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Analysis of Polycyclic Aromatic Hydrocarbon Using Programmable Temperature Vaporization Inlet Couple with Gas Chromatography Mass Spectrometry (PTV-GC-MS)

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ABSTRACT

The conditions in programmable temperature vaporization inlet of a gas chromatography-mass spectrometry (PTV-GC-MS) were optimized to enhance the detection of five compounds of polycyclic aromatic hydrocarbon (PAH) namely acenaphthylene, fluorene, anthracene, phenanthrene and pyrene. PTV parameters such as injection volume, vent pressure, vent time, vent flow, initial heating rate, purge flow rate, purge time and injection delay time were optimized. The optimized injection volume was 150 μL , which was introduced into the inlet by six times repeating injection of 25 μL using automatic liquid sampler at an interval of 5 seconds between each injection. The optimized vent flow and pressure are 400 mL/min and 5 psi for 2 minutes, respectively. The purge flow rate and initial heating rate were optimized to 400 mL/min for 2 minutes and 400 $^{\circ}\text{C}/\text{min}$. The performance of PTV solvent vent mode was compared to the splitless injection mode. The obtained limit of detection (LOD) in solvent vent mode was approximately five to six times lower than the limit obtained in splitless injection mode. The determined recoveries varied from 98.1 to 98.9% with pooled relative standard deviations ranging from 9.8 to 11.4%.

Keywords: polycyclic aromatic hydrocarbon, PAHs, PTV injection, solvent vent mode, GC-MS (EI)

INTRODUCTION

PAHs are ubiquitous in the environment. Some of the PAH compounds are highly carcinogenic, mutagenic and toxic and usually found in drinking water [1]. The US EPA (US Environmental Protection Agency) has classified sixteen PAHs as priority organic pollutants [2]. PAHs usually contain two to seven benzene rings consist of carbon and hydrogen atoms and are able to bind strongly to soot, soil and dust particles. Most of the PAH compounds are colorless, white or pale yellow-green solid. PAHs are produced as by-products from

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incomplete combustion of organic materials such as coal, wood or petroleum. Leakages or accidents in extraction, delivery or refinery of petroleum are the main sources where huge amount of PAHs are released into the environment. Besides that, PAHs are also released into ambient air through dust from rubber products such as car tyres due to abrasion process [3]. Tobacco smoke [4], smoked meats [5], tar oil [6], soft toys, childcare products [7] and extender oils used to improve elasticity in rubber products [8] also contain PAHs, which could penetrate through human skin, lung and digestive system. Other than that, some PAHs are also used to make dyes, plastics, and pesticides including medicines [3]. The effects of PAHs on laboratory animals such as mice are damage to skin, body fluid, immune system and tumors formation [9].

PAHs are not very amenable to go through solid-phase extraction and liquid-liquid extraction due to their non-polar nature and adsorption onto walls of extraction vessels. Moreover, these methods may require large solvent volume which may not agree to environmental friendly practices. Besides that, solid-phase microextraction (SPME) and stir bar sorptive extraction (SBSE) techniques can effectively reduce the amount of solvent used. However, both techniques require expensive apparatus [10-14].

The levels of PAHs in air and water are found to be as low as a few pg/m^3 ; whereas the levels in sediment and soils are in the range of ng/kg . Such low concentration levels are impossible to make in-depth investigation of PAHs becomes successful due to insufficient amount of the collected samples for instrumental analysis even though large volume of sample is used. Most of the times, instruments do not have the capability to detect the PAHs and not detected results are reported quite often [15]. Because of this, a new pre-concentration methodology is necessary to be developed for investigation of trace amount of PAHs in environmental samples such as air, water, soil and etc.

Samples containing PAHs are usually analyzed using GC-MS splitless injection mode [16-21], which is most commonly used for trace analysis; however, it has several disadvantages since it is a hot vaporizing device. In order to improve the sensitivity of the analytical instrument and the low concentration analyte can be detected; PTV inlet was invented based on a splitless inlet in late 1970s. After that, PTV started to evolve from cool injection in split or splitless mode to temperature programmable mode, which allows large volume of sample solution to be injected into the inlet [22]. Currently, the Agilent Programmed Temperature Vaporization (PTV) Inlet System has five operating modes; i.e. split, pulsed split, splitless, pulsed splitless and solvent vent modes [23]. Due to its complexity compared to traditional splitless inlet, optimization of the PTV inlet conditions is necessary in order that it can handle sample with wide range of concentrations [15]. PTV may transfer maximum of 500 μL of a liquid sample to the GC inlet through multiple injection using a typical 50- μL syringe, which can inject up to 25 μL for each injection [24]. In PTV inlet, the samples are injected into a cold liner and subsequently, a temperature controlled program is used to quickly heat the liner. This technique is able to selectively eliminate injected solvent before transferring the analytes into the separation column [25, 26]. The inlet temperature is adjusted in order that it below

solvent boiling point, thus it can effectively decrease the discrimination of less volatile contents in the sample. In addition, since the resistance time of the injected sample at elevated temperature is shorter than that in the splitless injection mode, this can prevent thermal degradation and enhance the sensitivity [27]. Control of the time interval between each injection is necessary to ensure the elimination of solvent from the liner is completed.

