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Development and Application of Solid Phase Extraction Method for Polycyclic Aromatic Hydrocarbons in Water Samples in Johannesburg Area, South Africa

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ABSTRACT

A solid phase extraction (SPE) technique has been developed for the quantitative determination of polyaromatic hydrocarbons (PAHs) in aqueous samples. The SPE technique involved extraction of PAHs from a 100 mL sample containing 10 % methanol as a modifier onto C_{18} cartridges. 40 % methanol in water was used as conditioning solvent, and 3 mL acetone:THF (1:1) as eluting solvent. After eluting, the extract was reduced to 1 mL under nitrogen and then analyzed by GC-MS. The extraction was optimized for the addition of organic modifier, sample load volume, conditioning solvent, washing solvent and eluting solvent. In order to evaluate the practical applicability of SPE technique, water samples were spiked with the PAHs to give final sample concentrations between 3 and 7 μg L^{-1}. Enrichment factors of 81–135 were achieved with relative standard deviations (RSDs) of less than 6 %. Recoveries obtained ranged from 81 to 135 %. Detection limits ranged from 20.0–52.0 ng L^{-1}. The optimized method was validated by analyzing certified reference materials. The optimized method was then applied to spiked real river samples in and around the Johannesburg area, South Africa. The concentrations obtained varied from 22.0 to 1040.0 ng L^{-1}. The RSDs were between 2.3 and 13 %. The overall order of PAHs levels was: phenanthrene > acenaphthene > naphthalene > fluoranthene > pyrene.

KEYWORDS

Solid phase extraction, polycyclic aromatic hydrocarbons, water samples, Johannesburg, South Africa.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the most widespread classes of environmental pollutants.[1] Their inputs in coastal and inland waters usually account for discharges of sewage and industrial effluents as well as for urban and rural run-off. Their solubility in water is quite low and decreases with increasing molecular weight.[2] Their hazard potential even in trace amounts can be relatively high, hence making their presence in the water cycle a severe as well as protracted risk to human health and to the environment.[2] Acute toxicity is generally associated with the lower molecular weight PAHs and is correlated with aqueous solubility and octanol–water partition coefficients.[2] PAHs are found at low concentrations in aqueous samples due to their loss during sample extraction because they strongly adsorb to particulate matter. Due to their hazardous characteristics, identification and determination of PAHs is an important analytical issue. The main problem with PAHs monitoring is their very low concentration and complexity of environmental matrices. Pre-concentration is therefore required to achieve the required sensitivity and selectivity.[3]

Several modern extraction techniques suitable for the extraction of PAHs in aqueous samples have been introduced over the past two decades, to overcome the drawbacks of the conventional liquid–liquid extraction (LLE) method. These techniques include solid phase microextraction (SPME) and solid-phase extraction (SPE)[3] as well as hollow fibre liquid phase micro extraction technique.[4] Currently, SPE is the most popular sample preparation technique for aqueous samples.[3] The general approach to SPE is the sorption of the sample from the liquid phase onto the solid adsorbent. SPE utilizes a range of sorbents such as polymeric, activated carbon or silica modified with nonpolar or polar organic liquid.[5,6] The modified silica sorbents are the most common for extraction of organic compounds and various formats exist.[3] SPE is used to prepare liquid samples and extract semi volatile and non-volatile analytes, but also can be used with solid samples that are pre extracted into solvents.[4] It is excellent for sample extraction, concentration and cleanup.[7]

SPE offers many advantages compared to other sample preparation techniques like LLE, such as high recovery, sample enrichment, high clean up, easy automation, less time and consumption of organic solvent and compatibility with instrumental analysis. Other advantages of SPE are that many samples can be analyzed in parallel and it can be applied to wide variety of sample matrices. Disadvantages with SPE are that it involves many steps; therefore method development time is required.

Several SPE methods have been reported for the extraction of PAHs.[5,8–9] To increase analyte enrichment and recovery a number of parameters need to be optimized such as the addition of organic modifier, sample load volume, conditioning solvent, washing solvent and eluting solvent. In this work an SPE method for PAHs was optimized, validated with certified reference material and applied to water samples in Johannesburg area, South Africa. The status of PAHs in South African environment is not fully known due to insufficient data.[10–12] Further, few studies that have been done concentrated on looking at these compounds in soil, sediments.[10–11] and sludge.[13] This is the gap that this study attempts to fill.

