Original Research Article

An ultra-trace Quantification of Poly Aromatic Hydro carbons using Selected Ion Monitoring Gas Chromatography Mass Spectrometry in Sarawak, Mambong River

Abstract

By applying the selected ion monitoring (SIM) with optimization of GCMS parameter, the amount of polycyclic aromatic hydrocarbons (PAHs) at ultra-trce level in the environmental samples were estimated. The 16 PAHs identified by the USEPA as important pollutants were determined in the water surface of water river. Total PAHs concentrations ranged from 2.0 to 40 ng L^{-1} was detected in river water. Source analysis revealed that the posibilities of PAHs sources mainly came from waste treatment plant, quarry and combustion process. Gas Chromatography Mass Spectrometry Selected Ion Monitoring can be considered as sensitive and robust method to analyse PAHs contamination in environmental samples.

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

INTRODUCTION

During the last decades, tremendous improvements in analytical instrumentation have allowed a better detection of pollutant in diluted systems such as water. However monitoring of pollution of ecosystems is still an ongoing challenge. PAHs are one of the important indicator of the environmental pollutants due to their mutagenic and carcinogenic properties [1]. They are listed in the US Environmental Protection Agency (EPA) priority pollutant list [2]. PAHs are derivitazation of natural and anthropogenic sources. Natural sources such as forest and prairie fires [3] or post-depositional transformations of biogenic precursors [4] while anthropogenic sources are inclusive of combustion of fossil-fuel [5], long-range atmospheric transport of PAHs [6]; urban runoff [7] and spillage of petroleum and its refined products [8]. These organic pollutants are omnipresence. They are found, for example, in food , water, soils, sediments and air particulates [5]. In recent years, they have received considerable attention as, in addition to their toxicity, they are highly persistent and can accumulate in environmental aqueous systems. Presence of PAHs in water is now part of environmental concern.

Few years back, water pollution is becoming severe environemental issues in all over the world especially developing contries including Malaysia. Water has been contaminated heavily in some regions and quality of water is particulary concerning. In addition, the problem of water quality in industrial and abandoned mining lands was outstanding. Urban and road runoff waters contribute to pollution of river water. Previous studies show that PAHs are highly concentrated in sludge of some river water, i.e. 400-900 times the Dutch threshold value for polluted soils [6]. Thus, concentrations of such compounds in river water must be evaluated.

Various type of analytical techniques have been developed for the determination of organic compounds in water samples. PAHs can be extracted from aqueous matrixes by few methods 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 is performed by Gas Chromatography (GC), pyrolysis GCMS or High Performance Liquid Chromatography (HPLC). Detection limits for the EPA–PAHs depend on the selected concentration method and the detection.

SPE coupled to HPLC / fluorescence is the most common procedure to quantify PAH traces in water with a detection limit in the range of ngL-1. However, the extraction were 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. SIM–MS enables the analysis of organic molecule trace levels in the presence of interfering compounds without losing identification capability due to a drastic reduction of the background signal [9]. Triple quad technology directly enables the recovery of three different mass spectra (precursor ions, product ions and neutral fragments).

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 reproducable 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. Validation parameters such as linearity, reproducibility, limits of detection and quantification are determined. Finally, the procedure is applied to the real environmental samples. The method of extraction was modified for optimum, efficient and quick result.

MATERIALS AND METHOD

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.

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. A 50-uL amount of 35% ammonia solution was added by pipette, and the sample was diluted with ultrapure water to approximately 200-mL. The internal standard solution was spiked followed by 10mL of hexane. The vessel was then placed on a bottle roller overnight (12 hours) to extract the PAHs into organic phase.

A pipette was used to take a 5-mL aliquot of the organic hexane phase. This was then concentrated by using nitrogen gas to 200 uL and was transferred to insert glass tube for GCMS analysis.

Gas Chromatography Mass Spectrometry

A Shimadzu QP 2010 Plus GCMS equipped with an autojector AOC-20i, 30 m x 0.25 mm x 0.25 umof BP-X5 capillary column (SGE,USA) was used to separate and quantify the PAH compounds. The samples were injected in the splitless mode at an injection temperature of 300 °C. The transfer line and ion source temperatures were 320 °C and 200 °C. The column temperature was initially held at 50 °C for 5 min, raised to 180 °C at the rate of 25 °C/min, then to 220 °C at the rate of 10 °C/min, and finally to 300 °C at the rate of 5 °C/min, held at final temperature for 15 min. Detector temperature was kept at 320 °C. Helium was used as a carrier gas at a constant flow rate of 1 mL/min. 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.