The analytical sensitivity for analytes with low concentration can be greatly enhanced by increasing the injection volume from small to large volume. This is because for most PAHs, the response of the mass spectrometric detector increases proportionally to the total injection volume. Besides that, by eliminating or shortening the solvent evaporation step, which is time consuming and subject to loss of chemicals due to elevated high temperature or in vacuum condition, tedious sample pre-treatment procedures can be simplified [15]. The aim of this study was to optimize the conditions of PTV solvent vent injection mode in order that the sensitivity of the analysis of five PAHs can be enhanced. The performances between splitless injection and PTV solvent vent modes were compared in this study.

EXPERIMENTAL

Chemicals

Five PAHs i.e. acenaphthylene, fluorene, anthracene, phenanthrene and pyrene with purity of 99% were purchased from Sigma-Aldrich USA. Analytical grade toluene (99% purity), which was used as solvent to dissolve PAHs throughout this study, was purchased from SYSTERM®, ChemAR in Malaysia.

Instruments and apparatus

A gas chromatograph (Model 7890A, Agilent Technologies. Inc., USA) equipped with quadrupole mass spectrometer (Model 5975C), automatic liquid sampler (Model 7683B) and Enhanced Chemstation software (version E.02.00.493) was used to determine the concentration of PAHs. DB-XLB column with dimension of 30 m × 0.53 mm id × 1.5 μm film thickness and Hamilton 50μL syringe were purchased from IT Tech Research Limited, Malaysia.

Preparation of standard solutions

The stock mixture solution of five PAHs standard at concentration of 1000 ppm was prepared by diluting 0.01 g of acenaphthylene, fluorene, anthracene, phenanthrene and pyrene in 10 mL toluene. PAHs standard solutions at lower concentration were prepared by diluting the PAHs stock mixture solution in appropriate volume of toluene. All prepared standard solutions were stored in 4 °C before used.

Limit of detection (LOD)

Two series of PAHs standard solutions with concentrations in the ranges of 1.5-9 ppm and 0.02-1 ppm were prepared for the determination of limit of detection (LOD) of PAHs in

Table 1. The parameters of gas chromatographic and mass spectrometric used in the analysis of PAHs

Parameters	
Injector Port	Splitless mode
Injection Volume	10 μ L
Carrier gas–helium flow	1.0 mL/min
Column (capillary column)	DB-XLB
Column Diameter	30m \times 0.53mm \times 1.5 μ m film thickness
Oven temperature program	95 $^{\circ}$ C for 0.5 min then 5 $^{\circ}$ C/min to 300 $^{\circ}$ C for 28 min
Transfer line temperature	300 $^{\circ}$ C
Ion Source Temperature	230 $^{\circ}$ C
Quadrupole Temperature	150 $^{\circ}$ C
Electron energy	69.922 eV
Ionisation current	34.610
Electronic multiplier potential	1270.588 V
MS Mode	EI
Scanning mass range	80-330 amu
SIM mode monitoring ions:	
Acenaphthylene	152.00
Fluorene	166.00
Anthracene	178.00
Phenanthrene	178.00
Pyrene	202.00

the analytical instrument. All curves in peak area versus PAHs concentration were plotted to obtain standard error of estimate and slope of each curve for the calculation of the LOD. LOD for each PAH compounds was calculated based on three times of the ratio of standard error of estimate to the slope of the curve.

GC-MS analysis conditions

The GC-MS parameters used in splitless mode analysis of PAHs in this study was summarized in [Table 1](#). Syringe with the maximum volume of 50 μ L was used to inject 10 μ L of PAHs solution into a temperature programmed GC inlet. The inlet temperature was programmed at 95 $^{\circ}$ C for 0.5 minutes before ramped at 200 $^{\circ}$ C/min to 300 $^{\circ}$ C. The injected PAHs solution was carried by helium gas at constant flow of 1.0 mL/min into a 30 m \times 0.53 mm DB-XLB capillary column located in an oven with programmed temperature starting at 95 $^{\circ}$ C for 0.5 min before ramped at 5 $^{\circ}$ C/min to 300 $^{\circ}$ C. The eluted PAH compounds were detected using a quadrupole mass detector in EI modes; scanning in a mass range of 80 to 330 amu. The masses of the monitored ions in SIM mode were: 152.00 for acenaphthylene, 166.00 for fluorene, 178.00 for both anthracene and phenanthrene, and 202.00 for pyrene. The mass spectrometer transfer line, ion source and quadrupole temperatures were fixed at 300, 230 and 150 $^{\circ}$ C, respectively. The optimized mass spectrometer conditions showed electron energy of 69.922 eV, ionization current of 34.610 and electronic multiplier potential of 1270.588 V.

