

# Polycyclic Aromatic Hydrocarbons in Petroleum Sludge Cake: Extraction and Origin - a Case Study

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## Abstract

*The aim of this study was to determine the most effective solvent(s) of Acetone, Dichloromethane (DCM), n-Hexane solvents and their mixtures of PAH soxhlet extraction (SE) from petroleum sludge cake sample; also to determine the origin of PAH in petroleum sludge cake sample - a case study. Gas chromatograph-mass spectroscopy (GC-MS) was used for analytical determination of the selected PAH compounds. The result was revealed that the binary mixture solvent of Acetone+n-Hexane (1:1) (v/v) was the most effective of solvent common used because it was the only one which was able to extract the selected PAH compounds and yielded the highest amount of total selected PAH extracted from the petroleum sludge cake. Meanwhile, n-Hexane solvent and DCM+n-Hexane (1:1) were less effective ones. The quantitative result of analysis of selected PAH compounds: Phenanthrene/Ph, Anthracene/An (both 3-rings) and Fluoranthene/Fl, Pyrene/Py (both 4-rings) could be used to determine the origin of PAH. In conjunction with their molecular ratio: An/(An+Ph) of 0.045, and Fl/(Fl+Py) of 0.483, cross-plotting of An/(An+Ph) vs Fl/(Fl+Py) indicated that the PAHs compounds in petroleum sludge cake samples originated dominantly from pyrolytic (petroleum combusted) sources.*

**Keywords:** Gas chromatography-mass spectrometry, petroleum sludge cake, polycyclic aromatic hydrocarbons, soxhlet extraction

## 1. Introduction

Oil production and petroleum refining processes generate considerable amount of petroleum sludge as wastes. The sludge varies in composition but typically contains 10-30% hydrocarbons, 5-20% solids and 50-85% water [1]. One of the causes of the harmful characteristics of petroleum sludge is the presence of polycyclic aromatic hydrocarbons (PAHs), which are organic micro-pollutant (xenobiotics) compounds [2], persistent [3] with toxic and carcinogenic-mutagenic characteristics [4]. This sludge can pose serious threat to human health and environment if not rendered harmless and disposed properly. Of more than 10,000 known PAHs, about 200 compounds are possible carcinogens. The EPA has classified 16 as priority pollutants [5]. They are: Naphthalene/Np ( $C_{10}H_8$ ), Acenaphthylene/Ace ( $C_{10}H_8$ ), Acenaphthene/An ( $C_{10}H_{10}$ ), Fluorene/F ( $C_{13}H_{10}$ ), Phenanthrene/Ph ( $C_{13}H_{10}$ ), Anthracene/An ( $C_{13}H_{10}$ ), Fluoroanthene/Fl ( $C_{16}H_{10}$ ), Pyrene/Py ( $C_{16}H_{10}$ ), Chrysene/Ch ( $C_{18}H_{12}$ ), Benzo[a]Anthracene/BaA ( $C_{18}H_{12}$ ), Benzo[b]Fluoroanthene/BbF ( $C_{20}H_{12}$ ), Benzo[k]Fluoroanthrene/BkF ( $C_{20}H_{12}$ ), Benzo[a]Pyrene/BaP ( $C_{20}H_{12}$ ), Indeno[1,2,3-cd]Pyrene/Ind ( $C_{22}H_{12}$ ), Benzo[g,h,i]Perylene/BPer ( $C_{22}H_{12}$ ), and Dibenzo[a,h]Anthracene/DbA ( $C_{22}H_{14}$ ). The analysis for PAHs, especially in solid matrices such as sludge and soils, is not simple and requires careful sample pretreatment and sophisticated instrumental analysis. Isolation or extraction is the main sample pretreatment step; and if needed it may be followed by clean-up. Instrumental analysis relies on the equipment's ability to separate, identify, and quantify various constituent PAHs of the samples [6]. Quantitative result of selected PAH compounds could also be used to determine the origin of the PAH itself [7], [8] in certain matrices such as marine sediment [9], [10], road dust [11], river sediment [12], emission particulate matter [13], and surface soil [14].

