

Application of Selected Ion Monitoring -Gas Chromatography Mass Spectrometry (SIM-GCMS) for quantification of Poly Aromatic Hydro carbons in surface water from Sarawak, Mambong River (Malaysia)

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Abstract

Background:

Objective: The study presented here carried out the ultra-trace Quantification of Poly Aromatic Hydro carbons in surface water using Selected Ion Monitoring with optimization Gas Chromatography Mass Spectrometry parameter. **Methods:** A Shimadzu QP 2010 Plus GCMS equipped with an auto-injector AOC-20i, 30 m x 0.25 mm x 0.25 μ m of BP-X5 capillary column (SGE, USA) was used to obtain the result of poly aromatic hydrocarbons to separate and quantify the PAH compounds as well as to identify the Polyromantic Hydrocarbon using USEPA. **Result:** The amount of polycyclic aromatic hydrocarbons (PAHs) at ultra-trace level in the surface water samples were estimated. Sixteen Poly Aromatic Hydro carbons were identified among which Naphthalene Pyrene (45.7ng/L), Chrysene (59.38ng/L), Benzo (g, h, i) perylene (40.35ng/L) as the major pollutants in the water surface of Mambong River water. Total Poly Aromatic Hydro carbons (PAHs) concentrations ranged from 2.0 to 40 ng L⁻¹ was detected in the river water. **Conclusion:** The Selected Ion Monitoring -Gas Chromatography Mass Spectrometry (SIM-GCMS) can be considered as sensitive and robust method to analyse PAHs contamination in environmental samples. Thus, help the researchers to uncover the critical areas of environmental pollution at ultra-trace level that many researchers were not able to explore.

Keywords: SIM, GCMS, PAHs, River, Hydrology.

INTRODUCTION

Improper land practices and anthropogenic activities led to water pollution. Population increase, urbanization, industrial activities, agricultural activities, environmental degradation, deforestation, land clearing, domestic sewage pollution and contamination of pesticides and fertilizer are among the most common factors that affect the water quality of river [1,2].

Poly aromatic hydrocarbons (PAHs) are one of the pollutants that are potentially harmful to human beings and the environment. PAHs have the potential to harm living organisms due to their potential toxicity and the ability to bioaccumulate in aquatic ecosystem. Besides, PAHs are highly persistent, either essential or non-essential, and they have a particular significance in ecotoxicology [3]. When the intake of PAHs is in excess, they will also produce toxic effects.

In recent times there are great improvement in the detection of pollutant in the water system because of the upgrade in the equipment making it easier to analysis and monitor the pollution in the ecosystem. However, monitoring and management of the ecosystem has become a challenge especially in developed countries where system of disposal of waste is failing among industries and factories. Where they play a great role in the increase in water pollution.

Poly Aromatic Hydrocarbons (PAHs) are one of the important indicator of the environmental pollutants because of its function as having mutagens and carcinogens agents [1]. They were considered as a priority pollutant among the environmental protection agency around the world especially United State Environmental Protection Agency (EPA) [2]. PAHs are derivitazation of natural and caused or produced by human sources. Natural sources such as forest and ecosystems such as temperate grasslands, savannahs, and shrub lands biome by ecologists, engulfed with fires [3] or post-depositional transformations of secretions and metabolites of plants or animals' precursors [4] while anthropogenic sources are inclusive of combustion of fossil-fuel [5], distance change in atmospheric transportation of the poly aromatic hydro carbon (PAHs) [6]; leaching of the urban runoff [7] and spillage of crude oil from petroleum factories and its refined products from the sister companies [8]. These organic pollutants are omnipresence. They are found virtually in every aspect of our life, in the food we eat, the water we take, soils, sediments and as much as air [5].

Poly Aromatic Hydro carbons (PAHs) are now becoming a source of concern because they are highly persistent and can accumulate in the ecosystem. Thus, presence of these hydrocarbons (PAHs) in the food we take, water, soils, sediments and air water has currently become an environmental concern.

