

Method Validation for SPE Applied to Determination of PAH in Petroliferous Industry Effluent Water

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Abstract

The presence of polycyclic aromatic hydrocarbons (PAH) in produced water is of environmental concern due to their toxic properties. PAH analysis in complex samples requires pre-treatment to enrich the fraction containing analytes, and eliminate matrix interferences. The objective of this work was to develop and validate an analytical methodology for determination of PAH in produced water, using solid phase extraction (SPE) and analysis by gas chromatography with flame ionization detection (GC-FID). Average recoveries of PAH from produced water enriched at two concentration levels varied from 30.9% for naphthalene to 119.1% for chrysene (RSD between 3.8% and 22.2%). The linear range was between 0.5 and 50.0 $\mu\text{g}\cdot\text{mL}^{-1}$, with regression coefficients better than 0.998. Detection limits were between 0.01 and 0.04 $\mu\text{g}\cdot\text{L}^{-1}$, and quantitation limits were between 0.05 and 0.16 $\mu\text{g}\cdot\text{L}^{-1}$. The validated method was applied to samples of produced water treated for disposal, in which concentrations varied from 3.5 $\mu\text{g}\cdot\text{L}^{-1}$ for phenanthrene to 44.3 $\mu\text{g}\cdot\text{L}^{-1}$ for naphthalene ($\sum \text{PAH} = 177.7 \mu\text{g}\cdot\text{L}^{-1}$). The method was also applied to seawater samples, in which 13 PAH compounds were detected ($\sum \text{PAH} = 60.27 \mu\text{g}\cdot\text{L}^{-1}$), probably derived from pyrogenic sources.

Keywords: Produced Water, Effluent, PAH, SPE

1. Introduction

One of the most significant by-products of petroleum extraction is produced water, due to the large volumes that are discharged or reused, as well as its chemical composition, which can vary greatly depending on the characteristics of the underlying geology. It is a highly complex aqueous matrix, containing organic and inorganic, soluble and insoluble, compounds derived from petroleum fractions, with high levels of salinity (up to 250 $\text{g}\cdot\text{L}^{-1}$). Hydrocarbons predominate, with the major groupings including alkanes, alkenes, alkynes, complex hydrocarbons containing oxygen, nitrogen and sulphur, volatile monoaromatic compounds, and polycyclic aromatic hydrocarbons (PAH) [1-4].

Although around a hundred PAH are found in the environment, only 16, possessing 2 to 6 aromatic rings, are considered as priority compounds due to their toxicity, mutagenicity or carcinogenicity [5]. The solubility of these compounds in water varies greatly, and reduces as molecular mass increases [6-8].

Liquid-liquid extraction (LLE) is the technique most frequently used for analysis of PAH in complex matrices including petroliferous wastewaters [3,5]. Other studies of wastewaters have used Solid Phase Microextraction (SPME)⁹ or Solid Phase Extraction (SPE) [10-12]. Direct mode SPME is not feasible, due to attack on commercially used fibres by compounds present in produced water. Headspace mode SPME cannot efficiently extract the 5 to 6 ring PAH. In contrast to liquid-liquid extraction, SPE does not require large volumes of organic solvents, hence generating little laboratory waste, and analysis time can be greatly reduced, particularly when several cartridges are used simultaneously. The wide variety of available adsorbents means that extraction conditions can be adapted to achieve desired separation and preconcentration goals.

While SPE is a technique that seems to offer advantages compared to liquid-liquid extraction, in routine analysis laboratories new techniques using this procedure need to be validated so that PAH determinations in complex water samples can be undertaken with confidence.

The objective of this work was to validate an analytical method for determination of 16 PAH, including 15 of the 16 compounds designated as priority pollutants by the United States Environmental Protection Agency, in produced water, using solid phase extraction and analysis by gas chromatography with flame ionization detection.

2. Experimental

2.1. Standards, Reagents and Solvents

Methanol, ethyl acetate, toluene, dichloromethane, acetone and *n*-hexane were nanograde (Merck, Darmstadt, Germany), and dichlorodimethylsilane was 99% (ACROS Organics, New Jersey, USA). Analytical grade anhydrous sodium sulfate was supplied by Merck. "Prepsep" C-18 (500 mg, 6 mL) cartridges were from Fisher Scientific (Pittsburgh, PA, USA).