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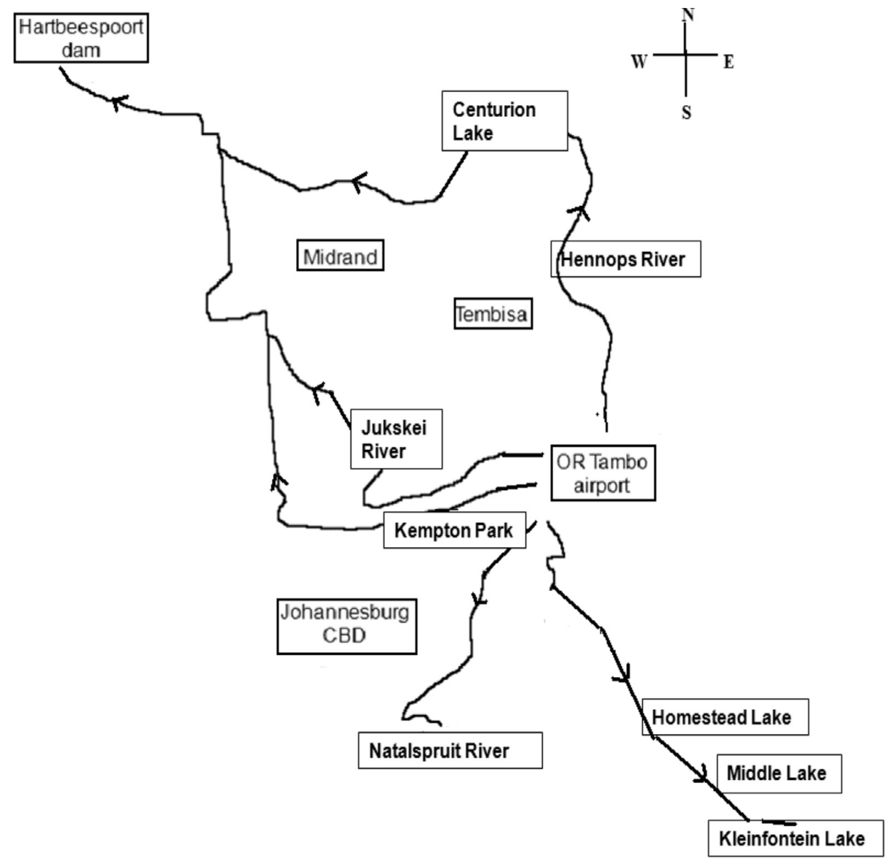

Figure 1 Sampling areas in and around Johannesburg, South Africa.

2. Materials and Methods

2.1. Standard and Reagents

Methanol (99.9 %) was purchased from Fischer Scientific (Loughborough, UK). Acetone (99.8 %) and acetonitrile (99.9 %) were from Lab Scan Analytical Scientific (Dublin, Ireland). Isooctane (99.5 %) was from Fluka (Steinheim, Germany) while phenanthrene and naphthalene (97.9 and 98 % purity, respectively) were from Supelco (Bellefonte, PA, USA). Tetrahydrofuran (99.5 %) was from Merck (Darmstadt, Germany). Acenaphthene, pyrene, fluoranthene and chrysene with 99 % purity were from Sigma-Aldrich (St Louis, MO, USA). All reagents were used without any further purification. Certified reference material QCO-259 was obtained from Industrial Analytica (Pty) Ltd (Johannesburg, South Africa).

2.2. Sampling

Water samples were collected from Centurion Lake, Middle Lake, Kleinfontein Lake, Homestead Lake, Hennops River, Hartbeespoort Dam, Blaauwpan and Jukskei River. The samples were collected between 19 May and 7 July 2011. Fresh water samples were collected in about 20–40 cm depth below the water surface in pre-cleaned brown glass bottles with Teflon caps. They were stored in the fridge at 4 °C prior to analysis. The pH and conductivity were measured as the samples got into the laboratory. Figure 1 shows the study area where samples were taken.

2.3. Instrument and Analytical Conditions

A Varian gas chromatography 3800 without an auto sampler, connected to an ion trap mass spectrometer Varian Saturn GC-MS 2000 was used. Analytes were separated using WCOT fused silica capillary column with dimensions, 30 × 0.25 mm ID, 0.25 μm film thickness. Helium was used as a carrier gas. The injector was set at 280 °C and the injections were done using a splitless mode. Injection volume was 1 μL. The temperature programme was held at 40 °C, held for 5 min, ramped at 10 °C min^{-1} to 179 °C, and held there for 2 min, ramped at 9 °C min^{-1} to a final temperature of 300 °C, and held for 10 min. Electron ionization (EI) was used in the mass spectrometer detector, while the full scan and the selective ion monitoring (SIM) modes were used for data acquisition. The scan range was 40–650 amu throughout. The target mass ions (m/z) used for quantification were 128 for naphthalene, 153 for acenaphthene, 178 for phenanthrene, 202 for fluoranthene and 228 for pyrene and chrysene.

2.4. Preparation of Calibration Solutions

Six PAHs (naphthalene, acenaphthene, phenanthrene, fluoranthene, pyrene and chrysene) were selected for the calibration of the instrument. The calibration standards were prepared in methanol, in the range 0.1–1.5 mg L^{-1}. The calibration curves gave good levels of linearity with correlation coefficients (r^2) between 0.9852 and 0.9958.

2.5. SPE Procedure

C_{18} SPE cartridges bond elute from Varian (Torrance, CA, USA) packed with 500 mg sorbent were used in this work. The cartridges were conditioned with 5 mL methanol, and then 5 mL methanol-water (40:60). 5 μg L^{-1} mixture of spiked PAHs in 100 mL deionized water sample with 10 % methanol as organic modifier was pumped through each cartridge at a flow rate of 1 mL min^{-1}, using SPE unit vacuum pump. Sample loading was followed by 5 mL for washing, using deionized water. The analytes were eluted by 3 mL acetone:THF (1:1) pumped at a flow rate of 0.5 mL min^{-1}. The volume was reduced to 1 mL under nitrogen flow. Finally, the concentrated eluate was injected in GC-MS. Each experiment was repeated three times. The river water samples were extracted in the same way as described above.