Few years back, water pollution is becoming severe in environmental issues all over the world especially developing countries such as Nigeria and Malaysia to mention are few. Water in such area especially in Mambong River Malaysia has been contaminated heavily in some regions and quality of water is particularly a source of concern. In addition, the problem of water quality in industrial and abandoned mining lands was outstanding. The Urban and road runoff waters also contribute to pollution of river water. It was reported [6], PAHs are more concentrated in sludge of some river water, within the range of 400-900 times the Dutch threshold value for polluted soils [6]. However, concentrations of PAHs in river water must be evaluated and controlled.

Different techniques and equipment was developed for the determination of organic compounds in ecosystem, especially rivers, wells, leaks and sea water samples. PAHs can be

studied using aqueous matrixes such as liquid-liquid phase extraction [14], Solid-liquid Phase Extraction (SPE) [12], Solid- Phase Micro Extraction (SPME) [13], micro wave Extraction (SBSE) [14, 15]. Detection of this organic compounds, the PAHs can be studied using Gas Chromatography (GC), pyrolysis GCMS or High Performance Liquid Chromatography (HPLC). Detection limits for the EPA-PAHs depend on the selected concentration method and as well as using SPE coupled to HPLC / fluorescence within the range of ngL-1. However, the extraction was complicated and exposed to the loss of PAHs and contamination.

Compared to normal scan MS modes, Selected Ion Monitoring Mass Spectrometry (SIM-MS) offers a higher degree of sensitivity. The use of SIM-MS enables the analysis of trace level of organic molecule in the presence of interfering compounds without losing identification capability due to a drastic reduction of the background signal [9]. The use of Triple quad technology has also made it easier and clearer to recover different mass spectra, the precursor ions, the product ions and the quantifier ions.

In this study, optimization method for GC-MS SIM was develop as a sensitive alternative tools for quantitative analysis. It is very important to use sensitive and reproducible method to analyse ultra-trace compounds in environment. Several parameters for temperature programming such as sampling time and temperature rate also studied to obtain excellent efficiency of detection. To confirmation the parameters such as linearity, reproducibility, limits of detection and quantification are all put in to consideration when it comes to application of Selected Ion Monitoring -Gas Chromatography Mass Spectrometry (SIM-GCMS) for quantification of Poly Aromatic Hydro carbons.

Thus, the procedure was then used for the real environmental samples. The method of extraction was modified for optimum, efficient and quick result. The aim of this study is the application of Selected Ion Monitoring -Gas Chromatography Mass Spectrometry (SIM-GCMS) for quantification of Poly Aromatic Hydro carbons in surface water.

MATERIALS AND METHOD

Standard

Low Level Standard Reference Material PAH (5ng/ml) was purchased from Sigma Aldrich.

Sample preparation

The water samples used in this study were collected from two different stations in Mambong, Sarawak River. These sampling stations called upper stream Sungai Sinai and downstream Sungai Endap. The locations of these sampling site are shown in Figure 1 and 2. The water samples collected was deposited to Water Research Lab for PAHs extraction.

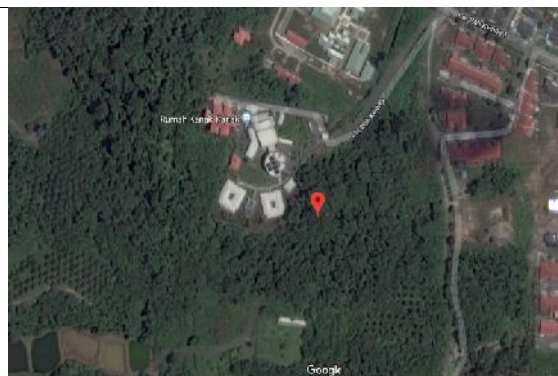


Figure 1. Upper stream Sungai Sinai



Figure 2. Downstream Sungai Endap.