Certified 2000 $\mu\text{g}\cdot\text{mL}^{-1}$ standards of the individual PAH in dichloromethane/benzene (1:1) were purchased from Ultra Scientific. The 16 compounds investigated were naphthalene (Nap), acenaphthylene (Acpt), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Py), benz[*a*]anthracene (BaA), chrysene (Chry), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenzo[*b,c*]fluoranthene (DBF), dibenz[*a,h*]anthracene (DBA), and benzo[*g,h,i*]perylene (BPe). PAH stock solutions were prepared in dichloromethane at 200 $\mu\text{g}\cdot\text{mL}^{-1}$ and stored at -10°C . Working standard solutions were prepared by diluting the stock solutions in dichloromethane as required.

2.2. Sampling

Produced water samples were collected from the lower part of the treatment station tank of a petroleum production company located in the city of Carmópolis, Sergipe, Brazil. The water had previously been processed for removal of the bulk of the oil content. For subsequent recycling and reuse for injection into wells during petroleum extraction [13], or discharge into the sea, the produced water passes through further processes involving filtration and chemical treatment. The samples were collected in amber glass flasks, fitted with closures lined with aluminium foil, and preserved by storing at 4°C prior to extraction.

2.3. Sample Preparation

5 mL aliquots of methanol were added to 100 mL subsamples of unfiltered produced water. The cartridges containing the C-18 solid phase were each conditioned

using 20 mL dichloromethane, 10 mL acetone, 20 mL methanol, and finally 20 mL ultrapure water, and then dried for 3 minutes. The water sample was adjusted to pH 7 with sulfuric acid (1:1), and then passed through the C-18 cartridge. The PAH were eluted with 5 mL acetone and 30 mL hexane. The organic extract was concentrated in a rotary evaporator (50°C , 60 rpm), transferred to a glass column filled with 5 g anhydrous sodium sulfate on silanized glass wool, and PAH were eluted from the column using 20 mL dichloromethane. After further concentration using the rotary evaporator, the extract was transferred to a 1 mL volumetric flask, and reduced under a flow of nitrogen before analysis.

2.4. Chromatographic Conditions

Quantification of PAH was performed using a Shimadzu (Kyoto, Japan) Model 17A gas chromatograph equipped with a flame ionization detector and split/splitless injector. The column was a Hewlett Packard (USA) fused-silica HP-5 (30 m \times 0.25 mm \times 0.25 μm film thickness), and 99.995% purity helium was used as carrier gas. Temperatures of the injector (splitless mode, 2 min) and detector were 250°C and 300°C , respectively. The column temperature was programmed as follows: 40°C for 1 min, increasing to 160°C at $25^\circ\text{C}\cdot\text{min}^{-1}$ and to 270°C at $5^\circ\text{C}\cdot\text{min}^{-1}$, with a hold for 11 min. The flow rate through the column was $1.32\text{ mL}\cdot\text{min}^{-1}$, and the injection volume was 1 μL .

3. Results and Discussion

Several parameters were examined at the sample preparation stage in order to optimize the performance of the SPE technique. Method validation was undertaken after formalization of the PAH extraction procedure, with recoveries determined using enriched produced water blank samples.

3.1. Filtration of the Matrix

Possible losses by sorption onto particulate matter present in the produced water, due to low compound solubility, were examined by filtration of three samples under vacuum through 0.45 μm cellulose acetate filters, and comparison with three unfiltered samples. PAH concentrations were lower for the filtered samples, and fluorene, phenanthrene, chrysene, benzo[*k*]fluoranthene, dibenzo[*b,c*]fluoranthene, dibenz[*a,h*]anthracene and benzo[*g,h,i*]perylene were not detected. With the exception of fluorene and phenanthrene, the PAH investigated possess between four and six aromatic rings. Hence, these compounds are strongly adsorbed onto matrix particulates.

In the absence of filtration, there was partial blockage of the C18 solid phase, which resulted in longer extraction times. This phase of the work resulted in the definition of a minimum sample volume without compromising sensitivity and the ability to quantify PAH, as a result of which subsample volumes were fixed at 100 mL.

