Extraction Techniques for Determination of Polycyclic Aromatic Hydrocarbons in Water Samples

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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 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 have 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]pyrene | 3.0         | 3.0             |
| Benzo[a]pyrene | 0.005          | 0.3             |
| Anthracene   | 3.0              | 3.0             |
| Fluoranthen | 3.0              | 3.0             |
| Acenaphthene | 3.0              | 3.0             |
| Acenaphthylene | 3.0           | 3.0             |
| Benzo[a]anthracene | 0.005       | 0.15            |
| Benzo[b]fluoranthen | 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              | –               |

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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 residual water. Then the cartridge was dried with an air stream for 10 min followed by 200 ml of dichloromethane (1:1 v/v). The water phase was drained and then the organic phase was re-extracted with 50 ml of the same solvent mixture. The extract was concentrated 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 |
|---------------------------------------------------------------|
| **Technique** | **Advantages** | **Disadvantages** |
| 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 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 µL 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].
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 polydimethylsloxane (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 desorbs 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 from complex matrices e.g., waste waters, beverages, biological and hydrothermal fluids [36 – 38].

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.

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