

**DISPERSIVE LIQUID-LIQUID MICROEXTRACTION-GAS
CHROMATOGRAPHY-MASS SPECTROMETRIC DETERMINATION OF
POLYCYCLIC AROMATIC HYDROCARBONS IN WATER**

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UNIVERSITI TEKNOLOGI MALAYSIA

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Alhamdulillah

Specially dedicated to my beloved father, Sharef Abdul Hadi Younes, my beloved mother Zizah AlSadiq, my siblings, friends and also my relatives.

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ABSTRACT

In this work, a sample preparation method based on dispersive liquid-liquid microextraction (DLLME) coupled with gas chromatography-mass spectrometry (GC-MS) was developed for the extraction of polycyclic aromatic hydrocarbons (PAHs), namely phenanthrene and fluoranthene from water sample. In this method, a mixture of carbon tetrachloride, CCl_4 (extraction solvent) and acetone (disperser solvent) was injected using a syringe into 5 mL water sample to form emulsion where the PAHs were extracted into the fine droplets of extraction solvent. The solution was then centrifuged for 3 min at 3000 rpm and the fine droplets were sedimented at the bottom of centrifuge tube. Sedimented phase (1 μL) was injected into the GC-MS for separation and determination of PAHs. The effects of various extraction parameters namely extraction solvent type, disperser solvent type, volume of extraction solvent, and volume of disperser solvent were investigated. The optimized conditions for DLLME of selected PAHs were carbon tetrachloride as extraction solvent, 60 μL of extraction solvent (CCl_4), acetone as disperser solvent and 1 mL of disperser solvent (acetone). The correlation coefficient (r^2) of the calibration curve for phenanthrene and fluoranthene were 0.9993 and 0.9973, respectively. The limits of detection (LODs) obtained for phenanthrene and fluoranthene were 0.0008 $\mu\text{g/mL}$ and 0.0006 $\mu\text{g/mL}$, respectively. The proposed method proved to be reproducible with relative standard deviations (RSDs) of 10.69 % and 9.72 % for phenanthrene and fluoranthene, respectively. The analyte recoveries were 100.5 – 107.8 %. The concentration of was 0.02-0.15 $\mu\text{g/mL}$. It was found that phenanthrene and fluoranthene were present in lake water sample at concentrations of 3.47×10^{-3} and 2.69×10^{-3} $\mu\text{g/mL}$. The DLLME method combined with GC-MS proved to be an efficient method and was applied successfully for the determination of PAHs from water sample.

ABSTRAK

Dalam kajian ini, kaedah penyediaan sampel yang berdasarkan kepada pengekstrakan mikro penyebaran cecair-cecair (DLLME) berganding dengan kromatografi gas-spektrometri jisim telah dibangunkan bagi pengekstrakan hidrokarbon aromatic polisiklik (PAHs), iaitu fenantrena dan fluorentena daripada sampel air. Dalam kaedah ini, campuran karbon tetraklorida, CCl_4 (pelarut pengekstrakan) dan aseton (pelarut penyebaran) telah disuntik menggunakan picagari 5 mL ke dalam sampel air bagi membentuk emulsi di mana PAHs diekstrak ke dalam titisan halus pelarut pengekstrakan. Seterusnya campuran tersebut telah diempar selama 3 minit pada 3000 rpm dan emulsi telah termendap di bahagian bawah tiub pengemparan. Fasa mendapan (1 μL) disuntik ke GC-MS bagi pemisahan dan penentuan PAHs. Kesan pelbagai parameter iaitu jenis pelarut pengekstrakan, jenis pelarut penyebaran, isipada pelarut pengekstrakan dan isipada pelarut penyebaran telah dikaji. Keadaan optimum DLLME bagi PAHs terpilih ialah carbon tetraklorida sebagai pelarut pengekstrakan, 60 μL pelarut pengekstrakan (CCl_4), aseton sebagai pelarut penyebaran dan 1 mL pelarut penyebaran (aseton). Nilai pekali kolerasi bagi regrasi linear (r^2) lengkung kalibrasi fenantrena dan fluorantena adalah masing-masing 0.9993 dan 0.9973. Had pengesanan yang rendah telah diperolehi bagi fenantrena dan fluorantena iaitu masing-masing 0.0008 $\mu\text{g/mL}$ dan 0.0006 $\mu\text{g/mL}$. Kaedah ini telah dibuktikan sebagai presis dengan nilai RSD 10.69% dan 9.72 % bagi fenantrena dan fluorantena. Peratusan perolehan semula adalah dalam julat 100.5 – 107.8 %. Kepekatan yang digunakan adalah dalam julat 0.02 – 0.15 $\mu\text{g/mL}$. Hasil kajian mendapati fenantrena dan fluorantena wujud di dalam sampel air tasik dengan kepekatan 3.47×10^{-3} dan 2.69×10^{-3} $\mu\text{g/mL}$. Kaedah DLLME berganding dengan GC-MS terbukti sebagai cepat dan telah berjaya diaplikasikan bagi penentuan PAHs dalam sampel air.

