

Extraction Techniques for Determination of Polycyclic Aromatic Hydrocarbons in Water Samples

Hiba Abdalla Mahgoub

Department of Chemistry, Al-Baha University, Saudi Arabia

Abstract: Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants in our environment and their importance appears from their toxicity and carcinogenicity to human. Water can become contaminated with PAHs from different sources such as runoff in urban areas, waste water from certain industries and petroleum spills. The selected extraction technique, not only influences the accuracy of the results, but also determines the total analysis time and costs. Different extraction techniques used to release PAHs from water samples have been overviewed since proper extraction procedures were necessary to achieve optimum analytical results. The extraction performance of each technique in terms of extraction conditions, time and further treatment required were also comparable. Selecting the suitable and effective extraction method for extracting PAHs from different water samples have been highlighted in this review; the aim was to provide an overview of current knowledge and information in order to assess the need for further extraction, analysis and quantification of these toxic compounds in water samples.

Keywords: Polycyclic aromatic hydrocarbons PAHs, water samples, extraction techniques

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic pollutants that are widely found in the environment. They may be found in air attached to dust particles, soil, sediments, water and food. Most PAHs enter the environment during burning of most organic materials such as coal, oil, wood, gasoline, garbage and tobacco. They are an important class of environmental contaminants because of their potential adverse health effects. They are known to have carcinogenic, mutagenic and teratogenic properties. Due to these properties as well as their persistence in the environment, they have been placed on the list of priority pollutants by the United States Environmental Protection Agency (US-EPA) and also the European Environment Agency [1]. The main sources of exposure to PAHs are from breathing PAHs (in wood smoke, traffic exhaust and other contaminated air) [2, 3], from eating contaminated food and drinking contaminated water. PAHs are generally carcinogenic and mutagenic and may induce lung, bladder as well as skin cancer [4]. In addition, exposure to high levels of PAHs has been shown to produce immunosuppressive effects and causing oxidative stress during its metabolism [5]. The maximum allowable concentrations of PAHs in soil and water are presented in Table 1. No standards exist for the amount of PAHs allowed in the air, but it is recommended that the levels be no higher than 0.004 ppm.

Different water sources can be contaminated with PAHs from dry and wet deposition, road runoff, industrial waste water and petroleum spills [6 – 8]. Different extraction techniques have been applied for extracting PAHs from water samples from sea, rivers, lakes, surface, ground, industrial waste and drinking water. The aim of this article was to provide an overview of different extraction techniques used to release PAHs from water samples, since proper sample preparation procedures were necessary to achieve optimum analytical results.

2. Collection of Water Samples

All water samples were collected in 1000 – 2000 ml dark glass bottles with Teflon caps and stored at 4 °C prior to extraction (normally within 48 h). For surface water samples, the samples were filtered through 0.45 µm micro porous filter membrane under vacuum in order to remove algae, zooplankton and suspended particles [9, 10]. Another pretreatment has been applied for industrial waste water that is if residual chlorine was present, 80 mg of sodium thiosulphate per liter of sample should be added and residual chlorine can be measured using EPA method 330.4 and 330.5 [11]. All industrial waste water samples must be extracted within seven days of collection and completely analyzed within 40 days of extraction [12].

Table 1: Maximum allowable Concentrations (MACs) of PAHs in water and soil, [1]

PAH	MAC (water), ppm	MAC (soil), ppm
Pyrene	3.0	3.0
Naphthalene	3.0	1.0
Phenanthrene	3.0	3.0
Benzo[h,g,i]perylene	3.0	3.0
Benzo[a]pyrene	0.005	0.3
Anthracene	3.0	3.0
Fluoranthene	3.0	3.0
Acenaphthene	3.0	3.0
Acenaphthylene	3.0	3.0
Benzo[a]anthracene	0.005	0.15
Benzo[b]fluoranthene	0.005	0.3
Dibenzo[a]anthracene	0.005	0.3
Fluorene	3.0	3.0
Indeno[1,2,3-ghi]pyrene	0.005	0.3
Indene	3.0	–

3. Extraction Techniques

Different extraction techniques have been developed and applied for extracting PAHs from water samples. The selected extraction technique, not only influences the accuracy of the results, but also determines the total analysis time and costs. Table 2 presents advantages and disadvantages of the currently applied extraction techniques. To better illustrate the extraction performance of each technique in terms of extraction conditions, time and further treatment required, comparison were given for some of the applications in table 3.

