



Determination of polycyclic aromatic hydrocarbons in water using dispersive liquid-liquid microextraction-gas chromatography-mass spectrometric

*Mohd Marsin Sanagi^{1,2}, Wan Aini Wan Ibrahim^{1,2}, Sarra Younes Sharef³, Nada Abusalah Almaabrouk Imrigha⁴

¹ Ibn Sina Institute for Basic Sciences Studies, Nanotechnology Research Alliance,

² Department of Chemistry, College of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

³ Department of Chemistry, Faculty of Science, Al-Zaytoonah University, Libay, Tarhuna

⁴ Department of Physics, College of Science, Sebha University, Libya

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ABSTRACT

For the extraction of polycyclic aromatic hydrocarbons (PAHs) from water samples, a new sample preparation approach based on dispersive liquid-liquid microextraction (DLLME) was developed. In this procedure, a water sample was injected with a mixture of carbon tetrachloride, CCl₄ (extraction solvent), and acetone (disperser solvent) to generate an emulsion in which the PAHs were extracted into fine droplets of extraction solvent. The impacts of several extraction parameters were explored, including extraction solvent type, disperser solvent type, extraction solvent volume, and disperser solvent volume. For phenanthrene and fluoranthene, the calibration curve correlation coefficient (r^2) was 0.9993 and 0.9973, respectively. For phenanthrene and fluoranthene, the limits of detection (LODs) were 0.0008 g/mL and 0.0006 g/mL, respectively. For phenanthrene and fluoranthene, the relative standard deviations (RSDs) were 10.69 percent and 9.72 percent, respectively. The analyte recovery rates ranged from 100.5 to 107.8%. Phenanthrene and fluoranthene were discovered in the samples.

تحديد الهيدروكربونات العطرية متعددة الحلقات في الماء استخدام غازات الاستخلاص الدقيق السائلة المشتتة مطيافية الكتلة الكروماتوغرافيا

*محمد مرسين سناجي^{1,2} و وان عيني وان ابراهيم^{1,2} و سارة يونس شريف³ و ندى أبو صلاح المعبروك إمرغية⁴

1 معهد ابن سينا لدراسات العلوم الأساسية ، تحالف أبحاث تقنية النانو

2 قسم الكيمياء ، كلية العلوم ، 81310 UTM Johor Bahru ، Universiti Teknologi Malaysia ، جوهور ، ماليزيا

3 قسم الكيمياء ، كلية العلوم ، جامعة الزيتونة ، ليبيا ، ترهونة ح

4 قسم الفيزياء ، كليو العلوم ، جامعة سبها ، ليبيا

الكلمات المفتاحية:

الملخص

تحليل المياه
الهيدروكربونات العطرية متعددة
الحلقات (PAHs)
مطياف الكتلة اللوني للغاز
استخلاص دقيق سائل-سائل مشتت
(DLLME)
(GC-MS)

لاستخراج الهيدروكربونات العطرية متعددة الحلقات (PAHs) من عينات المياه ، تم تطوير نهج جديد لتحضير العينات يعتمد على الاستخلاص الدقيق للسائل المشتت (DLLME). في هذا الإجراء ، تم حقن عينة من الماء بمزيج من رابع كلوريد الكربون ، و CCl₄ (مذيب الاستخلاص) ، والأسيتون (مذيب المشتت) لتوليد مستحلب يتم فيه استخلاص الهيدروكربونات العطرية متعددة الحلقات إلى قطرات دقيقة من مذيب الاستخلاص. تم استكشاف تأثيرات العديد من معاملات الاستخلاص ، بما في ذلك نوع مذيب الاستخلاص ونوع مذيب المشتت وحجم مذيب الاستخلاص وحجم المذيب المشتت. بالنسبة للفينانثرين والفلورانثين ، كان معامل ارتباط منحنى المعايرة 0.9993 (r^2) و 0.9973 على التوالي. بالنسبة للفينانثرين والفلورانثين ، كانت حدود الكشف (LODs) 0.0008 جم / مل و 0.0006 جم / مل على التوالي. بالنسبة للفينانثرين والفلورانثين ، كانت الانحرافات المعيارية النسبية (RSDs) 10.69 في المائة و 9.72 في المائة على التوالي. تراوحت معدلات استرداد المادة التحليلية من 100.5 إلى 107.8٪. تم اكتشاف الفينانثرين والفلورانثين في العينات

