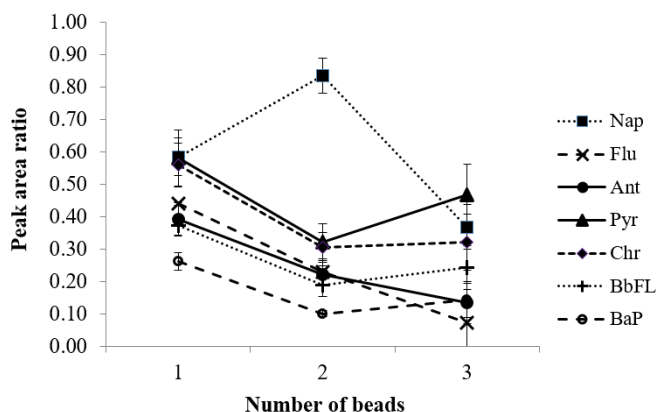


Figure 6 Effect of the number of PS-DVB monolithic beads on the extraction yield.

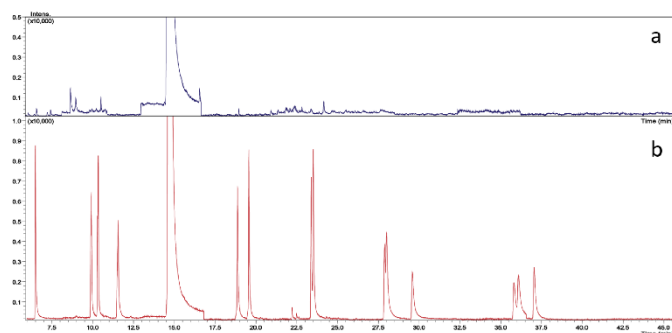


Figure 7 Chromatograms of waste water (a) without and (b) with spiking of 20 ng mL⁻¹ PAHs extracted by using the monolithic bead.

Table 1 Validation parameters for analysis of 16 PAHs in water using PS-DVB monolithic bead extraction followed by GC-MS.

PAH compounds	Intercept, a	Slope, b	r ²	LOD (ng mL ⁻¹)	% recovery ± SD (100 ng mL ⁻¹ , n=3)	% recovery ± SD (500 ng mL ⁻¹ , n=3)	% recovery ± SD (2500 ng mL ⁻¹ , n=3)
NaP	-0.0045	1.3810	0.9998	0.06	92.81 ± 1.34	96.43 ± 2.1	93.00 ± 3.75
AcPy	-0.0080	1.2961	0.9991	0.10	105.56 ± 3.92	107.14 ± 4.5	97.63 ± 1.14
AcP	-0.0053	0.9695	0.9992	0.10	106.73 ± 3.00	104.79 ± 4.3	103.51 ± 3.08
Flu	-0.0074	1.0585	0.9986	0.12	84.52 ± 2.42	78.41 ± 6.9	112.35 ± 4.62
Phe	-0.0004	1.4834	1.0000	0.02	98.69 ± 2.79	98.01 ± 4.9	87.20 ± 2.54
Ant	-0.0092	1.9363	0.9994	0.09	93.61 ± 0.48	84.76 ± 1.3	78.28 ± 5.89
FL	-0.0014	2.0105	0.9988	0.12	95.96 ± 2.30	96.46 ± 5.8	82.08 ± 2.23
Pyr	-0.0052	2.0331	0.9999	0.05	89.64 ± 3.22	95.91 ± 10.2	86.67 ± 1.46
BaA	-0.0104	1.6993	0.9992	0.10	83.11 ± 1.39	80.05 ± 9.8	96.87 ± 9.18
Chr	-0.0068	1.9518	0.9995	0.07	80.01 ± 1.62	72.35 ± 9.3	80.98 ± 1.97
BbFL	0.0002	1.2533	0.9998	0.01	98.72 ± 1.84	109.27 ± 3.6	69.45 ± 11.33
BkFL	-0.0130	1.8704	0.9999	0.12	103.62 ± 1.64	100.16 ± 3.2	74.33 ± 6.90
BaP	-0.0383	1.2742	0.9962	0.46	92.99 ± 6.32	105.99 ± 2.4	72.77 ± 6.73
InP	-0.0170	0.5519	0.9958	0.47	107.56 ± 3.09	88.07 ± 2.6	91.11 ± 4.23
DBA	-0.0084	0.6637	0.9998	0.20	106.98 ± 0.36	97.09 ± 6.1	69.87 ± 8.22
BghiP	-0.0126	0.7220	0.9989	0.27	91.68 ± 0.66	78.11 ± 1.2	79.68 ± 5.24

Table 2 Intraday and interday variability presented as %RSD for deionized water spiked at 500 and 2,500 ng mL⁻¹ PAHs (n=5).