Optimization of the PTV inlet

A standard solution containing five PAHs at concentration of 1 ppm was prepared in toluene for PTV solvent vent optimization. Eight parameters in PTV solvent vent mode were optimized as following sequence: injection volume (10-200 μL), vent pressure (0-25 psi), vent time (0.5-5 min), vent flow (50-400 mL/min), initial heating rate (10-500 $^{\circ}\text{C}/\text{min}$), purge flow to split vent (10-600 mL/min), purge flow time (0.5-5 min) and injection delay time (5-50 s).

Accuracy and Precision

The method efficiency was determined based on the recovery percentages and relative standard deviations (RSDs) obtained from the analysis of three standard solutions at the concentrations of 0.4, 0.6 and 1.0 ppm. All analyses were carried out using optimized PTV solvent vent mode and each analysis was repeated three times. A series of PAHs standard solutions with concentration ranging from 0.2 to 1.2 ppm was analysed using the optimized PTV conditions and the obtained results were used to plot calibration curves for the determination of the concentration of the analysed PAHs standard solutions. The recovery percentages were determined by obtaining 100% of the ratio of the calibrated concentration to the actual concentration of the PAHs in the standard solution.

RESULTS AND DISCUSSION

Optimization of PTV in the analysis of PAHs

LOD value can be lower down by injecting higher volume of analyte standard solution into the PTV inlet through multiple injection before transferred into the column for separation and eluted for detection. However, other parameters in PTV inlet such as vent pressure, vent time, vent flow, temperature programme, purge flow, purge flow time and injection delay time may limit the amount of PAHs being transferred from inlet liner into the column. Therefore, optimization of all these parameters is necessary if injection volume is to be increased to higher volume.

Injection volume was optimized by increasing the injection volume from 10 to 200 μL . Lowest injection volume of 10 μL was a single injection. Total injection volume of 60 μL was achieved by repeating six injections with each injection volume of 10 μL . Other total injection volumes, which were higher than 60 μL were achieved by repeating injection of 25 μL . Time interval between each injection in repeating injection was 12 sec. Solvent venting flow rate that was used in each injection was 400 mL/min for 0.5 minutes. According to the results shown in **Figure 1(A)**, peak areas for all five PAHs increase drastically when injection volume increases from 10 μL to 60 μL . The following increment of the injection volume does not show significant increasing of the peak area and this phenomenon most probably due to the saturation of the sample solution in the inlet. When total injection volume increased to 200 μL ,

peaks shown in the chromatogram become distorted and peak tailing is observed as shown in **Figure 2(B)** when compared to the peaks in chromatogram (**Figure 2(A)**), which is obtained from 10 μL injection volume. According to Norlock *et al.* [15], this is due to overloaded solvent that is injected into the inlet and subsequently flooding is occurred in the inlet liner. However, increasing the injection volume of PAHs solution into inlet produces more satisfactory RSD values (**Figure 1(A)**). When injection volume increased to 125 μL and 150 μL , RSD reduces to 4.50 % and 4.47 %. This shows that when more PAHs injected into the inlet, obtained responses are more precise. Optimized injection volume of 150 μL was used in the further optimization of other parameters.

When the sample is preconcentrated in the PTV inlet, excess solvent must be evaporated to avoid flooding in the liner and at the same time, losing analytes has to be minimized. Temperature used in PTV inlet to eliminate the excess solvent is very important and must be below solvent boiling point because it must prevent the analytes mix with the solvent vapour [28] especially during the temperature ramping process. Thus, in this study,