2.6. Optimization of Parameters Affecting SPE Technique

There are several parameters such as addition of organic modifier, sample load volume, conditioning solvent, washing solvent and eluting solvent that need to be optimized in order to enhance the extraction efficiency in the SPE. Thus all of the above-mentioned factors affecting the extraction efficiency were optimized. These factors were investigated using deionized water samples spiked with known concentrations of PAHs. The goal was to optimize the solid phase extraction procedure so as to obtain high analyte recovery and enrichment factors.

For the optimization, sample volume (100–200 mL), type of organic modifier (methanol, 2-propanol or acetonitrile), amount of organic modifier (0–20 %), type of conditioning solvent (acetone, methanol or 2-propanol), amount of conditioning solvent (20–40 %), as well as the type of eluting solvent (acetone:tetrahydrofuran (1:1), methanol:tetrahydrofuran (1:1) acetonitrile in tetrahydrofuran (1:1)) were tested one at a time with the other conditions kept constant. A concentration of 5 μg L^{-1} mixture of PAHs spiked in deionized water was used as sample.

In performing experiments to optimize the sample load volumes, the following parameters were kept constant: 20 % ACN as the organic modifier, 5 mL of acetone:water (40:60, v/v) as the conditioning solvent, 5 mL of deionized water as the washing solvent, 3 mL of acetone:THF (1:1) as the eluting solvent, and a concentration of 5 μg L^{-1} mixture of PAHs spiked in deionized water was used. This was followed by optimizing the effect of organic modifier on the amount extracted. Here parameters kept constant were: 5 mL of acetone:water (40:60, v/v) as the conditioning solvent, 5 mL of deionized water as the washing solvent, 3 mL of acetone:THF (1:1) as the eluting solvent, and a concentration of 5 μg L^{-1} mixture of PAHs spiked in 100 mL deionized water was used. This was followed optimizing the effect of the amount of organic modifier on the amount extracted. Here parameters kept constant were: 5 mL of acetone: water (40:60, v/v) as conditioning solvent, 5 mL of deionized water as washing solvent, 3 mL of acetone:THF (1:1) as eluting solvent, and a concentration of 5 μg L^{-1} mixture of PAHs spiked in 100 mL deionized water was used. This was followed by optimizing the effect of the conditioning solvent on the amount extracted. Here parameters kept constant were: 5 mL of deionized water as the washing solvent, 3 mL of acetone:THF (1:1) as the eluting solvent, and a concentration of 5 μg L^{-1} mixture of PAHs spiked in 100 mL deionized water and 10 % methanol as the organic modifier. This was followed by optimizing the effect of the amount of the conditioning solvent on the amount extracted. Here parameters kept constant were: 5 mL of deionized water as the washing solvent, 3 mL of acetone:THF (1:1) as the eluting solvent, and a concentration of 5 μg L^{-1} mixture of PAHs spiked in 100 mL deionized water and 10 % methanol as the organic modifier. This was followed by optimization of the effect of the eluting solvent on the amount extracted. Here parameters kept constant were: 5 mL of acetone: water (40:60, v/v) as conditioning solvent, 5 mL of deionized water as washing solvent, a concentration of 5 μg L^{-1} mixture of PAHs spiked in 100 mL deionized water, 10 % methanol as the organic modifier and 40 % methanol in water as the conditioning solvent.

2.7. Extraction of Certified Reference Material

The SPE method was validated by using a certified reference material. The sample was prepared according to the instructions by transferring 1 mL of the concentrated reference material standard containing different concentrations of PAHs compounds to 1 L volumetric flask and diluted to the mark. The PAHs concentrations in 1 L were 6.67 μg L^{-1} for naphthalene, 3.47 μg L^{-1} for acenaphthene, 1.15 μg L^{-1} for phenanthrene, 0.570 μg L^{-1} for fluoranthene and 1.48 μg L^{-1} for pyrene. 100 mL of the prepared sample was extracted in triplicates using the optimized SPE procedure. The concentrations of the compounds in the certified material were calculated from the calibration curves and the enrichment factors of the optimized SPE method.

2.8. Extraction of Real Samples

The analyzed real river water samples were collected from Blaauwpan, Homestead Lake, Middle Lake, Kleinfontein Lake, Hennops River, Centurion Lake, Hartbeespoort Dam and Jukskei River (see Fig. 1). 100 mL of each sample was extracted in triplicate using the optimized SPE procedure in this study.

3. Results and Discussion

3.1. Optimization of SPE Parameters

3.1.1. *Sample Load Volume*

Results of the optimum volume of sample to load into the cartridges are shown in Fig. 2. The recoveries obtained were almost constant with an increase in sample volume, which indi-