PAH compounds	Intraday		Interday	
	500 ng mL ⁻¹	2,500 ng mL ⁻¹	500 ng mL ⁻¹	2,500 ng mL ⁻¹
NaP	5.30	9.01	7.70	4.91
AcPy	2.48	5.82	4.74	4.99
AcP	5.33	9.61	4.93	6.22
Flu	7.19	5.43	7.80	9.46
Phe	5.20	6.43	1.13	2.03
Ant	3.95	3.06	2.51	3.18
FL	4.81	3.67	1.59	1.99
Pyr	6.63	3.75	3.62	4.86
BaA	6.74	3.68	9.04	2.57
Chr	7.66	1.06	8.70	2.43
BbFL	2.25	4.14	5.81	8.98
BkFL	5.84	1.70	5.96	2.24
BaP	7.50	1.78	7.27	2.67
InP	6.69	8.01	5.49	7.86
DBA	6.64	9.81	5.69	2.61
BghiP	7.64	7.71	3.09	8.37

Table 3 Results of analysis for 16 PAHs in water sampled from different locations (geodetic coordinate).

Water source	Concentration (ng mL ⁻¹)															
	NaP	AcPy	AcP	Flu	Phe	Ant	FL	Pyr	BaA	Chr	BbFL	BkFL	BaP	InP	DBA	BghiP
Industrial Facility, Samutprakarn (N13.547915, E100.66392)	4.89	9.27	8.26	10.53	0.44	7.23	10.6	4.19	9.34	5.57	0.06	10.61	45.18	46.22	<LOD	26.21
Market, Samutprakarn (N13.604431, E100.650970)	<LOD	<LOD	8.2	10.52	0.46	7.19	10.3	3.9	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Gas Station, Saraburi (N14.621458, E101.092814)	4.91	<LOD	8.21	10.52	0.44	7.17	<LOD	3.91	9.19	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Drainage from highway, Samutprakarn (N13.606901, E100.655853)	<LOD	<LOD	<LOD	<LOD	<LOD	7.18	10.3	3.9	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Tap water, Roi-et (N16.060462, E103.663788)	<LOD	<LOD	<LOD	<LOD	0.44	<LOD	<LOD	3.91	9.19	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Bottled water ^a	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Bottled mineral water (1) ^b	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Bottled mineral water (2) ^c	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Bottled mineral water (3) ^d	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Tap water, Bangkok (N13.8455883, E100.5713513)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

^a Loften Beverage Co.,Ltd. Mahasarakham (N15.5492077, E103.0604197)^b Evian, France^c Chang, Ayutthaya, Thailand^d Aura, Mae Rim, Chiang Rai, ThailandTable 4 Recoveries of 16 PAHs spiked in actual water samples at a concentration of 20 ng mL⁻¹.