3.2. Organic Solvents

The solvents used for conditioning the C18 cartridges and for subsequent elution were based on USEPA Method 3535 [14]. Dichloromethane, *n*-hexane and an *n*-hexane/dichloromethane mixture (70/30, v/v) were chosen for the elution test (in triplicate) of PAH through the C18 solid phase. Use of hexane gave the best recovery, varying between 37.0% for benzo[*a*]pyrene and 72.2% for acenaphthylene, while recoveries using the 70/30 v/v *n*-hexane/dichloromethane mixture were between 18.4% for benzo[*a*]pyrene and 61.2% for fluoranthene. Dichloromethane gave the lowest recoveries. Hence, *n*-hexane was selected as elution solvent.

3.3. Silanization

PAH adsorption was studied using both silanized and standard glassware. Silanization was achieved according to the procedure described by Doong [13], which requires filling all internal volumes with a solution of 10% dichlorodimethylsiloxane in toluene, and leaving for 8 hours. Subsequently the glassware was washed with toluene and methanol, and finally dried in a drying cabinet at 120°C. For unsilanized glassware, the average recovery for 14 PAH (acenaphthene and benzo[*b*]fluoranthene

were not extracted) was 54.0%. With silanization, the average recovery of all 16 PAH was 70.0%.

3.4. Sample pH

Since the hydrogen ion concentration influences sample preservation, tests were undertaken at pHs 2, 4 and 7. At acid pH, there was a decrease in recovery of between 10% and 20% compared to neutral pH. The best recoveries were obtained at pH 7 (Figure 1).

3.5. Solubilization of PAH in Produced Water

Due to the low solubility of PAH in water, which decreases as molecular mass increases, measurement errors can be incurred as a result of sorption of the compounds onto the walls of the glassware used throughout the procedure [15,16]. Addition of co-solvents or organic modifiers (methanol, acetonitrile or 2-propanol) is a technique used to increase the solubility of PAH [15,17,18]. In this work, methanol and acetonitrile were chosen, with a 5.0 mL volume of each solvent being added to the sample containing the PAH standard. Using methanol, recoveries varied from 45.9% for naphthalene to 93.9% for chrysene. Using acetonitrile, the variation was between 29.9% for naphthalene and 90.2% for dibenzo[*b,c*]fluoranthene. Although both solvents showed similar performance, slightly better results were obtained using methanol.

3.6. Comparison of FID and PID Detectors

The photoionization detector (PID) is capable of good

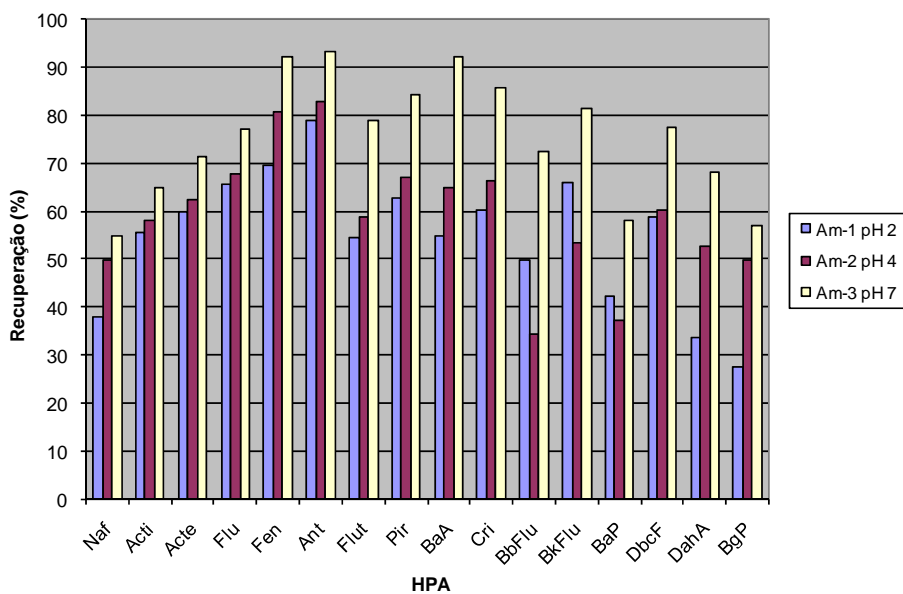


Figure 1. PAH recoveries obtained at pHs 2, 4 and 7.