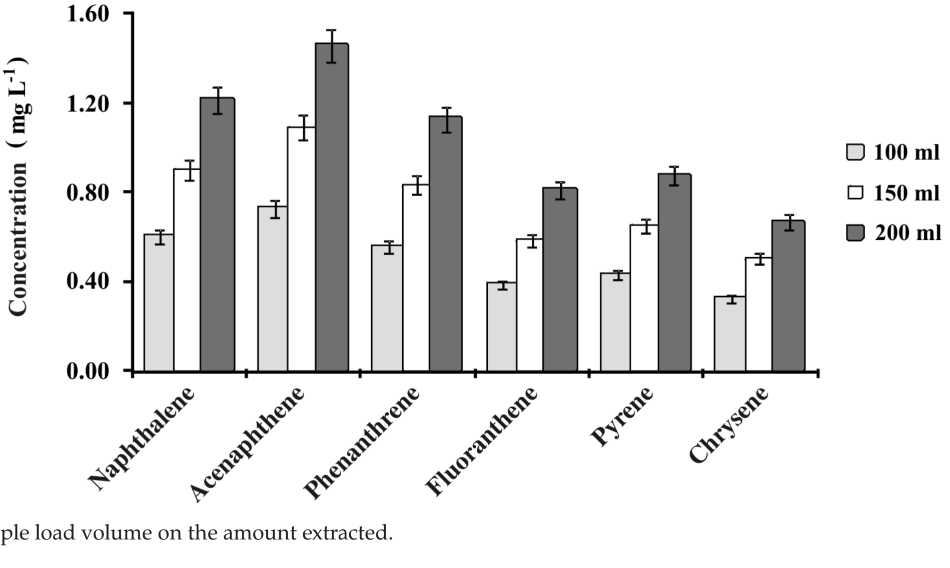

Figure 2 Effect of sample load volume on the amount extracted.

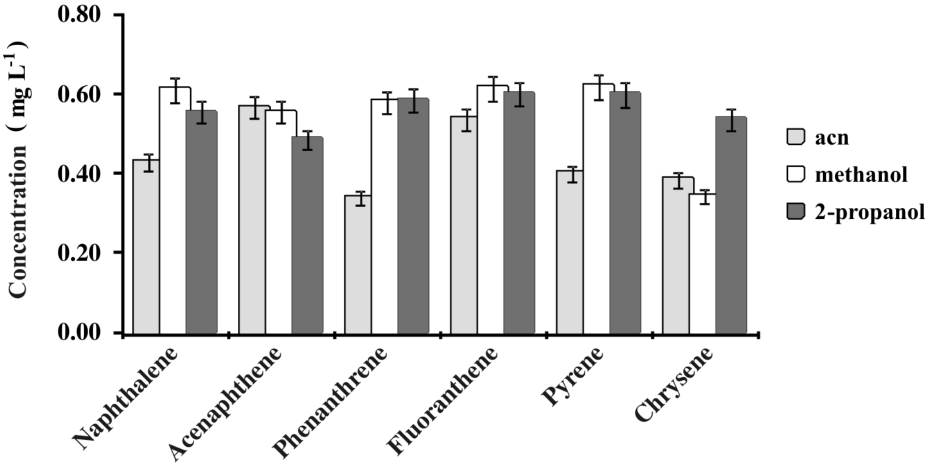

Figure 3 Effect of organic modifier on the amount extracted.

cated that the capacity of the sorbent was not exceeded in the volume range of the sample studied.100 mL sample value was then chosen to be the optimum volume in this work, taking into consideration the time required for the extraction. Xie *et al.*[9] reported to have varied the sample volume in determination of PAHs in aerosols using SPE. Sample volume was varied between 3–50 mL. The recoveries obtained decreased with an increase in sample volume. This decrease was attributed due to shift in the adsorption/desorption equilibrium favouring increased desorption from the packings and causing a net loss of adsorbate from the SPE cartridge.[9] The decrease in recovery at high sample volume becomes a capacity issue especially for non-polar compounds like PAHs.

Kouzyha *et al.*,[14] also investigated the effect of sample volume on the recoveries of PAHs in water. The sample volume was varied between 500 and 1500 mL and the cartridge used contained 200 mg of the sorbent. From sample volume of 1000 mL, a decrease in some of the PAHs was observed while there was no apparent decrease for others. With an increase of the volume to 1500 mL there was a significant decrease up to 40 % in the recoveries for some of the PAHs while there was no change for others. The contrast between the results obtained in this work with those of Kouzyha *et al.*[14] is that the recoveries in this work were almost constant with an increase in sample volume, while the recoveries obtained by Kouzyha *et al.*[14] were decreasing with increasing sample volume. This is because the volume of sample extracted by Kouzyha *et al.*[14] was much more compared to this study.

3.1.2. *Selection of Organic Modifier*

PAHs have very low water solubility that decreases with the molecular weight, which then lead to adsorption problem during sampling and storage. Their adsorption results in losses and underestimation of the real concentration.[15] To increase the solubility, an organic solvent or a surfactant is usually added to the sample. The concentration of the organic solvents is a critical parameter, because if it is too low it may not be enough to solubilize the high molecular weight PAHs, whereas if it is too high, the breakthrough volume will be low for the low molecular PAHs.[5]

Methanol, 2-propanol and acetonitrile were used at 10 % in order to investigate the effect of adding organic modifier. According to the results (Fig. 3), acetonitrile showed the lowest amount extracted. This could mean that 10 % acetonitrile is not enough to fully solubilize the PAHs. 2-propanol gave similar recoveries as methanol except in one instance where methanol recovered higher amount of chrysene than the earlier. As a trade off, and since methanol consistently gave slightly higher recoveries than 2-propanol, it was selected as the best extraction solvent in this study.