Sample collection

Samples were collected in 500-mL amber glass bottles. A 100-mL aliquot of the sample was taken and placed in a 250-mL amber screw cap bottle. Liquid-liquid extraction (LLE) was performed to separate compounds based on their relative solubilities in different immiscible liquids followed by [16,17]. In this method, the water sample poured into a Schott bottle with the mixture of hexane: dichloromethane (1:1 v/v) and sonicate for 10 minutes. The organic phase was poured into clean beaker and 10g of anhydrous magnesium sulfate was added. Re-extraction was performed by using 50 ml of the same solvent. Finally, the extract was concentrated and was transferred to insert glass tube for GCMS analysis.

Gas Chromatography Mass Spectrometry

A Shimadzu QP 2010 Plus GCMS equipped with an auto-injector AOC-20i, 30 m x 0.25 mm x 0.25 μ m of BP-X5 capillary column (SGE, USA) was the model used for the separation and quantification of the application of Selected Ion Monitoring -Gas Chromatography Mass Spectrometry (SIM-GCMS) for quantification of Poly Aromatic Hydro carbons (PAHs) compounds. The samples were introduced in the split less mode with an injection temperature of 300 °C. The transfer line and ion source temperatures was 320 °C and 200 °C. The column temperature was initially held at 50 °C for 5 min, and then raised to 180 °C at the rate of 25 °C per minutes, then to 220 °C at the rate of 10 °C per minutes, and finally to 300 °C at the rate of 5 °C per minutes, held at final temperature for 15 min. Detector temperature was kept at 320 °C. The carrier gas was Helium which was used at a constant flow rate of 1 mL per minutes. Mass spectrometry was acquired using the electron ionization (EI) and selective ion monitoring (SIM) modes. The ion mass program used for quantification is detailed in Table 1.

The validation calibration of Calibration curve

In this study, spiked calibration standard approach was used to overcome the problems caused by the matrix. In this approach, calibration standards were prepared by the addition of standard solution to blank water samples that are subjected to the same sample preparation procedure which is intended to be used for a new sample. In this way, the standard sample matrices will have the same composition as the new samples and therefore the effect of

matrix is reflected in both standards and the new (unknown) samples. The calibration curve will be obtained using the spiked calibration standards to calculate the concentration of analyte (s) in unknown sample without being concerned about the matrix effects. The developed method has the advantage of using spiked calibration curves that minimize the matrix interferences. The precision of this method corresponding to the values of relative standard deviation (RSD) values below than 10% for five-point calibration curve of individual compounds. Mean percentage error (MPE) computed using;

$$\frac{100\%}{n} \sum_{t=1}^n \frac{a_t - f_t}{a_t}$$

Where n= number of number of replicates (n=10), a_t approximate value and f_t is estimated value. Low MPE indicates that the calculated Limits of detection (LOD) and Limits of quantification (LOQ) in water are applicable.

Table 1. GC-MS SIM condition and parameter.

PAHs Individual	No.of rings	Retention Time (RT)	Retention Factor	Molecular mas	Selected m/z
Naphthalene	2	16.97	9.0	128	127,128,129
Acenaphthylene	3	19.388	8.7	152	151,152,153
Acenaphthene	3	22.525	8.7	154	154,153,152
Fluorene	3	23.176	8.4	166	166,165,167
Phenanthrene	3	24.95	7.7	178	178,179,176
Anthracene	3	28.323	11.0	178	178,176,179
d-10 Anthracene (I std)	3	28.53	10.0	188	188,186,189
Fluoranthene	4	32.505	8.8	202	202,201,203
Pyrene	4	33.227	7.7	202	202,200,203
Benzo(a)anthracene	4	37.495	3.7	228	228,229,226
Chrysene	4	37.669	6.1	228	228,226,229
Benzo(b)fluoranthene	5	41.11	2.7	252	252,253,125
Benzo(k)fluoranthene	5	41.223	2.6	252	252,253,125
Dibenz(a,h)anthracene	5	45.302	4.2	278	278,139,279
Benzo(g,h,i)perylene	6	45.894	2.3	276	276,138,277

RESULTS AND DISCUSSION

The aim of the present study was to develop and evaluate a rapid, simple and inexpensive technique to measure Poly Aromatic Hydro carbons (PAH) in surface water. Result have shown validation PAHs from the GC-MS as well as in water was perform by using five-point calibration curve (5 to 10 ng), procedural blank, check standard and sample duplicates were carried out for every set of samples. The LODs and LOQs were calculated based on the signal-to-noise ratio of equal to 3 and 10, respectively. Repeatability, RSD%, LODs and LOQs under optimized conditions are summarized in Tables 2. The validation parameters examined were in agreement with the European Union provision of No. 836/2011.