PAH compounds	%Recovery ± %RSD				
	Bottled water	Bottled mineral water (1)	Bottled mineral water (2)	Bottled mineral water (3)	Tap water, Bangkok
NaP	82.96 ± 1.55	83.19 ± 2.77	86.59 ± 6.17	85.02 ± 6.84	81.19 ± 4.34
AcPy	105.52 ± 3.18	105.67 ± 1.45	108.71 ± 3.35	107.82 ± 5.11	110.26 ± 0.61
AcP	110.00 ± 1.56	103.17 ± 3.85	108.14 ± 5.44	103.57 ± 3.48	108.76 ± 2.75
Flu	109.70 ± 0.75	105.97 ± 4.60	111.32 ± 4.23	113.02 ± 2.25	111.50 ± 2.58
Phe	96.90 ± 14.31	83.83 ± 4.23	81.86 ± 5.77	82.80 ± 4.21	70.76 ± 3.89
Ant	110.03 ± 1.31	104.98 ± 1.85	103.36 ± 3.19	104.80 ± 0.76	107.34 ± 2.04
FL	110.87 ± 1.75	106.48 ± 2.32	105.73 ± 0.96	103.63 ± 1.71	105.46 ± 2.29
Pyr	83.82 ± 1.13	77.29 ± 0.29	78.99 ± 2.96	77.95 ± 1.35	79.04 ± 3.13
BaA	88.31 ± 1.10	84.59 ± 2.19	85.76 ± 1.74	84.40 ± 2.43	85.71 ± 0.50
Chr	87.18 ± 1.44	84.28 ± 3.69	86.58 ± 2.41	83.65 ± 6.62	85.03 ± 1.73
BbFL	108.74 ± 11.75	91.06 ± 1.44	90.75 ± 0.36	88.64 ± 0.58	90.49 ± 1.28
BkFL	69.00 ± 2.38	85.31 ± 2.54	88.23 ± 2.20	82.79 ± 4.02	86.40 ± 3.23
BaP	109.27 ± 0.61	106.80 ± 1.72	114.50 ± 3.15	108.69 ± 0.56	110.56 ± 2.37
InP	106.92 ± 2.51	100.85 ± 1.35	100.94 ± 3.88	101.11 ± 3.15	99.87 ± 3.15
DBA	101.16 ± 0.35	101.35 ± 3.08	99.44 ± 2.54	101.20 ± 2.10	102.34 ± 1.88
BghiP	106.24 ± 0.32	107.27 ± 1.65	108.49 ± 0.36	108.92 ± 0.43	109.91 ± 1.22

Table 5 Comparison between various methods for determination of PAHs in water.

Extraction method	Sample matrix	Sample volume	Analytical method	% Recovery	Detection limit	References
PS-DVB monolith with DCM eluent	Water	100 mL	GC-MS	70-112	0.01-0.47 ng mL ⁻¹	Proposed method
SBSE ¹ with thermal desorption	Aqueous	10 mL	GC-MS	-	0.0001-0.002 ng mL ⁻¹	Kolahgar <i>et al.</i> (2002)
IL-SPME ²	Natural water	10 mL	GC-MS	80-110	0.004-0.005 ng mL ⁻¹	Hsieh <i>et al.</i> (2006)
C18 SPE with three mixed solvent elution	Water	10 mL	GC-FID	87.31-97.38	50-550 ng mL ⁻¹	Kanchanamayoon <i>et al.</i> (2008)
C18 SPE with centrifugation	Mineral spring water	500 mL	GC-MS	70-85	-	Kouzayha <i>et al.</i> (2011)
UDSA-DLLME ⁴ , WLSEME ⁵	River, lake and field water	5 mL	GC-MS	84-113 86-114	0.022-0.060 ng mL ⁻¹ 0.022-0.13 ng mL ⁻¹	Tseng <i>et al.</i> (2014)
Polypyrrole-polyaniline polymer on SBSE	Fountains, sea, and wastewater	12 mL	GC-FID	86-100	0.02-1.10 ng mL ⁻¹	Mollahosseini <i>et al.</i> (2016)
DLLME ⁶	Mineral water	10 mL	GC-MS	71-90	0.03-0.1 ng mL ⁻¹	Sadeghi <i>et al.</i> (2016)
Monolith polymer capillary microextraction	Lake water	3 mL	GC-MS	97-104	0.02-0.06 ng mL ⁻¹	Mugo <i>et al.</i> (2016)
SBME ⁷	Sea water	300 mL	GC-MS/MS ⁸	56-148	0.00021-0.00082 ng mL ⁻¹	Lopez-Lopez <i>et al.</i> (2017)

¹ SBSE = stir bar sorptive extraction

² IL-SPME = ionic liquid-solid phase microextraction

³ SWCNT-QDs = single-walled carbon nanotube-quantum dot nanocomposites

⁴ UDSA-DLLME = up and down shaker-assisted dispersive liquid liquid microextraction

⁵ WLSEME = water with low concentration of surfactant in dispersed solvent-assisted emulsion dispersive liquid-liquid microextraction

⁶ DLLME = dispersive liquid-liquid microextraction

⁷ SBME = solvent bar micro-extraction

⁸ GC-MS/MS = gas chromatography coupled triple quadrupole mass spectrometer