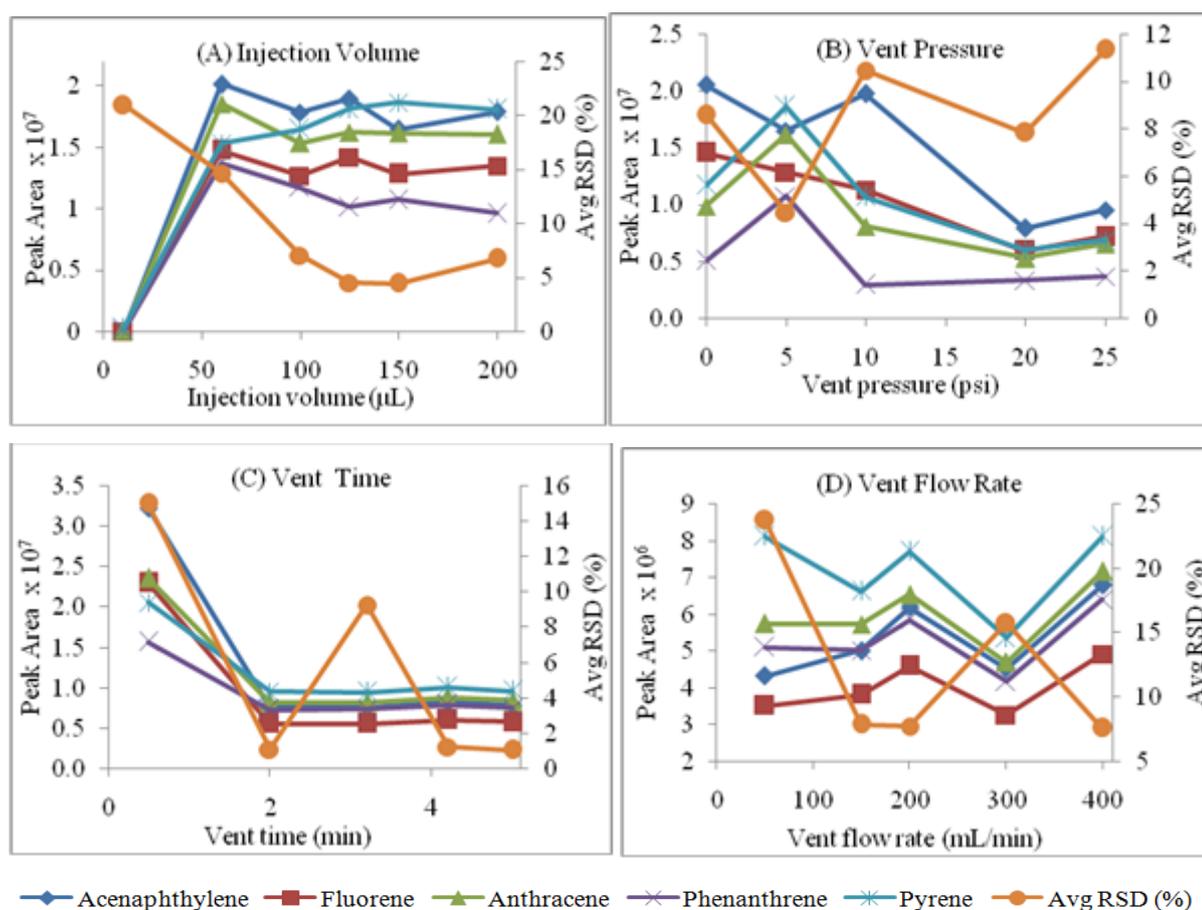


Figure 1. PTV injector parameters optimization: (A) injection volume; (B) vent pressure; (C) vent time; (D) vent flow

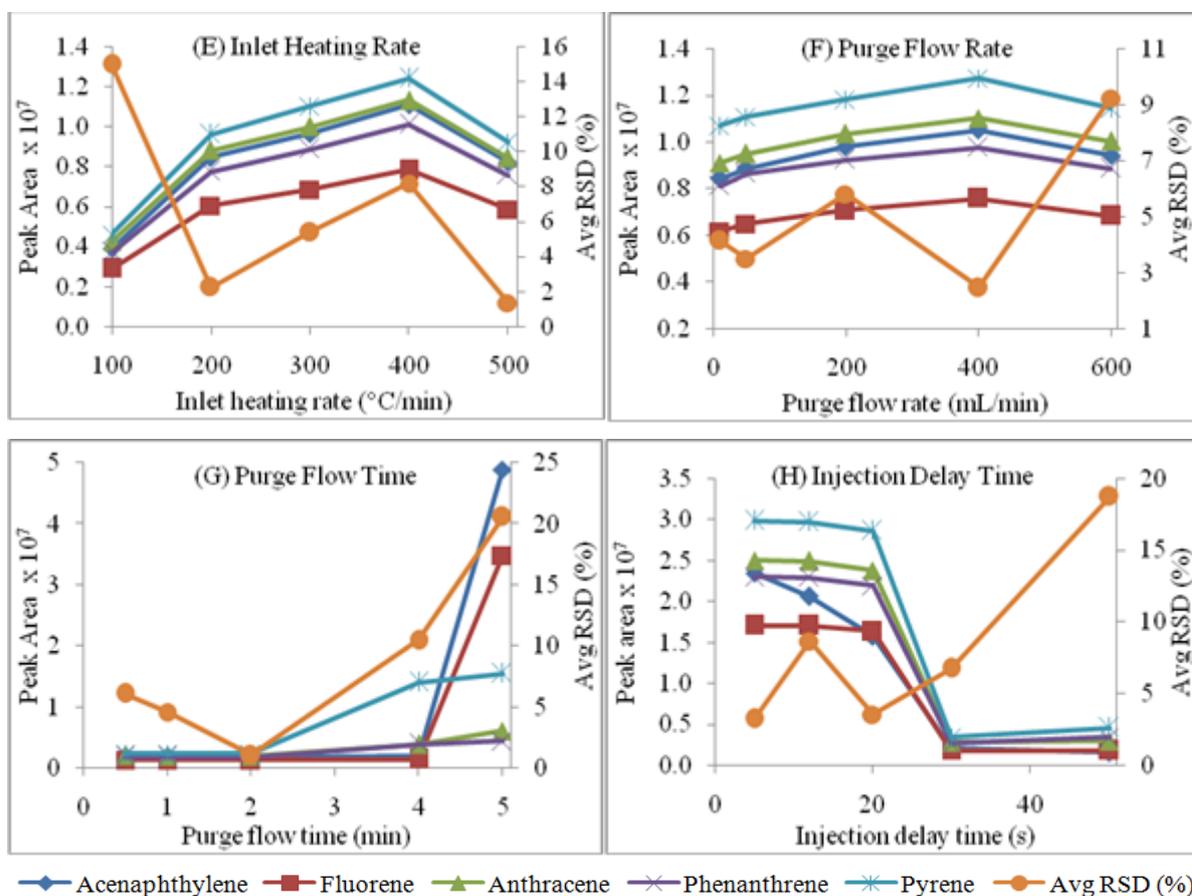


Figure 1 (continued). PTV injector parameters optimization: (E) initial heating rate; (F) purge flow rate; (G) purge time, and (H) injection delay time.