*Corresponding author:

E-mail addresses: nad.imrigha@sebhau.edu.ly, (M. M.Sanagi) Limos.far@utm.my, (S. Y. Sharef) sara_tabib2000@yahoo.com

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Introduction

Today, 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. The polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment [1] and they originated from both natural and anthropogenic sources. However, the term polycyclic aromatic hydrocarbons (PAHs) refers to a group of over a hundred substances that are environmentally persistent organic molecules with a wide range of toxicity. A range of causes, like as transportation, industry, and household heating, contribute to their extensive diffusion in the environment [2]. Because of the vast spread of these compounds, they are monitored in a variety of environmental matrices around the world, including drinking water, waste water, soil, and hazardous waste extracts. PAHs have been tracked as persistent organic pollutants (POPs) by various research organizations due to their high toxicity and carcinogenicity [3].

There have been developed and applied many analytical techniques for the analysis of PAHs compounds in the environment. These substances are typically extracted using liquid-liquid extraction (LLE) and/or solid-phase extraction (SPE)[4], as well as more classic methods including microwave-assisted extraction (MAE)[5]. Modern advancements in analytical chemistry, on the other hand, are geared at simplifying sample preparation. As a result, microextraction techniques play a significant role in the detection of PAHs. 3 As an alternative to the traditional LLE and SPE, solid-phase microextraction (SPME)[6], stirbarsortive extraction (SBSE)[7], and liquid-phase microextraction (LPME)[8] have been developed. Dispersive liquid-liquid microextraction (DLLME) is a simple and rapid preconcentration and microextraction method that has just been proposed and is widely used for determining organic pollutants in liquid samples, including PAHs[9]. According to a recent study, 16 dispersive liquid-liquid microextraction (DLLME) is a relatively novel approach used in analytical chemistry for sample pre-treatment that has great selectivity and sensitivity when compared to most classic extraction techniques[10].

Experimental

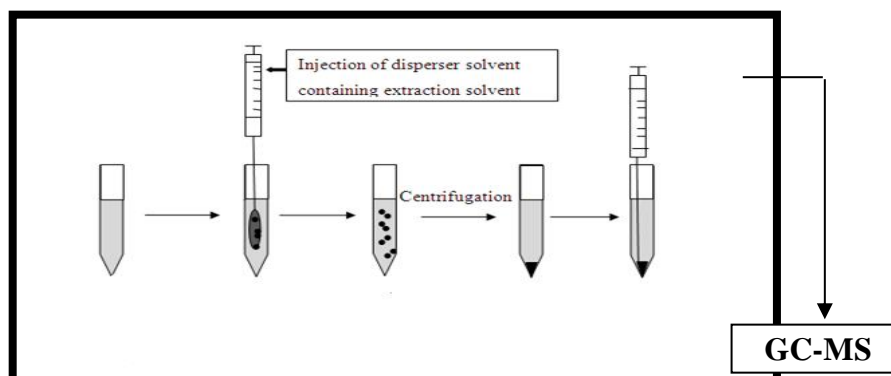


Figure 1: Schematic diagram of dispersive liquid-liquid microextraction procedure

Results and discussion

The efficiency of the dispersive liquid-liquid microextraction (DLLME) technique was studied using several parameters. The analytes were used in all of the parameter optimization studies (phenanthrene and fluoranthene). Extraction solvent and dispersive solvent, as well as volume of extraction and volume of dispersive solvents, were all evaluated. The DLLME technique was optimized using a solution of 0.1 mg/mL of each PAH in water. The findings are discussed in the next section.