3.1.3. *Amount of Organic Modifier*

Although the recovery of the analytes can be improved by addition of organic modifier, on the other hand the eluotropic strength of the sample increases with the modifier content.[8] It also promotes interaction of the hydrophobic C_{18} bonded phase with aqueous sample because of organic content added.[16] In order to investigate that effect, the methanol content in the sample was varied between 0 and 20 %. Figure 3 shows the results obtained. The results were best at 10 % methanol. Kiss *et al.*[8] reported to have varied the amount of organic modifier on the determination of PAHs in precipitation using SPE. The amount was varied between 2 and 40 %. The extraction showed to decrease at high amount of the organic modifier. The decrease was attributed to the breakthrough because of the increased eluotropic strength of the sample. Figure 4 shows the RSD obtained in varying the organic content in the sample. At 10 % methanol in the sample, the highest amounts of the PAHs were extracted and RSD values were also within the accepted range, and not very different from others. The amount of organic modifier that have been used in the literature are 25 % of 2-propanol with C_{18} sorbent.[5,8,16] This value is not far from what was obtained in this study, as 20 % methanol in the sample also gave good results close to those of 10 % methanol for many PAHs.

3.1.4. *Selection of Conditioning Solvent*

Conditioning is an important step in the SPE procedure. The first step of conditioning is to wet the SPE cartridge. Wetting the cartridge opens up the groups of the sorbent surface and thus increases the surface area available for interaction with the analyte. It can also remove residues from the packing material that might interfere with the analysis. The second step is to wash the sorbent bed with a solvent to prepare the suitable surface for the adsorption of the analyte. The second solvent has to be weaker or having equal eluting strength compared to the sample solution[9]. Acetone, methanol and 2-propanol were evaluated at 40 % in water, in order to investigate the effect of the conditioning solvent. Figure 5 shows the results obtained. All the tested solvents showed more or less similar results. Methanol was, however, chosen as the conditioning solvent in this work. Xie *et al.*[9] reported to have used hexane as the conditioning solvent on the determination of PAHs in aerosol by SPE. The

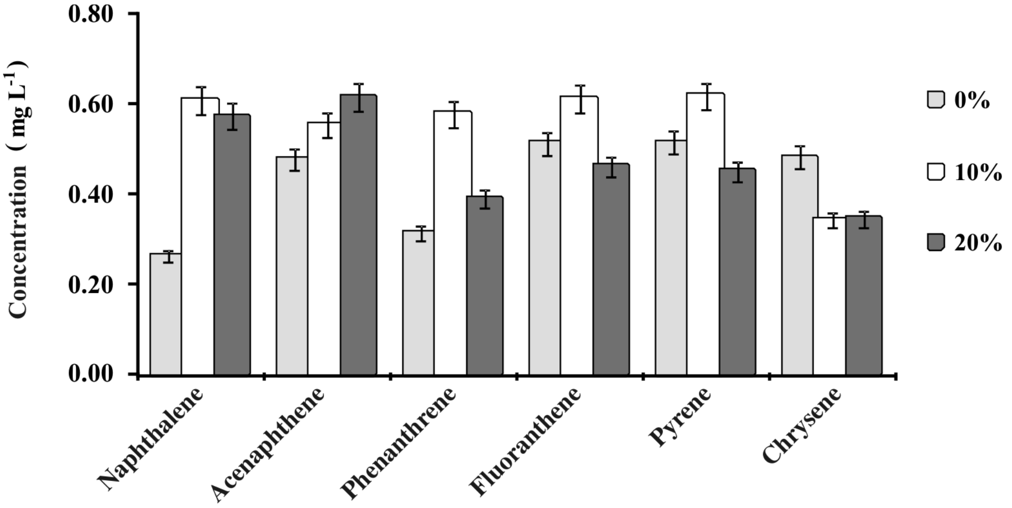

Figure 4 Effect of the amount of organic modifier on the amount extracted.

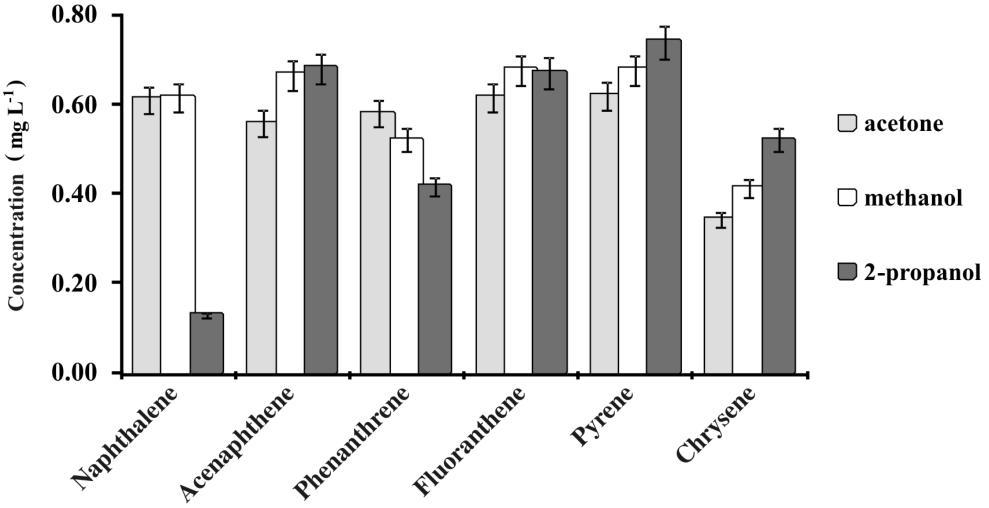

Figure 5 Effect of the conditioning solvent on the amount extracted.

choice was due to the sample solution that was prepared in hexane. Kiss *et al.*[9] used dichloromethane then methanol or 2-propanol as conditioning solvent, depending on the organic modifier of the sample. The reason was that it has to be the same composition as that of the organic modifier in the sample[8].