## Extraction methods: mini review

Various methods used for PAH extraction can be classified into two types namely, extraction conducted with pressurized fluids and extraction conducted at atmospheric pressure [15]. The first category includes Accelerated Solvent Extraction (ASE), Supercritical Fluid Extraction (SFE), and Sub-Critical Fluid Extraction; the second category includes Soxhlet Extraction (SE), Solvent Washing, Surfactant Promoted Extraction, Extraction by Vegetable Oils and Extraction by Cyclodextrins.

Soxhlet extraction (SE) process is a well-known simple classical technique for the extraction of organic non-polar compounds [3], hydrophobic substances [15], semi-volatiles and non-volatiles [16] from solid samples. It is applicable to a wide range of analytes in solid matrices. The procedure involves repeated percolation of re-condensed solvent vapors through a sample to desorb and solubilize target compounds (e.g. PAH). SE is one of the most commonly used laboratory techniques for organic contaminant extraction [17]. The test does not require high cost or expertise and yields good overall recovery [6], [18]. However, it has inherent disadvantages of long extraction duration and large volume of organic solvent consumption [6], [18]. SE process has been used to extract PAH from various samples, such as contaminated soil [19], [20], [21], waste water sludge [9], soils and sediments [22], wood ash [23] and fly ash [18]. Organic solvents like Acetone [9], [12], Dichloromethane (DCM) [24], [25], [22], n-Hexane [19], [26] and their combinations [19], [20], [21], [9], [22], [3], [6], [27], [18] have been employed for PAH extraction from solid samples.

Previous studies have mentioned Dichloromethane (DCM) (non-polar) as an effective solvent for PAH extraction [28] from samples of solid hydrocarbon [29], [25], sewage sludge [24], soil and sediment [22]. However, DCM as a chlorinated solvent is also considered to be toxic and its use will probably be limited in the future. Acetone and n-Hexane are less toxic chemicals [26]. n-Hexane, because of its non-polar nature, does not form dipole interactions with PAHs [30]. The use of Acetone as a solvent or in solvent mixture composition can also improve the results of some soil samples [30], [28]. Toluene has been shown to provide higher recoveries of PAHs than DCM [25] however it is highly toxic [6] and considered not suitable from an environmental view point. Therefore, toluene was not used as a solvent in this work. The choice of a suitable solvent (or solvent mixture) and amount vis-à-vis the samples (matrices) type, quantity and target compounds is of prime importance for the extraction process. Table 1, lists some studies of SE of PAH by different researchers.

**Insert table (1) about here**

### **Determination of origin of PAH**

A number of studies have been conducted on the presence of selected parent PAH compounds for environmental forensic purposes. The information has been used to trace the origin of petroleum in spill investigations [7], [10], [8] and in identification of road dust [11]. The presence of PAH analytes in unknown hydrocarbon samples is a useful tool for its source identification [7]. Some PAHs compounds, including Phenanthrene/Phen, Anthracene/Ant, Fluoroanthene/Fla, and Pyrene/Py in conjunction with their molecular ratios: Ph/An, An/(An+Ph), Fl/Py, and Fl/(Fl+Py) have been used to identify the origin of PAHs in various environmental samples such as soils and sediments [8], [28]. However, many reports also noted that Ph/An has low discrimination capacity. Since the pair of compounds, Ph and An, has small relative difference in thermodynamic stability between isomers, the Ph/An ratio is likely less effective for identification of the origin of PAHs [8], [12]. On the other hand, the Fl/(Fl+Py) ratio has a more detailed combustion sources boundary and the pair, Fl and Py, has higher relative difference in thermodynamic stability between their isomers than Ph and An. Therefore, the use of these would generally give a better interpretation for determination of the origin of PAHs [8], [11].