1. Extraction Solvent Selection

In order to achieve successful extraction in the DLLME process, the extraction solvent must be chosen carefully. There are three things to think about. To begin, the solvent must have a high affinity for the chemicals being studied. Second, it should have a low water

Chemicals and Reagents

Fluka Chemika provided phenanthrene (397.0 percent as determined by HPLC) and fluoranthene (397.0 percent as determined by GC) 14. J.T Baker provided methanol (HPLC-grade) (Phillipsburg, USA). Each analyte's stock solution (1000 mg/mL) was produced in a 10 mL volumetric flask using methanol as the solvent. By diluting the stock solution with methanol, working standard solutions were created. When not in use, the stock solution and working standard solutions were kept in the freezer. Millipore Simplicity(Simpak®-2) filtered distilled water. (QRCTM) provided the AR-grade acetone, and Riedel-deHonR provided the acetonitrile ACN. Carbon tetrachloride CCl_4 (99.5%) and dichloromethane CH_2Cl_2 (99.5%) were acquired as extraction solvents from (QRCTM). The water sample was taken from a lake near UTM campus.

Instrumentation

Gas chromatograph 6890N networks system (Agilent Technologies 6890N) paired with mass spectrometer (Agilent Technologies 5973i) were used to analyze PAHs (USA). The HP5-MS column was used. Injector temperature was 200°C, beginning oven temperature was 180°C for 3.5 minutes, rose at a programmed rate of 10°C/min, and final temperature was 245°C for 0 minutes. The injector was set to split mode with a 1:30 ratio and a 1 μL injection volume.

Dispersive Liquid-Liquid Microextraction (DLLME)

In a 10mL screw cap glass test tube with conic bottom, 5mL of aqueous sample solution was inserted and spiked with an adequate amount of 0.1mg/L of working solution (2500 mL). A 3mL syringe was used to inject 1 mL acetone as disperser solvent and 60 mL CCl_4 as extraction solvent into the sample solution. The sample was then gently agitated in the test tube until an emulsion (water, acetone, and carbon tetrachloride) formed. The extraction phase settled at the bottom of the conical test tube after centrifugation at 3000rpm for 3 minutes. A 10mL HPLC microsyringe was used to remove the sedimented phase, which was then injected into the GC-MS. The DLLME process is shown in Figure1.

solubility. Third, it must have a density greater than that of water. Finally, when injected directly for chromatographic analysis, the organic solvent should cause no interference with the analyte peaks [11]. Two distinct extraction solvents were chosen based on these requirements: 1 carbon tetrachloride, CCl_4 (density 1.59g/mL) and dichloromethane, CH_2Cl_2 (density 1.33g/mL). A series of sample solutions were evaluated, each containing 60 μL of the extraction solvents and 1mL of the disperser solvent (CCl_4 or CH_2Cl_2). In general, CCl_4 was more efficient in terms of emulsion formation and a large volume of sedimented phase, whereas CH_2Cl_2 was less efficient. Therefore, carbon tetrachloride was preferred as extraction solvent.

2. Dispersive Solvent Selection

The miscibility of the disperser solvent in the organic phase

(extraction solvent) and the sample is the most important criterion for choosing it. As a result, acetone, acetonitrile(ACN), and methanol were investigated. 2 mL of each disperser solvent containing 60 µL of carbon tetrachloride was used to test a series of sample solutions

(as extraction solvent). The peak area of acetone as a disperser solvent is the largest (Figure 2.6). As a result, acetone was chosen as the dispersive solvent in this research.