sensitivity for detection of the volatile monoaromatic hydrocarbons benzene, toluene, ethylbenzene, and the xylene isomers [2]. The operating conditions of this detector have been reported previously [1,2]. A test was undertaken to measure the performance of the PID for PAH. At a concentration of $0.4 \mu\text{g}\cdot\text{mL}^{-1}$, only the first seven compounds eluting from the column were detected, while all 16 PAH were detected at a concentration of $5 \mu\text{g}\cdot\text{mL}^{-1}$.

3.7. Validation of the SPE Method

Validation was based on parameters defined in standard protocols describing chromatographic methods [15-17].

3.8. Linearity

A five-point calibration curve was constructed for each compound over the concentration range of interest ($0.5 - 50 \mu\text{g}\cdot\text{mL}^{-1}$), using external standards. Calibration curve regression coefficients (R^2) were higher than 0.998 in all cases (Table 1).

3.9. Recovery

Recoveries were measured at two enrichment levels, 10

and $100 \mu\text{g}\cdot\text{L}^{-1}$ (Table 2). At the first level ($10 \mu\text{g}\cdot\text{L}^{-1}$), recoveries varied from 55.0% for naphthalene to 93.1% for anthracene. At the second level ($100 \mu\text{g}\cdot\text{L}^{-1}$) recoveries were from 30.9% for naphthalene to 119.1% for chrysene. At these levels, the efficiency of the SPE method was satisfactory, with recoveries lying close to the range normally considered acceptable, between 70% and 130% [18] (with the exception of naphthalene). At the first level, recoveries of acenaphthylene, benzo[*a*]pyrene and benzo[*g,h,i*]perylene were below 70%. Table 3 lists previously reported PAH recoveries, with some values below 30%.

3.10. Precision

Repeatability was measured using relative standard deviations (RSD) at two concentration levels (10 and $100 \mu\text{g}\cdot\text{L}^{-1}$), and ranged from 3.8% to 22.2% (Table 2). All RSDs were below 30%, the value considered acceptable. [18] Confidence limits at 95% probability were also obtained for each PAH.

3.11. Limits of Detection (LOD) and Quantification (LOQ)

These were determined using the standard deviation ($n =$

Table 1. Analytical curves, and limits of detection and quantification, for the PAH investigated.

PAH	Regression equation	R^2	LOD ($\mu\text{g}\cdot\text{L}^{-1}$)	LOQ ($\mu\text{g}\cdot\text{L}^{-1}$)
Naphthalene	$y = 2362.5x - 204.2$	0.9998	0.02	0.08
Acenaphthylene	$y = 2315.3x - 216.9$	0.9996	0.02	0.07
Acenaphthene	$y = 2391.1x - 213.7$	0.9996	0.01	0.05
Fluorene	$y = 2288.0x - 269.1$	0.9995	0.03	0.11
Phenanthrene	$y = 2471.6x - 322.2$	0.9992	0.02	0.08
Anthracene	$y = 2327.7x - 341.3$	0.9987	0.03	0.11
Fluoranthene	$y = 2449.8x - 207.6$	0.9988	0.03	0.12
Pyrene	$y = 2379.2x - 331.0$	0.9986	0.03	0.13
Benz[<i>a</i>]anthracene	$y = 2250.8x - 293.2$	0.9994	0.02	0.08
Chrysene	$y = 2468.1x - 356.9$	0.9980	0.03	0.13
Benzo[<i>b</i>]fluoranthene	$y = 2281.6x - 268.1$	0.9993	0.02	0.08
Benzo[<i>k</i>]fluoranthene	$y = 2312.9x - 228.2$	0.9987	0.03	0.13
Benzo[<i>a</i>]pyrene	$y = 2067.8x - 134.3$	0.9998	0.03	0.12
Dibenzo[<i>b,c</i>] fluoranthene	$y = 1336.3x - 269.3$	1.0000	0.04	0.16
Dibenz[<i>a,h</i>]anthracene	$y = 1591.5x - 321.5$	0.9999	0.04	0.15
Benzo[<i>g,h,i</i>]perylene	$y = 1579.0x - 277.4$	0.9995	0.03	0.11

LOD: Limit of detection; LOQ: Limit of quantification.