initial inlet temperature was fixed at 95 °C which is below toluene boiling point that is approximately 110 °C. The efficient of the elimination of the injected solvent in the inlet is controlled by three parameters that are (i) the time the split vent is open (also known as vent end time), (ii) the inlet pressure during solvent elimination (vent pressure), and (iii) the flow through the split vent (vent flow) [29]. High peak response could be obtained if these three parameters are optimized properly.

Figure 1(B) indicates that when higher vent pressure was applied to the inlet, the obtained peak responses reduced gradually and at the same time, gradual increment of RSDs can be observed. This is probably due to the losing of PAHs at high vent pressure condition, which causes slower elimination of the solvent introduced into the inlet [29,30]. Anthracene, phenanthrene and pyrene have highest peak area at vent pressure of 5 psi except acenaphthylene and fluorene, which have highest peak area at 0 psi. The vent pressure of 5

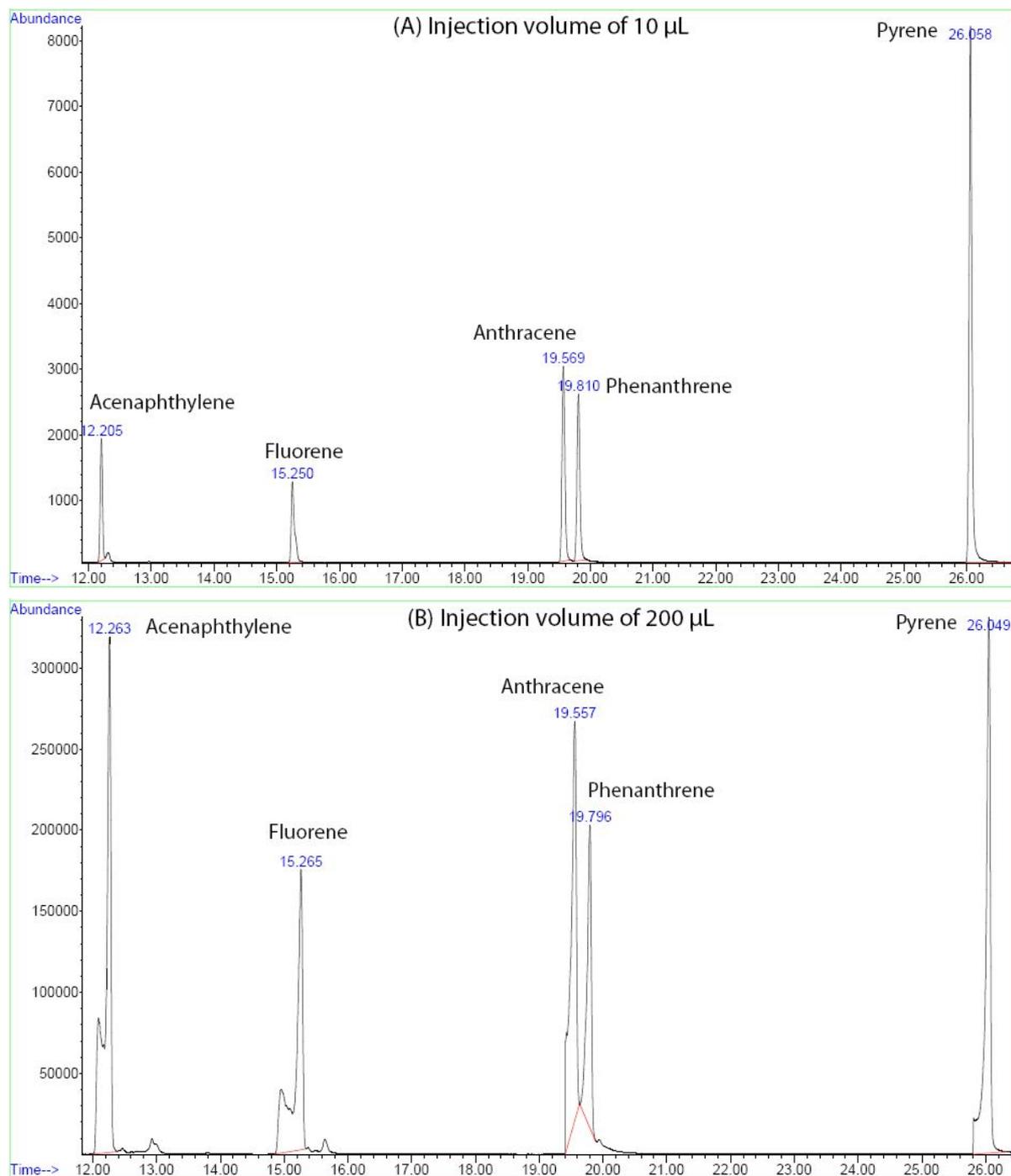


Figure 2. The chromatograms obtained from the analysis of a mixture containing five PAHs at the concentration of 1 ppm with the injection volume of (A) 10µL and (B) 200 µL

psi was chosen to be used in the further optimization due to the lowest average RSD is obtained at this pressure.