3.1 Solid phase extraction (SPE):

Solid-phase extraction (SPE) is a separation process which removes compounds from a mixture based on their physical and chemical properties. The general approach to SPE is the sorption of the sample from the liquid phase onto the solid adsorbent. The analyte or interference of samples are retain on a sorbent by different mechanism [22]. A range of sorbents have been used in SPE such as polymeric, activated carbon or silica modified with nonpolar or polar organic liquid [13, 14]. In the SPE procedure, C₁₈ SPE cartridges packed with sorbent were conditioned with 5mL methanol, and then 5mL methanol:water (40:60). The water sample (1000ml) was passed through the cartridge at a flow rate of 20ml/min; the cartridge was centrifuged at 2500 rpm for 10 min to remove residential water. Then the cartridge was dried with an air stream for 10 min followed by 200 ml of acetone. The elution was performed with 5 ml cyclohexane and the volume was reduced to 1ml under nitrogen flow prior for PAHs analysis [15 – 18].

3.2 Liquid – liquid Extraction (LLE):

LLE is a method to separate compounds based on their relative solubilities in different immiscible liquids. In the LLE procedure, the water sample poured into a separatory funnel and the mixture of 100 ml n-hexane and dichloromethane (1:1 v/v) was added and shaken for 2min. the water phase was drained and then the organic phase was poured into a glass funnel containing 20g of anhydrous sodium sulfate and re-extracted with 50 ml of the same solvent mixture. The extract was concentrated prior for PAHs analysis [19, 20].

3.3 Automated SPE

Automated SPE provide extraction system for extraction of liquid samples via SPE methods, it is easy operation and use commonly available SPE columns. The SPE-DEX[®] 4790 (horizon technology) can handle sample volumes ranging from 20 ml to 4 L. The concentrator system provides automated sample drying, with a patented PTFE membrane technology that automatically removes residual water from the organic solvent and concentrates each dried extract by applying heat, vacuum, and sparge flow for up to six samples at once [23]. In the automated SPE procedure, water samples were modified by the addition of isopropanol (IPA)

to provide a final concentration of 25 % IPA in each sample. This addition of the IPA enhances extraction efficiency and causes desorption of any analytes from vial walls. Using a large volume liquid handling syringe, 10 ml of sample is introduced to a stainless steel sample loop on the MPS 3XL. Using a dedicated sample enrichment pump incorporating a solvent selection valve, the sample is concentrated using an on-line solid phase extraction cartridge. Following sample enrichment, the cartridge is eluted using one of the analytical pumps with 100 % acetonitrile, thus ensuring efficient desorption from the cartridge. Post cartridge, eluent flow is mixed with water from a second pump, using a high pressure mixing tee to provide the analytical gradient conditions for separation and detection [24].

Table 2: advantages and disadvantages of extraction techniques

<i>Technique</i>	<i>Advantages</i>	<i>Disadvantages</i>
Liquid – liquid Extraction (LLE)	extracts PAHs both dissolved in the water and adsorbed upon any suspended particles in the sample	Use of large volumes of solvents and numerous pieces of laboratory glassware. Time consuming and is not easy to automate
Solid Phase Extraction (SPE)	Easy automation, many samples can be analyzed in parallel. Require no human intervention.	Adsorption of PAHs on to the wall of extraction vessels. Large solvent volume. Involve many steps.
Solid-Phase Micro Extraction (SPME)	Solvent minimization. Fewer steps involve. Minimum sample volume and preparation.	Limited capacity of the fiber. Potential contamination of the SPME needle.
Stir bar Sorptive Extraction (SBSE)		Further sample preparation, e.g., pH adjustment, back extraction and derivatisation required for extraction of certain compounds.
Dispersive Micro-Solid Phase Extraction (D- μ -SPE)	Lower cost Solvent minimization Materials used were more convenience in handling	Solvent type, extraction and desorption time have significant effect on the method performance