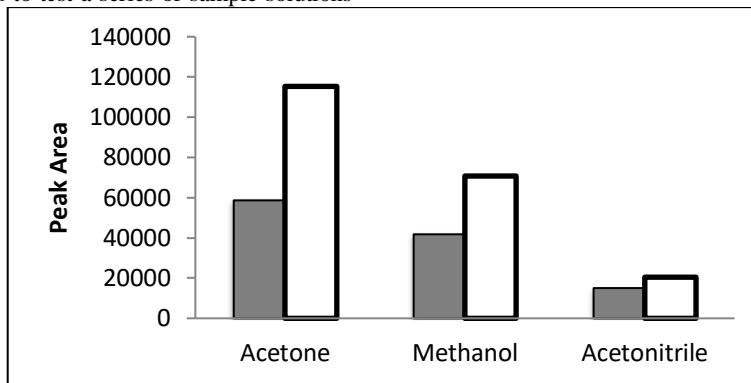


Figure 2: The disperser solvent selection.

3. Extraction Solvent Volume Effect

Solutions comprising varied amounts of carbon tetrachloride (CCl₄) were submitted to identical DLLME methods under the optimal conditions. The best condition is usually the least volume of extraction. However, when the amount of extraction solvent decreases, the sediment phase shrinks, and the sediment becomes too small to remove with a microsyringe[12]. To investigate the influence of extracting solvent volume on extraction efficiency, DLLME mixes

having various volumes of CCl₄ (60, 80, and 100 mL) and a fixed volume of acetone (1 mL) were utilized. The results demonstrate that increasing the volume of CCl₄ from 60 to 100mL reduced the volume of the sediment organic phase (Figure 3). As a result, the optimum volume of extraction solvent was determined as 60µL, which gives the maximum recoveries for all PAHs.

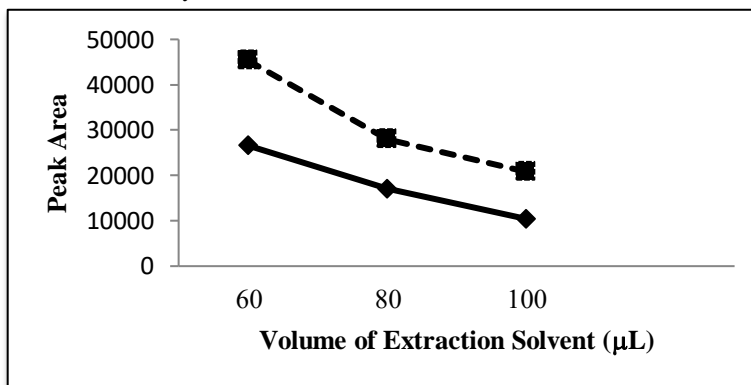


Figure 3: Extraction solvent volume effect on DLLME.

4. Dispersive Solvent Volume Effect

The volume of dispersive solvent is critical for the extraction solvent to form very fine droplets, which have a direct impact on extraction efficiency. However, because changing the volume of the dispersive solvent would change the volume of the sediment phase, it is impossible to quantify the effect of the dispersive solvent volume on extraction efficiency[13]. The effect of acetone volume 1 as a disperser solvent was investigated using various volumes (0.5, 1, and 1.5 mL) of carbon tetrachloride (CCl₄) as the extracting solvent. The

results (Fig.4) revealed that as the disperser solvent volume increased from 0.5 to 1 mL, the extraction efficiency increased. However, as the volume of acetone was increased from 1mL to 1.5mL, the extraction efficiency declined. The results also revealed that when using a little amount of acetone, the emulsion state did not form adequately, and the extraction recovery was reduced. However, as the solubility of PAHs in water increases in the presence of a large amount of acetone, the extraction efficiency declines. As a result, 1mL of acetone was chosen as the best disperser solvent volume.