RESULTS

Table 1. GC-MS SIM condition and parameter.

Comment [CP1]: center values

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 (Istd)	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)antharacene	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

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

Comment [CP2]: center values

PAHs Individual	Recovery	Limit of detection (LOD)	Limit of Quantitation (LOQ)	R^2
	%	(ngL^{-1})	(ngL^{-1})	
Naphthalene	45	1.3	3.8	0.995
Acenaphthylene	60	1.3	7.6	0.999
Acenaphthene	75	1.2	7.5	0.998
Fluorene	75	1.4	2.7	0.996
Phenanthrene	57	1.3	2.5	0.999
Anthracene	48	0.5	2.5	0.995
d-10 Anthracene (Istd)	53	1.1	2.5	0.999

Fluoranthene	78	1.1	3.2	0.998
Pyrene	40	2.5	4.5	0.996
Benzo(a)antharacene	55	2.5	4.5	0.999
Chrysene	92	3.0	4.8	0.995
Benzo(b)fluoranthene	46	3.0	5.5	0.999
Benzo(k)fluoranthene	85	1.5	5.5	0.998
Dibenz(a,h)anthracene	78	2.0	6.8	0.996
Benzo(g,h,i)pery lene	90	1.5	4.0	0.999

Table 3. PAHs from environmental samples.

PAHs Individual	Upper stream	Down stream
	Concentration (ngL^{-1})	
Naphthalene	-	7.80
Acenaphthylene	-	11.50
Acenaphthene	-	9.2
Fluorene	-	2.6
Phenanthrene	-	3.2
Anthracene	-	31.4
d-10 Anthracene (Istd)	-	2.4
Fluoranthene	-	2.0
Pyrene	-	45.7
Benzo(a)antharacene	-	10.76
Chrysene	-	59.38
Benzo(b)fluoranthene	-	17.76
Benzo(k)fluoranthene	-	4.56
Dibenz(a,h)anthracene	-	3.45
Benzo(g,h,i)perylene	-	40.36

Comment [CP3]: center values and -

DISCUSSIONS

Method validation

Comment [CP4]: To delete if it is the only subtitle

The calibration graphs showed that the linearity for Naphthalene, Acenaphthene, Flourene and for Phenanthrene, Anthracene, Pyrene, Benz[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Dibenz[a,h]anthracene, Benzo[ghi]perylene were observed over the concentration range of 0.1-2.8 and 0.35-2.8 ngmL^{-1}, respectively. The coefficients of determination (r^2) were between 0.983 and 0.999 for all PAHs. It shows that the extraction process and analytical method after validation have enough efficiency for the determination of PAHs at trace levels. In the present study, we used spiked calibration standard approach to overcome the problems caused by the matrix. In this approach, calibration standards are 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 unknown samples. In this way, the standard sample matrices will have the same composition as the unknown samples and therefore the effect of matrix is reflected in both standards and unknown samples. The calibration curve is constructed using these spiked calibration standards and it is easily used 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.

Limits of detection (LODs) and Limits of quantification (LOQs) were calculated based on the signal-to-noise ratio of equal to 3 and 10, respectively. Recovery, repeatability, RSD%, R^2, LODs and LOQs of the method under optimized conditions are summarized in Tables 2. As shown in these tables, all of the validation parameters examined were in compliance with EU provision No. 836/2011. Therefore, the attained validation parameters are acceptable and the optimized and validated method can be used to analyze the real samples. Hence, the optimized method were applied to analyze 50 mineral water samples which were collected from Tehran market.

Comment [CP5]: For what purpose? Where are the results?

Concentration distributions of ΣPAHs in these rivers water shown in Table 3 reveal that the PAHs can be detected in ultra-trace level in river water whilst not detected at upper stream in the direction toward the waste treatment plant. This indicates that the the SIM method with optimization of GCMS parameter can increase the response sensitivity.

CONCLUSION

Selected Ion Monitoring can be use 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 down stream 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.

SIGNIFICANCE STATEMENT

This study discovered the important of optimization parameter of GCMS in SIM mode that can beneficial the detection and quantification of ultra-trace level of compounds. This study will help the researchers to uncover the critical areas of environmental pollution at ultra-trace level that many researchers were not able to explore. Thus a new theory on quantification of ultra-trace level may be arrived at.

CONFLICT OF INTERESTS

We declare that we have no conflict of interest.

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