According to **Figure 1(C)**, increasing inlet vent time reduces PAHs peak areas. Same trend was obtained in the study carried out by Gómez-Ruiz *et al.* [31]. Zhang *et al.* [32] suggested that longer vent time causes substantial loss of target compounds via the split vent. Stajnbaher & Zupancic-Kralj [33] explained in their studies of PTV optimization that when longer vent time is used to avoid flooding at the column entrance that causes peak distortion, most of the time the recoveries of volatile compounds will drop to unacceptable levels. Due to the higher average of RSD obtained at 0.5 minutes vent time (**Figure 1(C)**), 2 minutes vent time was chosen to be used in the further optimization. According to Zhao and Meng [30], the vent flow rate has linear effect on solvent elimination; denoting that the faster solvent vaporization is attributed to the higher vent flow. Nevertheless, the faster solvent elimination also can result in the loss of volatile compounds. Hoffmann and MacNamara [34] explained that when the split vent flow of a PTV inlet is correctly optimized, solvent that is introduced into the inlet will be selectively removed and the analytes of interest will be concentrated in the liner before transferred into the column. Based on the results shown in **Figure 1(D)**, the peak areas of the PAHs obtained in this study fluctuate across 50 to 400 mL/min vent flow rates. The results show that the lowest vent flow rate gives highest RSD average of the analysis. The vent flow rate of 400 mL/min was chosen to be used in the further optimization because it has slightly higher peak area across the studied vent flow rates and slightly lower RSD average of 7.55%.

Figure 1(E) shows the effect of the inlet heating rate on the obtained peak areas of PAHs analysis. The results indicate that the higher peak areas were obtained when the inlet heating rate was increased from 100 to 400 °C/min. This is attributed to the reason that more PAHs were evaporated in the inlet at higher temperature before being carried into the column by the mobile carrier gas. Other than this, it was probably caused by the fact that analytes tending to adsorb in the liner are better detached from the active sites by “shock” heating [35]. The decreasing of the peak areas at the heating rate of 500 °C/min most probably due to the thermal degradation of PAHs in the inlet with high temperature condition. Same pattern obtained in the study carried out by Godula *et al.* [35]. Additional explanation given was that too rapid heating might lead to liner overflow with sample vapors, resulting potential losses of the more volatile compounds. Inlet heating rate at 400 °C/min was chosen for further optimization.

The inlet purge is achieved by actuating the split (purge) valve that allows a high split flow through the liner, which quickly purges the residual vapours from the inlet [36], which can prevent inlet from contamination [25]. As shown in **Figure 1(F)**, when the purge flow rate was increased from 0 to 400 mL/min, it causes merely gradual increment in the peak areas obtained from the PAHs analysis. Nonetheless, when the purge flow rate was increased to 600 mL/min, the obtained peak areas reduced slightly but RSD average increases significantly compared to the RSD average at 400 mL/min. Similar observation was reported in the study carried out by Pinto *et al.* [37]. It was regarding less reproducible chromatograms were pronounced when high purge flow values were used in the analysis. The purge flow times ranging from 0.5 to 5 minutes were studied and the obtained results are shown in **Figure 1(G)**.