This study also uses selected PAH ratios to determine the origin of petroleum sludge cake; whether it is pyrolytic (petroleum combustion) or petrogenic (unburned petroleum) represented by Phenanthrene/Ph, Anthracene/An (both 3-rings) and Fluoroanthene/Fl, Pyrene/Py (both 4-rings) in conjunction with their molecular ratios: An/(An+Ph), and Fl/(Fl+Py). The aim of this study is to determine a suitable solvent or solvent mixture for PAH (selected compounds only: Ph, An, Fl, and Py) extraction for petroleum sludge cake samples using Soxhlet Extraction and with the objective to determine the origin of PAH in petroleum sludge cake sample.

## **2. Methodology**

### **2.1 Sample**

Sludge cake was collected from decanter unit after sludge dehydration treatment of petroleum refinery. The samples were placed in dark glass bottles and stored at 4 °C in a cold room. Prior to extraction, the samples were placed in a dessicator cabinet.

### **2.2 Experimental**

The identification and quantification of four selected PAH in petroleum sludge cake samples were conducted using Gas Chromatography-Mass Spectrometry. The sludge cake samples were pre-treated by soxhlet extraction (SE) using seven combinations of solvents viz. Acetone, Dichloromethane (DCM) and n-Hexane as shown in Table 2.

### 2.3 Chemicals and standards

Acetone (Merck), DCM (R&M, HPLC grade), and n-Hexane (Merck) were used as solvents for selected PAH extraction. Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) (Merck) was of analytical reagent grade. The 17 compounds PAH Mixture Standard Solution 2.0 mg/ml in DCM+Benzene (1:1) was purchased from AccuStandard USA.

**Insert table (2) about here**

### 2.4 Extraction procedure

The selected PAHs were extracted from petroleum sludge cake using soxhlet extraction of the EPA 3540 (1996) modified method. 10 g sample was mixed with an equal amount of  $\text{Na}_2\text{SO}_4$  [25], [6], wrapped in Kimwipes tissue paper and placed in a Whatman® cellulose extraction thimble. 180-ml of solvent (Table 2) was added into a 250 ml receiving flask for PAH extraction. Extractions were carried out below the solvent(s) boiling temperature for 24 hours [6]. The extracts were then vacuum concentrated [6] on a rotary vacuum evaporator (Büchi, RE 125) at 40 °C [33], [34] and a pressure of 350 mbar [26]. Solid Phase Extraction (SPE) using Resprep (Restek™) C-18 Cartridge has been done followed by filtration with 0.45  $\mu\text{m}$  PTFE (polytetrafluoroethylene) syringe filter prior to GC-MS analysis.

### 2.5 GC-MS analysis

In this experiment, Shimadzu QP5050-A GC-MS and SIM Mode was used to determine the selected PAH concentrations based on USEPA Method 8270D (2007). The GC-MS was equipped with BPX-5 (5% phenyl polysilphenylene-siloxane) capillary column (30 m length, 0.25 mm dia., 0.25  $\mu\text{m}$  film thickness) with operating conditions: GC inlet pulsed 75 kPa, 1.2 ml/min; carrier gas Helium (He) flow 93 mL/min; injection volume 5  $\mu\text{L}$ , splitless injection at 300 °C, detector at 280 °C, and initial oven temperature 70 °C held for 2 min, then increased at 8 °C/min to final temperature 290 °C. Retention time and mass spectra (Table 3) of the selected PAH were set for the GC-MS analysis.

**Insert table (3) about here**

PAHs are complex matrices and gas chromatography-mass spectrometry (GC-MS) is often used as the preferred approach for their separation, identification, and quantification. GC-MS generally affords greater selectivity, resolution, and sensitivity [35]. The identification of selected PAH was accomplished by comparing retention time of their standards and appropriate components identified in petroleum sludge cake samples. The quantitative analysis of individual PAHs in the samples was carried out by comparing it with the peak areas of the PAHs in the standard mixture [35], [27]

## 3. Results and Discussion

The GC-MS results obtained for the selected PAHs extraction from sludge cake samples using different solvents are shown in Table 4 and Figure 1.