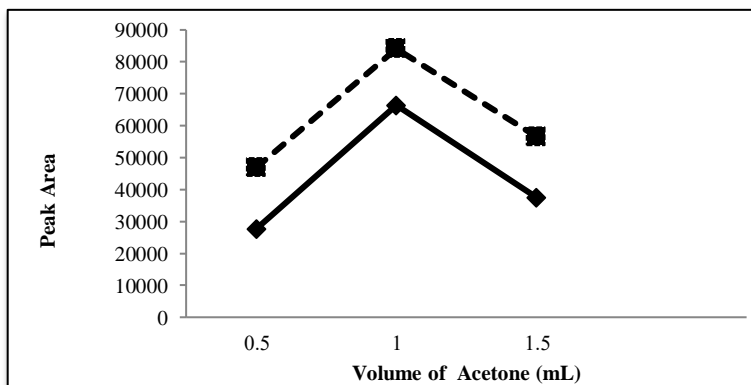


Figure 4: Disperser solvent volume effect on DLLME

Analytical performance

With four concentration levels, phenanthrene and fluoranthene calibration curves were created in the range of 0.02–0.15 µg/mL. Under optimal conditions, the correlation coefficients (r^2) 1 0.9993 and 0.9973 were obtained. The PAH compounds had LODs of 0.0008

and 0.0006 µg/mL, respectively. The recovery rates for phenanthrene and fluoranthene were 100.5 and 107.8%, respectively, with relative standard deviations (RSDs) of 10.69 and 9.972 percent.

Table 1. The correlation coefficients (r^2), LODs and LOQs of PAHs form water sample.

PAHs	Correlation coefficient (r^2)	LOD (µg/mL)	LOQ (µg/mL)
Phenanthrene	0.9993	0.0008	0.002
Fluoranthene	0.9973	0.0006	0.001

Real sample analysis

The proposed approach was used to analyze the PAHs in the real sample utilizing the newly designed DLLME method under optimal conditions. Lake water was gathered from the UTM campus's lake (JB, Malaysia). The findings for lake water 2 revealed that the target analytes were present in trace amounts in the sample. To confirm the

presence of PAHs, the sample was spiked with 0.1 µg/mL of a combination of fluoranthene and phenanthrene. Figure 5 shows the chromatogram of a lake water sample spiked at 0.1 µg/mL concentration level.

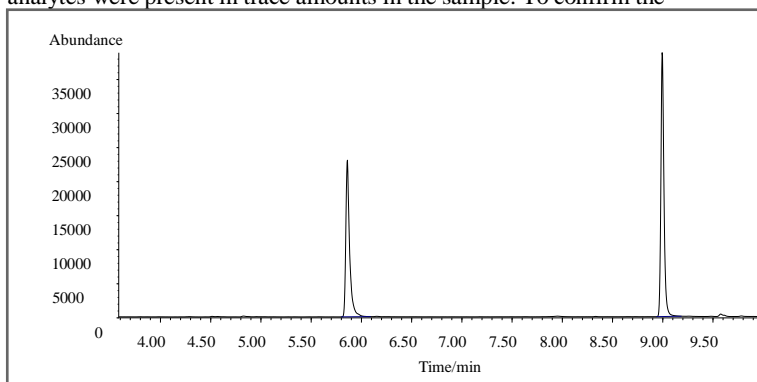


Figure 5: DLLME- GC-MS analysis of PAHs in water sample. Extraction conditions: disperser solvent volume, 0.5 mL, 1 mL, and 1.5 mL; extraction solvent volume, 60 µL of CCl₄; sample volume, 5 mL; stirring rate, 3000 rpm; extraction time, 3 min; concentration of phenanthrene and fluoranthene, 0.1 µg/mL.

Conclusion

The measurement of phenanthrene and fluoranthene in water samples was done using dispersive liquid-liquid microextraction combined with gas chromatography-mass spectrometry (GC-MS). The method's attractive qualities have brought value to the analysis procedure of phenanthrene and fluoranthene in water samples, such as simplicity of operation, speed, low cost, high recovery, high enrichment factor, and extremely short extraction time (a few seconds). The selection of extraction solvent, disperser solvent, extraction solvent volume, and disperser solvent volume were all explored as factors affecting DLLME performance. However, the DLLME approach in combination with GC-MS was successfully used to analyze PAHs in a lake water sample.

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