3.6 Dispersive Micro-Solid Phase Extraction (D- μ -SPE):

The uses of polymeric material have been developed for extraction of PAHs in water samples in order to minimize the solvent waste [25, 26]. In one of the D- μ -SPE procedure, 50 mg of nanoporous CaCO₃ was first conditioned with dichloromethane for 5 min and then placed in 5 ml water sample in a 10 ml glass centrifuge vial. This was then ultrasonicated for 30 min and centrifuged at 13500 rpm for 2 min. The aqueous was discarded and the material was dried by placing on a lint-free tissue to remove excess moisture. A 100 μ L of dichloromethane was added to the nanoporous CaCO₃ crystals and ultrasonicated for 15 min for analyte desorption and final volume of analyte was ready for PAHs analysis [27].

Table 3: Comparison of technique performances for the extraction of PAHs

Technique	Solvent	Pre-conditioning	Condition	Treatment after extraction	Recovery rate for PAHs (%)	Ref.
SPE C ₁₈ column	Methanol, cyclohexane	5ml methanol under vacuum followed by 5ml ultra pure water	1000 ml of water, flow rate 20ml/min	Centrifuge, concentration	36.28 - 132.57	15
SPE C ₁₈ column	methanol, acetone:THF (1:1)	5ml methanol, then 5ml methanol-water (40:60)	100ml of water with 10% methanol, elution by 3ml acetone:THF (1:1), flow rate 0.5ml/min	concentration	81-135	16
SPE C ₁₈ microcolumns (6ml, 1000mg)	CH ₂ Cl ₂ , ACN	10ml of: dichloromethane, isopropanol, ethanol, methanol, distilled water and deionized water	1000 ml of water, flow rate 2-3 ml/min, eluted by 10ml ACN and CH ₂ Cl ₂	concentration	28.28-104.38	17
LLE	n-hexane and dichloromethane (1:1 v/v)	All glasswares washed with detergent and hot water then rinse with distilled water	800ml of water and 100 ml of solvent, shake for 2 min.	concentration	96.80	19
LLE	n-hexane		0.5-1 L of water extracted twice with 150 and 100 ml of solvent.	concentration	80-120	21
Automated SPE	isopropanol	The cartridge, loop, injector and sample lines were cleaned and equilibrated	10 ml of water introduced to a sample loop MPS 3XL	Automatic concentration	97	24
D-μ-SPE	dichloromethane	nanoporous CaCO ₃ conditioned with dichloromethane for 5 min	5 ml water in 5 ml solvent extracted for 30 min	Centrifuge	84-110	27
SPME	Solvent free	Fiber conditioned in temperature of injection port for 2 h	Fiber inserted into 14 ml water sample @ room temp. for 60 min.	None	75.6-107	32
SBSE	Solvent free	stir bar was conditioned at 50°C for 24 h, put into a glass tube containing 10 mL of MeOH/CH ₂ Cl ₂ (50:50 v/v), sonication for 30 min and dried at 50°C for 1 h.	Stir bar was immersed into a 20 mL of water sample extracted with stir bars was @ room temperature on a magnetic agitator	Desorption in equivalent mixtures of acetonitrile-methanol	93 to 101	35

3.4 Solid-Phase Micro Extraction (SPME):

SPME was first introduced by Arthur and Pawliszyn in 1990 [28] as alternative extraction method for analysis of trace organic components in a variety of matrices. It is based on the partitioning of the analytes between the extracting phase immobilized on a fused silica fiber substrate and the analyte matrix [29]. The commercially available coating fiber was polydimethylsiloxane (PDMS) which is a nonpolar coating. PDMS has been used successfully, but the disadvantage of it, is its little selectivity [30]. In SPME procedure, the PDMS fibers (100 μm film thickness) were conditioned in the injection port of the instrument for 3 h for 270 °C. 8 ml of water sample was placed in 100 ml vial capped with PTFE-coated septa. The fibers were immersed into the water samples with agitation at 250 rpm for 60 min. and then the fiber was thermally desorbed for 10 min into the injection system [31]. Different experiments have been carried out to determine the optimum range of conditions for the application of SPME for PAHs analyses such as temperature, equilibration time, salinity and compound concentration [33].