3.1.5. *Amount of Conditioning Solvent*

The conditioning solvent is used to activate the octadecyl chains in the cartridge. It is therefore important to use enough amounts. In order to investigate the proper volume for conditioning, 20–40 % methanol in water was used. Figure 6 shows the results obtained on varying methanol amount. At 20–30 %

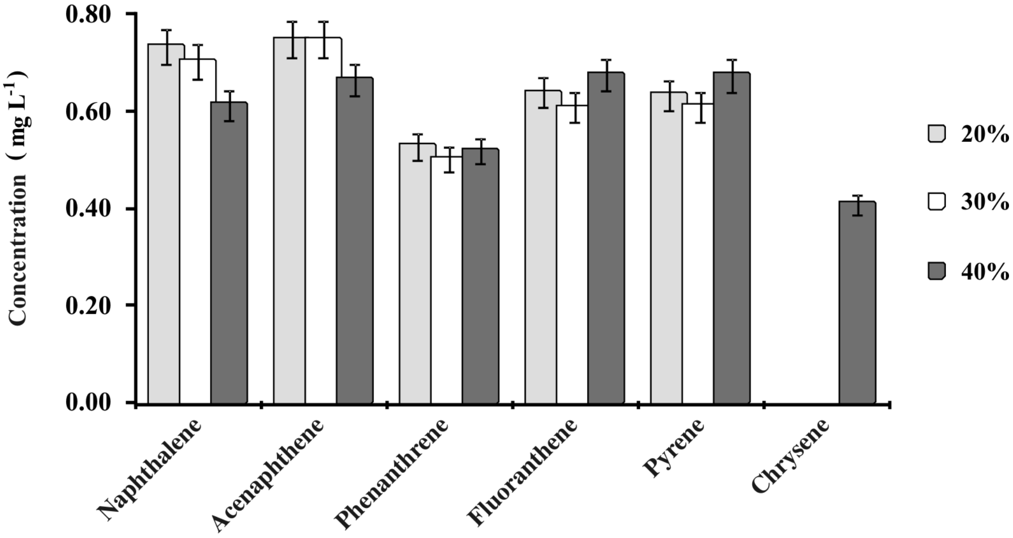

Figure 6 Effect of the amount of the conditioning solvent on the amount extracted.

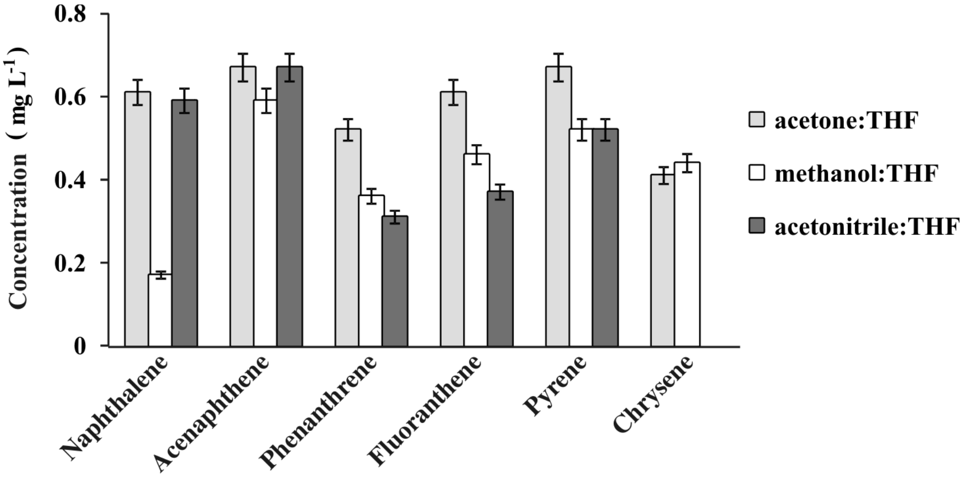

Figure 7 Effect of the eluting solvent on the amount extracted.

methanol, chrysene was not detected, although the results were slightly better for the lower molecular weight compounds. At 40 % all compounds were detected and this composition was used in all further experiments.

3.1.6. *Selection of Eluting Solvent*

Once the analytes are retained on the cartridge they are eluted by an appropriate organic solvent. The choice of eluting solvent should be carefully considered. If the solvent is too powerful, more interfering compounds will be eluted out. If the elution strength of the solvent is not enough, a larger elution volume will be needed, and then it will dilute the sample and lower the sensitivity.[9] Recoveries of low molecular weight PAHs are better eluted with moderately polar solvents, but for higher molecular weight PAHs a more non-polar solvent is required. Therefore to ensure high recoveries of all PAHs, mixtures of solvents are usually recommended.[5] A suitable strength of the eluting solvent was determined by examining 3 mL acetone in tetrahydrofuran (1:1), 3 mL methanol in tetrahydrofuran (1:1) and 3 mL acetonitrile in tetrahydrofuran (1:1). Figure 7 shows the results obtained on the selection of eluting solvent. 3 ml acetone:THF (1:1) showed the highest recovery for all analytes and it was then considered as the suitable eluting solvent for this work. Other researchers such as Pixteren *et al.*[17] used acetonitrile/methanol as eluting solvent, which was not tested in our experiments.