Table 2. Summary of validation of GC-MS SIM method.

Poly Aromatic Hydrocarbons	Mean	SD	%RSD	LOD	LOQ	Water		Mean % Error
						LOD	LOQ	
Naphthalene	2.17	0.05	2.23	2.31	2.65	0.02	0.03	-56.62
Acenaphthylene	4.71	0.27	5.82	5.54	7.46	0.06	0.07	-5.72
Acenaphthene	4.79	0.07	1.42	5.00	5.47	0.05	0.05	-4.18
Fluorene	4.84	0.09	1.96	5.13	5.79	0.05	0.06	-3.14
Phenanthrene	4.63	0.13	2.85	5.03	5.95	0.05	0.06	-7.38
Anthracene	4.94	0.04	0.79	5.05	5.33	0.05	0.05	-1.30
Fluoranthene	4.74	0.05	1.07	4.89	5.25	0.05	0.05	-5.14
Pyrene	4.95	0.04	0.90	5.09	5.40	0.05	0.05	-0.94
Benzo(a)anthracene	4.87	0.01	0.26	4.90	4.99	0.05	0.05	-2.70
Chrysene	4.86	0.02	0.42	4.92	5.06	0.05	0.05	-2.84
Benzo(b)fluoranthene	4.47	0.03	0.59	4.54	4.73	0.05	0.05	-10.68
Benzo(k)fluoranthene	4.56	0.01	0.32	4.61	4.71	0.05	0.05	-8.76
Benzo(a)pyrene	4.92	0.01	0.28	4.96	5.06	0.05	0.05	-1.56
Dibenz(a,h)anthracene	4.99	0.14	2.90	5.43	6.44	0.05	0.06	-0.14
Benzo(g,h,i)Perylene	4.97	0.13	2.57	5.35	6.25	0.05	0.06	-0.60
Indeno(1,2,3-cd)Pyrene	4.95	0.12	2.38	5.31	6.13	0.05	0.06	-0.96

*%RSD: Percent Relative Standard Deviation, SD: Standard Deviation

The validation calibration graphs indicated the linearity for Naphthalene, Acenaphthene, Fluorene and the Phenanthrene, Anthracene, Pyrene, Benz [a] anthracene, Chrysene, Benzo [b] fluoranthene, Benzo[k]fluoranthene, Benzo[a] pyrene, Dibenz [a, h] anthracene, Benzo [g, h, i] perylene were observed within the concentration range of 0.1-2.8 and 0.35-2.8 ngmL⁻¹, respectively. The coefficients of determination (r²) was between the range of 0.983 and 0.999 for all PAHs. It was observed that the extraction process and analytical method after validation have enough efficiency for the determination of PAHs at trace levels. This information can be used in assessment of the pollution status of the ecosystem as well as the risk to human who consume PAH contaminated animals [18,19,20].