3.5 Stir bar Sorptive Extraction (SBSE):

Like SPME method, SBSE is a solvent less technique based on the sorption of analytes onto a thick film of PDMS coated on a stir bar. In the SBSE procedure, stir bar (conditioned in

empty thermal desorption tube at 300 °C for 4 h with helium flow rate at 50 ml/min) coated with PDMS inserted into 100ml of water and 10 ml of methanol. Sample was stirred at 700 rpm at room temperature for 6 h, after extraction, the stir bar was removed and dried with lint free tissue and placed in the automatic sampler in order to thermally desorb the compounds [34]. The SBSE technique has shown great potential to extract organic compounds even from complex matrices e.g., waste waters, beverages, biological and hydrothermal fluids [36 – 38].

4. Conclusion

PAHs are an important class of environmental contaminants because of their potentially adverse health effects. The main sources of exposure to PAHs are from breathing contaminated air, eating contaminated food and drinking contaminated water [39]. Water can become contaminated with PAHs from runoff in urban areas, waste water from certain industries and petroleum spills. One of the main sources of PAHs contamination in drinking-water is the coating of the drinking-water distribution pipes. After the passage of drinking-water through those pipes or after repair work, significantly increased PAHs levels have been detected in the water [40, 41].

Different extraction techniques have been applied for extracting PAHs from water samples of sea, rivers, lakes,

surface, ground, industrial waste and drinking water. The different extraction techniques used to release PAHs from water samples have been overviewed since proper extraction procedures were necessary to achieve optimum analytical results. In terms of extraction efficiencies once correctly optimized for a given solute matrix couples all techniques are comparable. Different results may be obtained for the same class of compounds when several matrices have to be extracted.