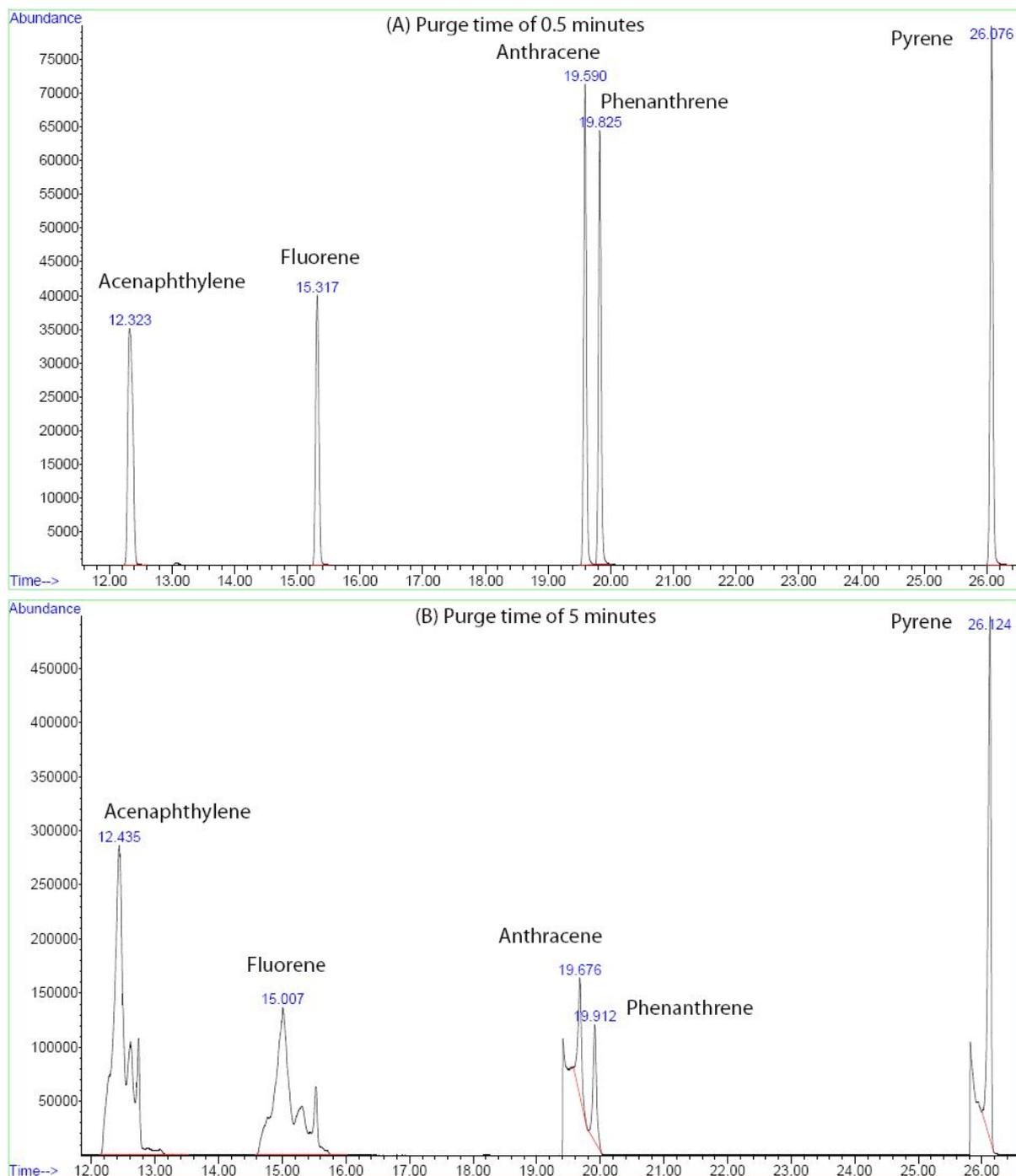


Figure 3. The chromatograms of 150 μ L injection volume of five PAHs at the concentration of 1ppm and purge time of (A) 0.5 minutes and (B) 5 minutes

The results show that the shorter purge flow times do not have much effect on the obtained peak areas in PAHs analysis until this parameter was increased to 4 and 5 minutes. The RSD

Table 2. Limit of detection (LOD) for each PAHs in splitless mode and PTV solvent vent mode analyses

PAHs compounds	LOD (ppm)		LOD _{splitless} /LOD _{colvent vent}
	Splitless injection (1.5-9 ppm)	PTV solvent vent injection (0.02-1 ppm)	
Acenaphthylene	2.01	0.39	5
Fluorene	1.75	0.36	5
Anthracene	1.85	0.37	5
Phenanthrene	4.14	0.40	10
Pyrene	2.45	0.39	6

averages increase significantly at these two purge flow times as well and the increment most probably due to the extraneous peaks were obtained in the analysis where purge flow times are at 4 and 5 minutes as shown in **Figure 3(B)**. According to Chromacademy [36], if the purge flow time is too long, it will cause extraneous peaks, baseline rising and subsequently the reproducible integration becomes difficult to be carried out. However, if the purge flow time is too short, it will cause the analyte still resident in the liner and lead to poor analytical sensitivity and reproducibility. The optimum purge flow rate and time of 400 mL/min and 2 minutes were used for further optimization.

The time interval between each injection (injection delay time) in the multiple injection mode needs to be long enough in order that the injected solvent could have sufficient time to be evaporated in the inlet. Otherwise, the excess solvent may accumulate and cause flooding in the inlet liner and subsequently damage the analytical column. On the other hand, if the time interval is too long, it may also cause the loss of the volatile analytes and therefore, shortest total injection time is desirable [5]. Several injection delay times between 5 to 50 seconds were chosen to study. The continuous injection was repeated six times in each multiple injections with injection volume in each injection was 25 μ L. Obviously as shown in **Figure 1(H)**, the peak areas of PAHs decrease significantly and in the other hand, the RSD average increases sharply when injection delay time higher than 20 seconds was used. The injection delay time of 5 seconds was considered as optimum value for this parameter due to its lowest RSD average and shorter delay time which can minimize the loss of the volatile PAHs.