Table 2. Recoveries using the proposed SPE method for determination of PAH in saline samples (n = 5).

PAH	Fortification ($\mu\text{g}\cdot\text{L}^{-1}$)	Recovery (%)	
		Mean \pm CI ¹	RSD ²
Naphthalene	10	55.0 \pm 10.26	15.0
	100	30.9 \pm 8.53	22.2
Acenaphthylene	10	65.0 \pm 12.37	15.3
	100	83.3 \pm 9.76	9.4
Acenaphthene	10	71.3 \pm 14.57	16.4
	100	88.1 \pm 14.26	13.0
Fluorene	10	77.2 \pm 12.80	13.3
	100	104.1 \pm 14.47	11.2
Phenanthrene	10	92.1 \pm 15.51	13.5
	100	115.8 \pm 11.88	8.3
Anthracene	10	93.1 \pm 10.48	9.0
	100	107.5 \pm 12.57	9.4
Fluoranthene	10	78.8 \pm 18.29	18.7
	100	111.7 \pm 9.50	6.9
Pyrene	10	84.1 \pm 11.72	11.2
	100	107.2 \pm 7.60	5.7
Benz[<i>a</i>]anthracene	10	92.3 \pm 10.33	9.0
	100	117.7 \pm 8.66	6.0
Chrysene	10	85.5 \pm 10.87	10.2
	100	119.1 \pm 5.59	3.8
Benzo[<i>b</i>]fluoranthene	10	72.3 \pm 10.51	11.7
	100	90.4 \pm 5.93	5.3
Benzo[<i>k</i>]fluoranthene	10	81.4 \pm 20.13	19.9
	100	95.0 \pm 5.12	4.3
Benzo[<i>a</i>]pyrene	10	58.1 \pm 14.01	19.4
	100	91.1 \pm 11.27	10.0
Dibenzo[<i>b,c</i>]fluoranthene	10	77.4 \pm 20.77	21.6
	100	71.8 \pm 4.33	4.9
Dibenz[<i>a,h</i>]anthracene	10	68.0 \pm 9.38	11.1
	100	69.7 \pm 3.92	4.5
Benzo[<i>g,h,i</i>]perylene	10	56.9 \pm 11.85	16.8
	100	71.8 \pm 4.27	4.8

¹CI: confidence interval; ²RSD: relative standard deviation.

Table 3. Previously reported PAH recoveries for aqueous matrices.

PAH	Recovery (%)						
	(SPE) ¹ Subsoil water	(SPE) ² Milli-Q water	(SPE) ³ Sewage	(LLE) ⁴ Seawater	(SPE) ⁴ Seawater	(LLE) ⁵ Seawater	(LLE) ⁶ Seawater
1.Nap	35		99	nd	nd		x
2.Acpt	46		104	nd	nd		x
3.Ace	105		64	nd	nd		x
4.Flu	97	x	93	nd	nd	x	x
5.Phe	102		72	10	52	x	x
6.Ant	86		82	3	10	x	x
7.Flt	113		81	13	34	x	x
8.Py	112		90	13	32	x	x
9.BaA	68	x	106	12	23		x
10.Chry	67		96	13	18	x	x
11.BbF	86	x	91	14	25		x
12.BkF	73	x	87	13	18		x
13.BaP	61	x	77	7	10	x	x
14.DBF	63	x	81	13	22		x
15.DBA	58	x	72	16	20		x
16.BPe	67	x	69	13	16		x
Range	35 - 112	95 - 104	64 - 106	3 - 16	10 - 52	95 - 112	65 - 92

nd = not detected; x = PAH analysed; ¹Martinez *et al.* (2004); ²Garcia-Falcón *et al.* (2004); ³Oleszezuk and Baran (2004); ⁴Filipkowska *et al.* (2005); ⁵Nemr and Abd-Allah (2003); ⁶Anyakora *et al.* (2005).