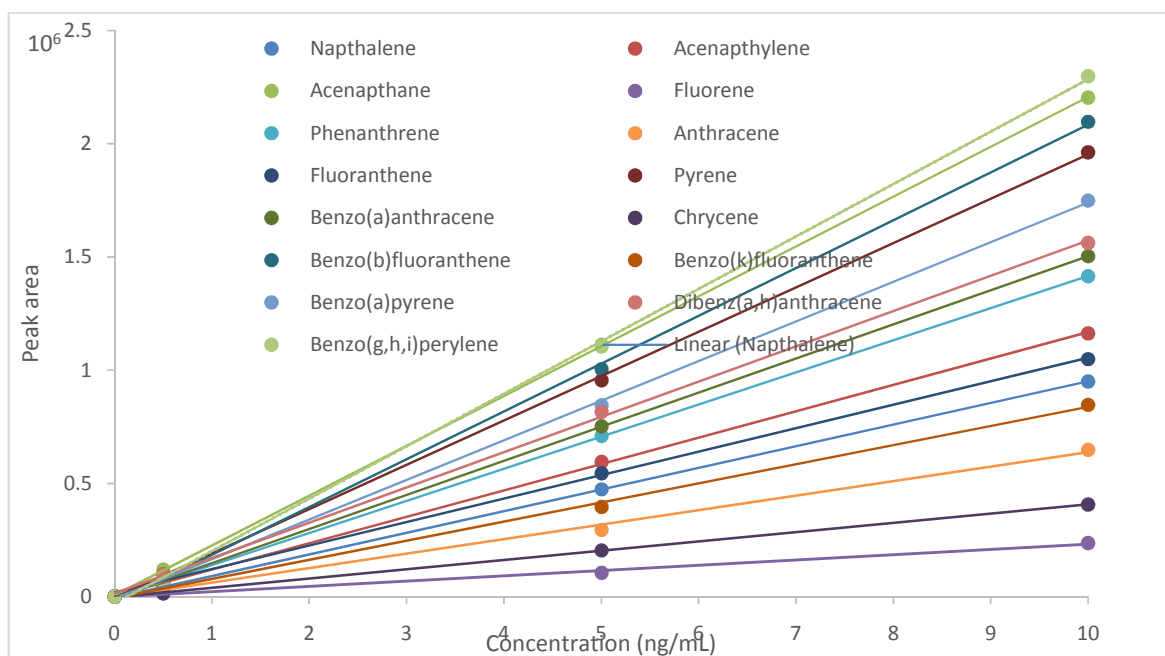


Figure 1. Calibration curve for individual PAH with coefficients of determination (r^2) was between the range of 0.983 and 0.999 for all PAHs.

Concentration distributions of Σ PAHs in water from Sarawak, Mambong River, and these rivers water result shown in Table 3 reveal that the PAHs detected in ultra-trace level in downstream river water whilst not detected at upper stream in the direction toward the waste treatment plant. This indicates that the SIM method with optimization of GCMS parameter can increase the response sensitivity. However, these detected PAH will help awareness as to the ingestion of this sediment and suspended particles containing PAH or PAH contaminated prey which can result in this PAH being absorbed by human [21].

Table 3. Concentration of PAHs from environmental samples.

PAHs Individual	Upper stream	Down stream
		Concentration (ng/mL)
Naphthalene	-	7.80
Acenaphthylene	-	5.71
Acenaphthene	-	9.20
Fluorene	-	2.60
Phenanthrene	-	3.20
Anthracene	-	7.40
d-10 Anthracene (Istd)	-	2.40
Fluoranthene	-	2.07
Pyrene	-	7.70
Benzo(a) anthracene	-	5.72
Chrysene	-	9.38

Benzo(b)fluoranthene	-	7.76
Benzo(k)fluoranthene	-	4.56
Dibenz(a,h)anthracene	-	3.45
Benzo(g,h,i)perylene	-	6.36

CONCLUSION

Selected Ion Monitoring can be used to perform quantification analysis in ultra-trace level. Optimization of GCMS parameter can enhance the response of detection. In this study, SIM method shows that the concentration of PAHs in downstream river water was successfully detected on ultra-trace level. On the contrary, all the PAHs was not detected in upstream river water. This may be related to the sources of PAHs in the study area. Thus, it is expected for researchers to uncover the critical areas of environmental pollution on the sediment, Aquatic organisms, and plants at ultra-trace level of PAH that were not explored using selected ion monitoring (SIM).

SIGNIFICANCE STATEMENT

This study will help the researchers to explore the critical areas of environmental pollution at ultra-trace level that many researchers were not able to explore. As well as to understand the potential of optimization parameter of GCMS in SIM mode that can be used for detection and quantification of ultra-trace level of compounds in an environment.

CONFLICT OF INTERESTS

We declare that we have no conflict of interest.

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