References

- [1] ATSDR, Agency for Toxic Substances and Disease Registry, (2006). Toxicological profile for polycyclic aromatic hydrocarbons. Atlanta, GA, USA.
- [2] Hiba, A. M., Nimir A. S., and Tawfeeg, E. M., (2015). Identification of polycyclic aromatic hydrocarbons emissions from Oud Incense – Al – Baha City Southwest Saudi Arabia. *International journal of chemical science and research*, 5 (6), 12 – 22.
- [3] Hiba, A. M., and Nimir A. S., (2015). Identification of polycyclic aromatic hydrocarbons emissions from wood of aromatic plants (Dokhan Incense) used in Sudan. *Journal of chemistry and chemical sciences*, 5(10), 575-584.
- [4] Binková B, Šrám RJ., (2004). The genotoxic effect of carcinogenic PAHs, their artificial and environmental mixtures (EOM) on human diploid lung fibroblasts. *Mutat Res-Fund Mol M*, 547(1-2),109-121.
- [5] Singh V. K., Patel D. K., Jyoti, R. S., Mathur N, Siddiqui M. K., (2008). Blood levels of polycyclic aromatic hydrocarbons in children and their association with oxidative stress indices: an Indian perspective. *Clin Biochem*, 41(3),152-161.
- [6] Wu, B., Zhang, R., Cheng, S. P., Ford, T., A. Li, M. and Zhang, X. X., (2011). Risk assessment of polycyclic aromatic hydrocarbons in aquatic ecosystems. *Ecotoxicology*, 20 (5),1124-1130.
- [7] Hong, Y. W., Yuan, D. X., Lin, Q. M., and Yang, T. L., (2008). Accumulation and biodegradation of phenanthrene and fluoranthene by the algae enriched from a mangrove aquatic ecosystem. *Marine Pollution Bulletin*, 56 (8), 1400-1405.
- [8] Ngabe B, Bidleman TF, Scott GI., (2000). Polycyclic aromatic hydrocarbons in storm runoff from urban and coastal South Carolina. *Sci Total Environ*, 255(1-3),1-9.
- [9] Joil J. C., Henry X. C., Marilda F., Gisele M. H., (2012). Persistent toxic substances in surface water of Todos Os Santos Bay, Brazil. *Resources and Environment*, 2(4), 141-149.
- [10] Badawy, M. I., Emababy, M. A., (2010). Distribution of polycyclic aromatic hydrocarbons in drinking water in Egypt. *Desalination*, 251, 34 – 40.
- [11] Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for chlorine total residual, (1979). *Methods for Chemical Analysis of Water and Wastes*, EPA-600/4-79-020. U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.
- [12] Determination of polynuclear aromatic hydrocarbons in industrial and municipal wastewaters, (1982). EPA 600/4-82-025, National Technical Information Service, PB82-258799, Springfield, Virginia 22161.
- [13] R.M. Marcé and F. Borrull, *J. Chromatog. A*, (2000). Solid-phase extraction of polycyclic aromatic compounds , 885(1-2), 273-290.
- [14] Oliferova, L., Stakus, M., Tysin, G., Shpigun, O. and Zolotov, Y., (2005). On-line solid-phase extraction and HPLC determination of polycyclic aromatic hydrocarbons in water using fluorocarbon polymer sorbents , *Anal. Chim. Acta*, 538(1), 35-40.
- [15] Hamid K., Masud Y., Simin N., Amir H. M., Reza A., Noushin R., and Ramin N., (2013). Polycyclic Aromatic Hydrocarbons in drinking water of Tehran, Iran. *Journal of Environmental Health Sciences & Engineering*, 11:25.
- [16] Sibiyaa, P., Potgietera, M., Cukrowskaa, E., Jönssonb, J.Å and Chimukaa, L., (2012). Development and application of solid phase extraction method for polycyclic aromatic hydrocarbons in water samples in Johannesburg Area, South Africa. *S. Afr. J. Chem.*, 65, 206-213.
- [17] Kabzinski, A.K.M., Cyran, J., and Juszczak, R., (2002). Determination of polycyclic aromatic hydrocarbons in water (including drinking water) of Lodz. *Polish Journal of Environmental Studies*, 11(6), 695-706.
- [18] Shadung, J. M., and Fanyana, M., (2013). Application of solid phase extraction (SPE) method in determining polycyclic aromatic hydrocarbons (PAHs) in river water samples. *Journal of environmental chemistry and ecotoxicology*, 5(11), 278-283.
- [19] Farshid, K., Amir, H. S., and Rokhsareh, M., (2011). Determination of polycyclic aromatic hydrocarbons (PAHs) in water and sediments of the Kor River, Iran. *Middle-East journal of scientific research*, 10(1), 1-7.
- [20] Okoli, C. G., Ogbuagu, D. H., Gilbert, C. L., Madu, S., Njoku, R. F., (2011). Proximal input of polynuclear aromatic hydrocarbons (PAHs) in groundwater sources of Okrika Mainland, Nigeria. *Journal of environmental protection*, 2, 848-854.
- [21] Manoli, E. , Samara, C. , Konstantinou, I. , Albanis, T., (2000). Polycyclic aromatic hydrocarbons in the bulk precipitation and surface waters of Northern Greece. *Chemosphere*, 41, 1845-1855.
- [22] Kanchanamayoon, W., and Tatrahun, N., (2008). Determination of polycyclic aromatic hydrocarbons in water samples by solid phase extraction and gas chromatography. *World journal of chemistry*, 3(2), 51-54.
- [23] Salem, NH. Determination of PAHs from sea water using automated SPE. Brett Holmes, Horizon Technology, Inc., 03079 USA.
- [24] Paul, R., (2009). Automated Analysis of PAHs by HPLC. AWE international, (18).
- [25] Bagheri, H., Babanezhad, E., and Es-haghi, A., (2007). An aniline-based fiber coating for solid phase microextraction of polycyclic aromatic hydrocarbons from water followed by gas chromatography-mass spectrometry. *Journal of chromatography A*, 1152 (1-2), 168-174.
- [26] Yan, X., Wu, D., Peng, H., Ding, K., Duan, C., and Guan, Y., (2012). Array capillary in-tube solid-phase microextraction: a rapid preparation technique for water samples. *Journal of chromatography A*, 1244, 69-76.