LODs of PAHs in splitless mode and optimized PTV solvent vent mode analyses

The LODs of the PAHs were determined using splitless and optimized PTV solvent vent modes. Two series of PAHs standard solutions with concentrations ranging from 1.5 to 9 ppm and 0.02 to 1.00 ppm were used to determine LOD in each condition, respectively. The determined LOD for each PAH compound is tabulated in **Table 2**. It is very noticeable that LODs determined using optimum PTV solvent vent mode analysis are approximately five to six times lower than LODs determined using splitless mode analysis and it even can ascend to 10 times higher for phenanthrene. This shows that PTV solvent vent mode was optimized by evaporating most of the solvent and pre-concentrating all PAHs in the inlet liner before being carried by the carrier gas into the column. Both analysis modes were carried out in the same

Table 3. Recovery Percentage and relative standard deviation (RSD) for each PAHs

PAHs compounds	Concentration			Average % recovery	RSDp	Linearity (r^2)
	0.4 ppm	0.6 ppm	1.0 ppm			
Acenaphthylene	96.1±0.9	95.9±2.2	102.4±16.8	98.1	9.8	0.997
Fluorene	97.4±4.6	96.2±4	102.2±18.7	98.6	11.4	0.998
Anthracene	96.7±3.9	96.3±4.3	101.5±17.5	98.2	10.6	0.998
Phenanthrene	96.8±2.9	96.4±5.2	102±17	98.4	10.4	0.998
Pyrene	97±4.9	96.9±4.6	102.7±16.9	98.9	10.5	0.997

Note: * Pooled Relative Standard Deviation

oven programmed temperature and mass spectrometric conditions. Thus, the differences between both LODs are due to the conditions that have been optimized in the inlet. Such enhancement is a great significance in the determination of trace amount of PAHs in environmental samples.

Recovery percentage and RSD in PAHs analysis using optimum PTV solvent vent mode

Three PAHs standard solutions with concentrations at 0.4, 0.6 and 1.0 ppm in toluene were analyzed using optimum PTV solvent vent mode. The obtained peak areas were calibrated using regression equations obtained from standard calibration curves established by a series of PAHs standard solutions with concentration ranging from 0.2 to 1.2 ppm. The obtained concentrations were used to calculate recovery percentages in each concentration by multiplying the ratio of the calibrated concentration to the actual concentration with 100%. Each standard solution was analysed three times and RSD for each concentration was calculated to determine their precision. The obtained results are tabulated in **Table 3**. All obtained standard calibration curves show good linearity with R square values more than 0.99. The recovery percentages for concentrations of 0.4 ppm and 0.6 ppm are approximately 96%; whereas, 1.0 ppm shows recovery slightly higher than 100%. However, average recovery percentages among 0.4, 0.6 and 1.0 ppm range from 98.1 to 98.9% with pooled relative standard deviation (RSD_p) of 9.8 to 11.4%.

Comparison between optimized PTV solvent vent and splitless injection modes on PAHs analysis

The conditions of conventional splitless injection and optimized PTV solvent vent injection modes are summarized in **Table 4**. The aim of the present study was to investigate the enhancements in performance of PAHs analysis between optimized PTV solvent vent and splitless injection modes. The benefits of PTV are the injection volume can be increased from 10 to 150 μ L without flooding the inlet as less solvent vapour is delivered to the GC column and the loss of the analyte from the thermal degradation or evaporation can be minimized. The temperature of PTV inlet was quickly elevated at rate of 400 $^{\circ}$ C/min to remove the toluene solvent before the PAHs were delivered into the column; whereas the temperature of the oven was kept below the boiling point of the toluene in order that PAHs can be refocused at the

Table 4. Summary of the parameters between splitless and optimized PTV solvent vent modes

GC inlet method stages	GC inlet parameters	Splitless mode	PTV solvent vent multiple injection mode
Solvent venting process	Injection volume (μL)	10	150 (6 \times 25)
	Injection delay time (s)	-	5
	Vent pressure (psi)	-	5
	Vent time (min)	-	2
	Vent flow (mL/min)	-	400
Transfer of analytes	Inlet heating rate ($^{\circ}\text{C}/\text{min}$)	200	400
Inlet purge process	Purge flow to split vent (mL/min)	50	400
	Purge flow time (min)	1	2

starting point of the column, which is similar to the conditions was mentioned in the study carried out by Delgadillo-Marín *et.al.* [28]. In such a way, the obtained response signal in the form of peak area could be enhanced to multiple times. The disadvantages of the splitless mode are the injection sample volume, which is allowed to be introduced into the inlet is limited and the injected solvent could not be evaporated and vented out from the inlet to pre-concentrate the analyte. Thus, all solvent together with the analyte are forced to the column for separation, which produces limited response from the mass spectrometric detector.

CONCLUSION

In present study, all necessary parameters in PTV solvent vent inlet for the determination of five PAH compounds were successfully optimized. The LODs for the five PAHs ranging from 0.36 to 0.40 ppm were determined using the optimized PTV solvent vent mode with the injection volume of 150 μL . The LODs obtained from the optimized PTV solvent vent mode are better than those from splitless injection mode, which is merely ranging from 1.75 to 4.14 ppm. All the studied parameters are found to be critical in investigating the sensitivity of PAHs except purge flow rate and vent flow rate. As a conclusion, the optimized PTV solvent vent injection mode in GCMS is a suitable method for the determination of PAHs with concentration below 1 ppm because its sensitivity was increased by approximately five to six times of magnitude compared to the conventional splitless injection mode.

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