**Insert table (4) about here**

**Insert Figure (1) about here**

Phenanthrene/Ph was identified in the extraction of all solvents tested except Acetone+DCM mixture. Meanwhile, Fluoroanthene/FI was only identified in the extraction of Acetone+DCM mixture and Acetone+n-Hexane mixture. The Acetone+n-Hexane mixture was able to extract all four target PAHs and also yielded the highest amount of total selected PAH extracted (31.711 ppm). The result also revealed that n-Hexane solvent and mixture solvents of DCM+n-Hex were less effective since only able extracted Phenanthrene/Ph only with amount of 2.483 ppm and 0.811 ppm, respectively. Carabias-Martinez et al. [36] mentioned that the polarity of the solvent should be close to the target compound. Both DCM and n-Hexane are non-polar, water immiscible solvents, whereas Acetone is a polar water soluble solvent which has the ability to break-up solid aggregates and allow intensive contact between particles [2]. Carabias-Martinez et al. [36] noted that mixtures of low- and high-polar solvents are more efficient than single solvents when extracting analytes with a wide range of polarities. Song et al., [37] have also shown solvent mixtures to be more effective than single solvents in extracting PAHs from moist samples. These results corroborate well with the present study as it is based on sludge (moist) samples.

Figure 2 shows the cross-plotting of  $\text{An}/(\text{Ph}+\text{An})$  vs  $\text{Fl}/(\text{Fl}+\text{Py})$  for determination of the origin of the sludge cake sample.

**Insert Figure (2) about here**

The An/(An+Ph) value of 0.045 (Table 4) was located in the petroleum zone i.e. below the border line (0.1) of petroleum zone, whereas the Fl/(Fl+Py) value of 0.483 (slightly below 0.5) was located in 'the petroleum combustion zone'(range of 0.4-0.5). As the sludge was heated (80-90 °C) in a pretreatment tank before decanting to produce the sludge cake, therefore the heating affected the sludge PAH composition and hence the inference about its origin.

#### 4. Conclusion

The aliquot of soxhlet extracted samples was without clean-up pretreatment prior to determine with Gas Chromatograph-Mass Spectroscopy (GCMS). The results showed that binary solvent mixture of Acetone+n-Hexane (1:1) (v/v) was the most effective in PAH extraction using soxhlet extraction. Not only it was able to detect the four selected PAH compounds: Phenanthrene/Ph, Anthracene/An, Fluoroanthene/Fl, and Pyrene/Py, but also the amount of PAH extracted was the highest. Meanwhile, in this experiment, n-Hexane solvent and DCM+n-Hexane (1:1) were less effective ones. The selected PAH compounds through their nominal concentrations, ratios, and cross-plotting indicated PAH in the petroleum sludge cake sample is dominantly originated from pyrolytic (petroleum combusted) sources. This is related to the history of the sample which was heated in a pretreatment tank during sludge treatment.

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Table 1 Solvent(s), matrices, and results in soxhlet extraction of PAH

Solvent(s)	Matrices	Remarks	References
Acetone	soil	Relative Standard Deviation (RSD) of data was about 5% and comparable with DCM and better than n-Hexane alone	[30]
DCM	marine- sediment	recoveries of Certified Reference Material/CRM was about 66.0-111.1% and comparable with Microwave Assisted Solvent Extraction/MASE which was 73.5-136.8%	[31]
n-Hexane	contaminated- soil	recovered 71% of total PAH	[19]
	soil	poor recovery of the high boiling group of PAH compounds (range of 50–90%)	[32]
Acetone+DCM (1:1) (v/v)	contaminated- soil	poor recovery rate which was only 16% only of total PAH	[19]
	contaminated-soil	mean concentrations (mg/kg) of PAHs extracted slightly lower than PLE but higher than super fluid extraction (SFE) and sub-critical water extraction (SCWE)	[20]
	contaminated- soil	RSD of data was about 6% and comparable with pressurized liquid extraction (PLE) performance	[21]
DCM+n-Hexane (1:1) (v/v)	sewage sludge	the extraction recoveries: 65.0-91.8%	[3]
	marine- sediment	the recovery (internal standard) of PAH was 70-123%	[27]
Acetone+n-Hexane (1:1) (v/v)	soil and sediment	the extraction of high molar mass (HMM) n-alkanes and PAH were more efficient than PHWE, however not for smaller compounds	[22]
	wastewater sludge	the percentage recoveries of 63.45-80.65% were higher than SCWE	[9]
Acetone+DCM+n-Hexane (30:20:50) (v/v)	fly ash from boiler	better recovery for HMM PAH than ultrasonic extraction, but not good for lighter compounds.	[18]