- [27] Abdulmumin A. N., Chanbasha B., Amjad A.S., and Abdul Rahman A., (2012). Determination of polycyclic aromatic hydrocarbons in water using nanoporous material prepared from waste avian egg shell. *Journal of nanomaterials*, article ID 305691.
- [28] Arthur, C.L., and Pawliszyn, J., (1990). Solid phase microextraction with thermal desorption using fused silica optical fibers. *Analytical chemistry*, 62, 2145-2148.
- [29] Pawliszyn, J., (1997). *Solid Phase Microextraction: Theory and Principles*. Wiley-VCH, New York.
- [30] Lord, H. and Pawliszyn, J., (2000). Evolution of solid-phase microextraction technology. *J. Chromatogr. A* 885, 153-93.
- [31] Rami, K., Stephane, L. F., Jan, T. A., Karyn, L. M., and Helene, B., (2012). Extraction of polycyclic aromatic hydrocarbons (PAHs), polycyclic aromatic sulfur heterocycles (PASHs) and alkylated derivatives from sea water using solid phase microextraction (SPME) gas chromatography mass spectrometry (GCMS). *Proceeding of the Thirty-fifth AMOP technical seminar on environmental contamination and response*. Canada, Ottawa, 928-940.
- [32] Qingling, L., Xiaoqin, X., Lee F. S., and Wang, X., (2006). Determination of trace PAHs in seawater and sediment pore-water by solid-phase microextraction (SPME) coupled with GC/MS. *Science in China Series B, Chemistry*, 49(6), 481-491.
- [33] Amanda, J. K., James, W. R., and John, L. Z., (2003). Application of solid-phase microextraction (SPME) to the analysis of polycyclic aromatic hydrocarbons (PAHs). *Environmental geochemistry and health*, 25, 69-75.
- [34] Rami, K., Helene, B., Karyn, L. M., Jan, T. A., and Stephane, L. F., (2012). Chemical characterization of oil-water system using stir bar sorptive extraction (SBSE)-thermal desorption (TD)- gas chromatography mass spectrometry (GCMS). *Proceeding of the Thirty-fifth AMOP technical seminar on environmental contamination and response*. Canada, Ottawa, 994-1000.
- [35] Margoum, C., Guillemain, C., Yang, X., Coquery, M., (2013). Stir bar sorptive extraction coupled to liquid chromatography-tandem mass spectrometry for the determination of pesticides in water samples: method validation and measurement uncertainty. *Talanta*, Elsevier, 116, 1-7.
- [36] Cecile K., Jean, L. C., Jean, P. D. and Nils G H., (2012). Characterisation of dissolved organic compounds in hydrothermal fluids by stir bar sorptive extraction gas chromatography – mass spectrometry. Case study: the Rainbow field (36°N, Mid-Atlantic Ridge). *Geochemical transactions*, 13, 8.
- [37] Poulain, M., Geffroy, R. C., Canaff, C., Ruban, V., and Ambles, A., (2014). Quantification of polynuclear aromatic hydrocarbons in retention pond waters using gas chromatography-tandem mass Spectrometry. *Austin Chromatogr.*,1(3).
- [38] Barbara, H., Peter, P., and Coretta, B., (2002). Semi-automated stir bar sorptive extraction (SBSE) in combination with HPLC - fluorescence detection for the determination of polycyclic aromatic hydrocarbons in water. *Global analytical solutions*, AN, 1-5.
- [39] Hiba Abdalla, M., (2015). Polycyclic aromatic hydrocarbons in food samples: methods of extraction, a review. *International journal of current research*, 7(12), 23603-23606.
- [40] Davi M. L., (1994). Determination of polycyclic aromatic hydrocarbons in drinking water by mass spectrometry. *Life chemistry reports*, 10, 181-188.
- [41] Basu D. K., Saxena, J., Stoss, F.W., Santodonato, J., Neal, M.W., Kopfler, F.C., (1987). Comparison of drinking water mutagenicity with leaching of polycyclic aromatic hydrocarbons from water distribution pipes. *Chemosphere*, 16, 2595-2612.