3.1.7. *Spiked Concentration and Detection Limits*

Since PAHs usually exist in low concentration ranges in the natural water due to their low solubility,[18] the developed method should have high sensitivity to be able to detect them. This means that the developed method should have high enrichment factors for the target PAHs. For accurate quantification, the enrichment factors should also be independent of sample concentration, assuring a direct proportionality of the amount extracted to that in the sample. In order to investigate the effect of spiked water concentration on the concentration enrichment factor, the sample was spiked with 3, 5 and 7 μg L^{-1} mixture of PAHs. Results obtained on varying spiked concentration showed that the amount extracted increased with the initial sample concentration (data not shown). This is expected and shows that loss due to adsorption is minimal. According to the results obtained in Table 1, the enrichment factors or recoveries were not much influenced by sample concentration. Some of the extraction efficiencies were higher than 100 % and the reason could be factors such as matrix effect, but they are still acceptable.[19] The detection limits were as follows (ng L^{-1}): 20 for naphthalene, 30 for acenaphthene, 52 for phenanthrene, 25 for fluoranthene and 21 for pyrene. These detection limits allow detecting trace levels of the PAHs in the environment. The same experiments were done in real water samples and results obtained were not very different from what was obtained in deionized water in terms of recovery and detection limits.

3.2. Validation of SPE Optimized Method

The SPE method was validated using a standard reference material (SRM) under the optimized conditions described above. The analyses were carried out in triplicates. The results are presented in Table 2. The concentrations obtained were slightly lower than certified values, but accepted considering the challenges involved in analysis of PAHs at trace levels. The RSDs, (n = 3) were less than 4 %.

3.3. Application of the Optimized Method to Real Water Samples

The optimized conditions were applied to real water samples obtained from rivers, lakes and dams in and around Johannes-

Table 1 Recoveries at three different spiked sample concentration (μg L^{-1}) under optimum conditions. Values in brackets are % RSD (n = 3).

Compounds	3.0 % Recovery	5.0 % Recovery	7.0 % Recovery
Naphthalene	122 (2.0)	123 (1.6)	122 (1.1)
Acenaphthene	130 (2.3)	133 (1.6)	134 (2.6)
Phenanthrene	103 (2.6)	104 (1.8)	104 (5.7)
Fluoranthene	135 (1.6)	135 (1.9)	135 (6.0)
Pyrene	135 (5.2)	135 (1.9)	134 (4.0)
Chrysene		81 (4.9)	82 (5.1)

Table 2 Results obtained on the validation of SPE method

Compounds	Certified values /μg L^{-1}	Obtained values /μg L^{-1}	Acceptable limits /μg L^{-1}
Naphthalene	4.83 (0.71)	6.99 (2.27)	2.49 to 7.17
Acenaphthene	2.90 (0.58)	2.24 (0.96)	1.25 to 4.54
Fluoranthene	0.51 (0.06)	0.49 (2.54)	0.30 to 0.73
Pyrene	1.20 (0.169)	0.78 (3.76)	0.23 to 2.17

Table 3 Levels of PAHs (ng L^{-1}) obtained with SPE for real water samples (n = 3) and relative standard deviations expressed in percentage.

	Concentration/ng L^{-1}					
	Naphthalene	Acenaphthene	Phenanthrene	Fluoranthene	Pyrene	Sum
BP	128.5 (5.3)	406.6 (13.0)	615.7 (4.3)	890.0 (7.7)	89.8 (6.0)	1329.6
HL	202.8 (4.3)	53.0 (6.7)	279.7 (4.1)	125.8 (4.2)	41.8 (9.3)	731
ML	62.6 (9.9)	168.0 (5.3)	105.6 (11.9)	125.7 (5.6)	38.8 (7.2)	500.7
KL	21.6 (10.9)	278.6 (1.9)	419.3 (4.9)	281.4 (2.7)	43.7 (9.5	1044.6
HR	46.5 9.9)	75.8 (8.3)	53.5 (5.8)	56.4 (7.2)	28.5 (9.2)	260.7
CL	33.4 (8.8)	115.7 (7.7)	168.8 (4.2)	29.7 (7.3)	23.6 (10.3)	371.2
HD	238.6 (2.3)	112.4 (8.8)	64.3 (8.2)	37.6 (9.9)	82.3 (4.2)	535.2
JR	64.7 (7.8)	136.8 (6.3)	74.0 (7.4)	21.4 (10.7)	35.7 (10.9)	332.6
Sum	993.1	1346.9	1780.9	767.0	384.7	

Note: BP = Blaauwpan, HL = Homestead Lake, ML = Middle Lake, KL = Kleinfontein Lake, HR = Hennops River, CL = Centurion Lake, HD = Hartbeespoort Dam, JR = Jukskei River.

burg. Table 3 below shows the results obtained. pH of the water samples showed Centurion Lake, Homestead Lake, Blaauwpan and Hennops Rivers' pH to be close to neutral (pH ~7.2). Middle Lake, Kleinfontein Lake, Hartbeespoort dam and Jukskei River water samples' pH were basic (pH ~8.3) . This could be due to contamination of wastewater and solid waste. The conductivity of Centurion Lake, Hennops River, Jukskei River and Hartbeespoort Dam were high (~562–874 μS cm^{-1}) and could be attributed to anions such as sulphates, phosphates and nitrates associated with sewage wastewater and solid wastes. Middle Lake and Kleinfontein Lake, Blaauwpan and Homestead Lake conductivity were low (187–332 μS cm^{-1}). This could mean that they are not polluted with metals and anions.