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LIST OF ABBREVIATIONS

PAHs	-	Polycyclic Aromatic Hydrocarbons
PCBs	-	Polychlorinated Biphenyls
POPs	-	Persistent Organic Pollutants
LLE	-	Liquid-Liquid Extraction
SPE	-	Solid Phase Extraction
HPLC	-	High-Performance Liquid Chromatography
GC/MS	-	Gas Chromatography/Mass Spectrometry
LPME	-	Liquid-phase microextraction
DLLME	-	Dispersive Liquid-Liquid Microextraction
LC	-	Liquid Chromatography
GC	-	Gas Chromatography
HF-LPME	-	Hollow fiber- liquid phase microextraction
mg	-	Milligram
m	-	Meter
mm	-	Milimeter
g	-	Gram
cm ³	-	Centimeter
µg	-	Microgram
mL	-	Milliliter
µm	-	Micrometer
I.D	-	Inner diameter
min	-	Minute
ppm	-	Part per million
LOD	-	Limit of Detection

LOQ	-	Limit of Quantification
S/N	-	Signal to Noise ratio
rpm	-	Revolutions per minute
°C	-	Degree Celsius
CH ₂ Cl ₂	-	Dichloromethane
CCl ₄	-	Carbon Tetrachloride
SD	-	Standard deviation
RSD	-	Relative Standard Deviation

CHAPTER 1

INTRODUCTION

1.1 Background of Research

The public concern over contamination of the built environment has rapidly grown as the potential health hazards of the agricultural and industrial pollutants have become recognised. One important area of modern environmental analysis is the determination of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) where both of them are ubiquitous in the environment (Potted & Pawliszyn, 1994). These compounds originate from both natural and anthropogenic sources and include suspected and known carcinogens. The term polycyclic aromatic hydrocarbons (PAHs) refer to a group of over hundred different chemicals which are environmentally persistent organic compounds of various structures and varied toxicity. Their widespread distribution in the environment is the result of a variety of natural and anthropogenic sources such as traffic, industry, and domestic heating (Bodzek *et al.*, 1997). The distribution of these compounds is extensive and consequently is monitored worldwide in a wide range of environmental matrices, including drinking water, waste water, soil, and hazardous waste extracts. Due to their high toxicity and carcinogenicity PAHs have been monitored as persistent organic pollutants (POPs) by several research institutions (King *et al.*, 2004).

Many analytical techniques have been developed and applied for the analysis of PAHs compounds in the environment. Generally, these compounds are extracted either by liquid–liquid extraction (LLE) and or by solid-phase extraction (SPE) (Kootstra *et al.*, 1995) and other traditional methods such as

microwave-assisted extraction (MAE) (Bartolom *et al.*, 2005). However, modern trends in analytical chemistry are approached towards the simplification of sample preparation. Thus, the microextraction techniques are playing an important role in the determination of PAHs. Solid-phase microextraction (SPME) (Fernández-González *et al.*, 2007), stir bar sportive extraction (SBSE) (Kolahgar *et al.*, 2002) and liquid-phase microextraction (LPME) (Charalabaki *et al.*, 2005) have been developed as alternative techniques to the classical LLE and SPE. Recently, a simple and rapid pre-concentration and micro extraction method named dispersive liquid-liquid microextraction (DLLME) has been introduced and frequently used for determination of organic contaminants in liquid samples including of PAHs (Rezaee *et al.*, 2006).

1.2 Statement of Problems

The toxicity of some PAHs has warranted their inclusion in environmental control legislation. Many environmental agencies have adopted very low levels of PAHs for drinking and natural waters, designed to protect the environment and human health (Charalabaki *et al.*, 2005). These compounds are emission from countless natural processes such as incomplete combustion of organic materials (coal and wood) or forest fires and human activities (Ma *et al.*, 2010). Due to hazardous characteristics the identification and determination of PAHs is an important analytical issues. However, extraction is a critical step in organic contaminant analysis because it is time-consuming and sometimes becomes the origin of quantification errors (Saleh *et al.*, 2009). Therefore, the preferable extraction technique is usually based on the extraction efficiency, selectivity, its simplicity of operation, smallest amount of solvent used, size of sample, rapidity, the ease of automation, sample throughput and cost.

Although, selectivity, sensitivity, and sample clean up can be achieved by the traditional techniques such as liquid-liquid extraction (LLE) and solid phase extraction (SPE), these methods are time consuming and generally labor intensive and requires relatively large amount of expensive, toxic and environmentally-

unfriendly organic solvent. Recently, Rezaee *et al.* (2006) introduced a novel microextraction technique named dispersive liquid-liquid microextraction (DLLME) as a high performance and powerful method. In this work, the application DLLME combined with GC-MS is explored for the extraction and determination of selected PAHs in selected water samples.

1.3 Research Objectives

The objectives of this study are:

- a) To study the effect of extraction and disperser solvents, effect of extraction and disperser solvent volumes in DLLME.
- b) To optimize the DLLME of phenanthrene and fluoranthene for sample-preparation prior to GC/MS.
- c) To apply the developed DLLME method coupled with GC/MS to the analysis of phenanthrene and fluoranthene in selected water sample.

1.4 Statement of Hypothesis

A previous study has shown that dispersive liquid-liquid microextraction (DLLME) is a relatively new technique used in analytical chemistry for sample pre-treatment that offers high selectivity and sensitivity compared to most traditional extraction techniques. It is expected that, DLLME can provide good enrichment factor within a short analysis time. PAHs were employed as model compounds to achieve the extraction procedure and were determine by GC-MS.

1.5 Significance of Study

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants emitted from a variety of natural and anthropogenic sources (Poster *et al.*, 2006). Due to the teratogenic and carcinogenic character of some of these molecules' more attention has been paid in environmental chemistry. In this work, DLLME was utilized to extract phenanthrene and fluoranthene from selected water sample and the optimization of selected important parameters were carried out in this technique. The major idea behind this study is to reduce the analysis steps and improve the quality, speed and sensitivity of analytical techniques as well as effective and of low cost

1.6 Scope of Study

The scopes of study are:

- a) The sample is limited to lake water sample.
- b) The quantification and identification of phenanthrene and fluoranthene will be carried out using gas chromatography-mass spectrometry (GC-MS).

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