7) of the concentration at the lowest level of enrichment and in the sample blank (LOD = $t_{95\%,s}$) [19]. Detection limits varied between 0.01 and 0.04 $\mu\text{g}\cdot\text{L}^{-1}$ (Table 1). Limits of quantification were calculated as ten times the standard deviation ($n = 7$), and varied between 0.05 and 0.16 $\mu\text{g}\cdot\text{L}^{-1}$.

3.12. Comparison with Liquid-Liquid Extraction

The proposed method employing SPE was applied to the determination of the 16 PAH in samples of produced water. Mean concentrations varied from 3.5 $\mu\text{g}\cdot\text{L}^{-1}$ for phenanthrene to 44.3 $\mu\text{g}\cdot\text{L}^{-1}$ for naphthalene, with a total combined PAH concentration of 177.7 $\mu\text{g}\cdot\text{L}^{-1}$ (Table 4). Previous work employing liquid-liquid extraction³ found the following PAH concentrations in produced water: naphthalene 26.68 $\mu\text{g}\cdot\text{L}^{-1}$; acenaphthylene 0.44 $\mu\text{g}\cdot\text{L}^{-1}$; acenaphthene 0.34 $\mu\text{g}\cdot\text{L}^{-1}$; fluorene 0.01 $\mu\text{g}\cdot\text{L}^{-1}$; phenanthrene 0.02 $\mu\text{g}\cdot\text{L}^{-1}$; anthracene 0.03 $\mu\text{g}\cdot\text{L}^{-1}$; fluoranthene 0.01 $\mu\text{g}\cdot\text{L}^{-1}$. The remaining PAH were not detected.

Seawater samples collected near Aracaju, Sergipe State, were analyzed in order to confirm the wider applicability of the SPE method. The total PAH concentration

was 60.27 $\mu\text{g}\cdot\text{L}^{-1}$ (Table 4), with the ratios between low molecular weight and high molecular weight compounds, phenanthrene/anthracene (<10) and fluoranthene/pyrene (>1), indicating that the likely source was pyrogenic (combustion). Furthermore, in pyrogenic material there is a predominance of 4 to 6 ring compounds ($\Sigma\text{PAH} = 44.0 \mu\text{g}\cdot\text{L}^{-1}$) relative to 2 to 3 ring compounds ($\Sigma\text{PAH} = 16.2 \mu\text{g}\cdot\text{L}^{-1}$) [20,21].

4. Conclusions

An analytical method for determination of the 16 priority polycyclic aromatic compounds in produced water using SPE and GC-FID analysis has been validated. The parameters linearity, recovery, precision, detection limits and quantification limits were all shown to be acceptable. The proposed method was compared with liquid-liquid extraction for real samples of produced water. Using SPE, 15 PAH were detected in these samples, at concentration levels ranging from 3.5 to 44.3 $\mu\text{g}\cdot\text{L}^{-1}$ ($\Sigma\text{PAH} = 177.7 \mu\text{g}\cdot\text{L}^{-1}$). Only seven PAH were detected using liquid-liquid extraction. To confirm that the method is suitable for typical saline samples, it was used for analysis of

Table 4. PAH concentrations measured in produced water and seawater (n = 2).

PAH	Produced water ($\mu\text{g}\cdot\text{L}^{-1}$)	Seawater ($\mu\text{g}\cdot\text{L}^{-1}$)
Naphthalene	44.30	2.64
Acenaphthylene	16.55	2.46
Acenaphthene	10.10	2.53
Fluorene	10.03	2.52
Phenanthrene	3.53	2.39
Anthracene	8.54	3.70
Fluoranthene	3.94	4.44
Pyrene	3.80	2.91
Benz[a]anthracene	8.29	12.95
Chrysene	12.10	9.53
Benzo[b]fluoranthene	6.02	9.13
Benzo[k]fluoranthene	14.44	1.97
Benzo[a]pyrene	18.58	3.10
Dibenzo[b,c]fluoranthene	7.81	nd
Dibenz[a,h]anthracene	nd	nd
Benzo[g,h,i]perylene	9.67	nd
Σ PAH	177.71	60.27

nd: not detected.

seawater, in which 13 PAH were detected (Σ PAH = $60.27 \mu\text{g}\cdot\text{L}^{-1}$).

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