In all the samples analyzed, all five PAHs were detected as shown in a typical chromatogram (Fig. 8). The concentrations obtained in all samples were lower than the maximum allowable concentration levels in water which is 3.0 mg L^{-1} for all of them.[20] Blaauwpan site showed to be the most polluted with PAHs followed by Kleinfontein lake. Jukskei and Hennops Rivers were found to have PAHs on the lower side. The low concentrations found in all samples may be due to the low solubility of PAHs in water and that they are removed by adsorption on particles.[3] The other reason may be due to the low emitting sources responsible for their presence in the rivers. The differences in the order

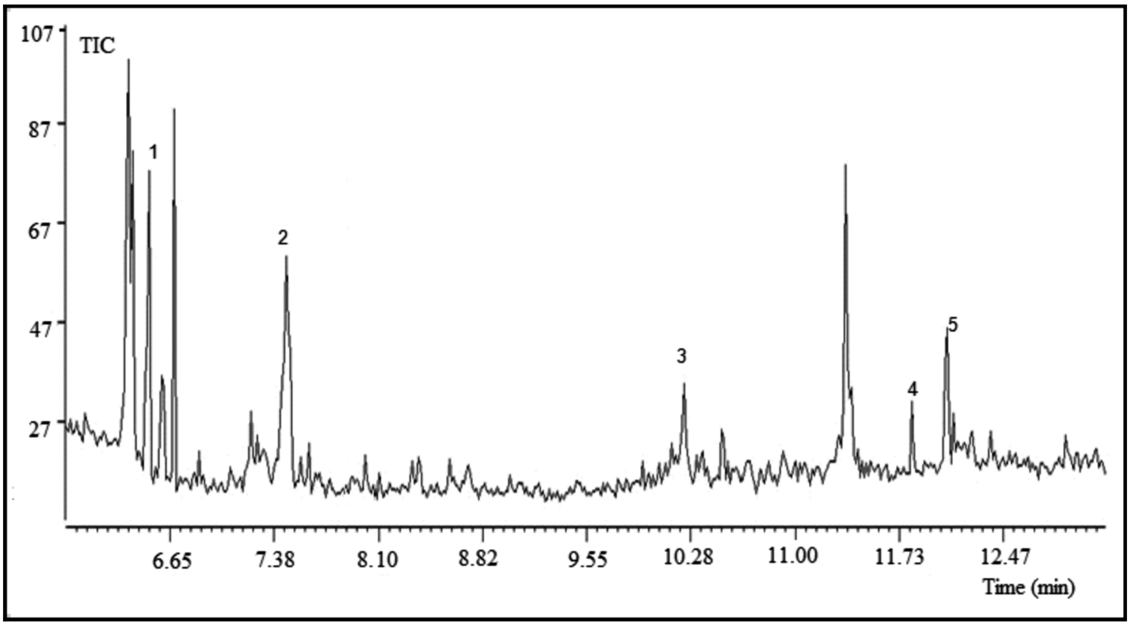

Figure 8 A typical chromatogram of the Blaauwpan water sample extracted by SPE and detected by GC-MS. Where: 1 = Naphthalene, 2 = acenaphthene, 3 = phenanthrene, 4 = fluoranthene, 5 = pyrene.

Table 4 Comparison of levels of PAHs (μg L^{-1}) obtained from water samples around the world.[2]

Compounds	Germany	Denmark	Greece	South Africa (including ours)
Naphthalene	0.007–0.051	0.0055	–	0.0216–1.6
Acenaphthene	0.0085–0.046	0.0004	0.010–0.064	0.0530–25.1
Phenanthrene	0.0041–0.022	0.021	0.030–0.132	0.0535–0.6157
Fluoranthene	0.0076–0.040	0.0054	0.010–0.065	0.0034–0.2814
Pyrene	0.0073–0.033	0.015	0.010–0.140	0.0001–2.5
Sum	0.0345–0.151	0.047	0.06–0.401	0.1316–30.10

of concentrations for PAHs in various samples could be attributed to diverse sources and physical properties of various water bodies. Comparing the results obtained in this study to what has been reported earlier in South Africa,[21] pyrene was the most dominant PAH, while in this study was the least. These differences in the most dominant PAHs could be attributed to the diverse sources of PAHs in each region and physical chemical conditions of the water samples especially suspended . So far, there are no detailed studies that have been done in trying to locate major sources of PAHs in these different regions.

Table 4 compares the results obtained in South Africa, including our study, to those of other countries. Results from South Africa are on the high side. Germany and Denmark has the lowest amount of PAHs reported. Off course these comparisons may not tell the whole picture of PAHs pollution of each country as much data may be needed. The dominant PAH in each country in Table 4 differs due to differences in sources.

4. Conclusion

The developed and validated SPE method was successfully applied to real water samples around Johannesburg area. Comparing the results obtained from those of the developed countries, they are on the high side. For this reason, further investigation is needed on possible sources. A seasonal variation on the levels of these compounds in the study area is also needed so as to have an idea of the possible flux changes. Further, investigation the presence of other much non-polar and heavier PAHs, especially those with five- and six-membered rings, are recommended.

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