Table 2 Solvent regime in the experiment

Solvent(s) (v/v)	Volume of solvent (mL)			Total
	Acetone	DCM	n-Hexane	
<u>Single</u>				
Acetone	180			180
DCM		180		180
n-Hexane			180	180
<u>Binary Mixture</u>				
Acetone:DCM (1:1)	90	90		180
DCM:n-Hexane (1:1)		90	90	180
Acetone:n-Hexane (1:1)	90		90	180
<u>Ternary Mixture</u>				
Acetone:DCM:n-Hexane (1:1:1)	60	60	60	180

Table 3 Retention time and mass spectra of the selected PAH

Compound	Retention time (min)	Target ions (m/z)
Phenanthrene/Ph	21.42	178
Anthracene/An	21.67	178
Fluoranthene/Fl	27.42	202
Pyrene/Py	28.55	202

Table 4 Amounts (ppm) of selected PAH extracted from petroleum sludge cake

Selected PAH		Solvent*						
		Single			Binary Mixture (v/v)			Ternary Mixture (v/v)
Number of Rings	Comp.	Ace	DCM	n-Hex	Ace+DCM (1:1)	DCM+n-Hex (1:1)	Ace+n-Hex (1:1)	Ace+DCM+n-Hex (1:1:1)
3	Ph	0.840	6.421	2.483	ND	0.811	28.936	8.268
	An	0.881	0.199	ND	ND	ND	1.363	0.399
4	Fl	ND	ND	ND	0.397	ND	1.164	ND
	Py	ND	0.361	ND	2.537	ND	1.248	0.246
Total		1.721	6.981	2.483	2.934	0.811	31.711	8.913

\* Ace: Acetone, DCM: dichloromethane, n-Hex: n-Hexane; ND: not detected

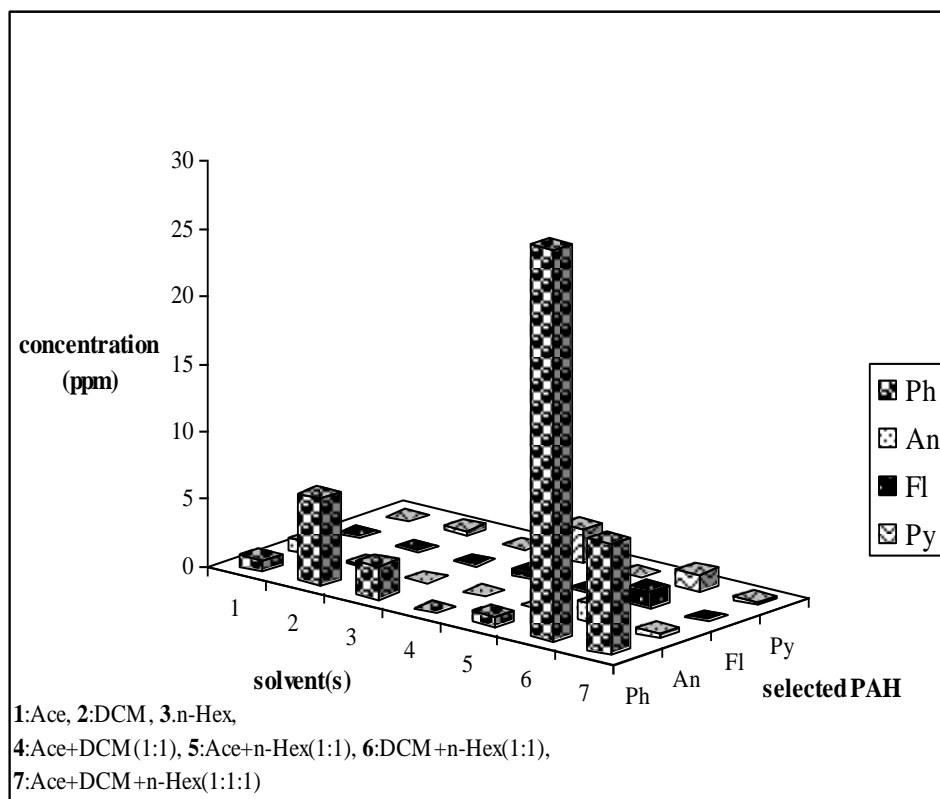


Figure 1 Selected PAH (ppm) in extracts of petroleum sludge cake

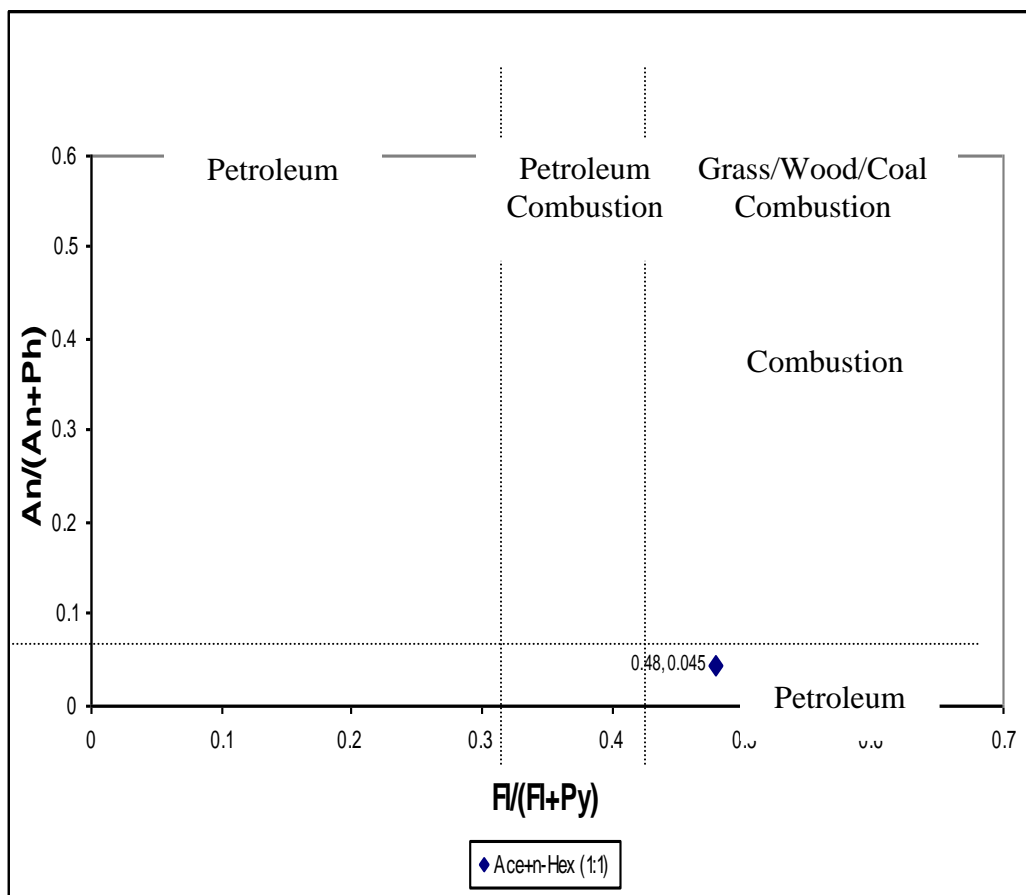


Figure 2 PAHs cross-plot of An/(An+Ph) vs Fl/(Fl+Py) of petroleum sludge cake