

Preliminary Analysis of Benzene, Toluene, Ethylbenzene, O-Xylene (BTEX) and Formaldehyde inside Vehicle Cabin

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ABSTRACT

Vehicle indoor air quality (VIAQ) has become a high important field of research since people spend much of their time inside vehicle cabin. Volatile organic compounds (VOCs) are one of the main pollutants inside vehicle cabin. There are various types of VOCs can be found inside vehicle cabin and high exposure to these organic compounds may affect the human health. This study was conducted to analyse the effect of indoor temperature to the concentration of formaldehyde, benzene, toluene, ethylbenzene and o-xylene inside vehicle cabin when a vehicle was parked under direct sunlight and driven under different ventilation modes. Among the sampling methods used in indoor air quality research, direct-reading instrument and active air sampling are the methods usually applied to measure the air quality level inside vehicle cabin. This study used direct-reading instrument to measure the concentration of formaldehyde and active air sampling to identify the concentration of benzene, toluene, ethylbenzene and o-xylene (BTEX). It was found that high indoor temperature with heat accumulation accelerated the melting process of interior material; thus, causing a high emission of

formaldehyde concentration inside vehicle cabin. The role of ventilation modes was more dominant compared to indoor temperature. Meanwhile, the concentrations for BTEX were not detected possibly due to age of studied vehicle.

Keywords: *Vehicle indoor air quality (VIAQ), Volatile organic compounds (VOCs), Benzene, toluene, ethylbenzene and o-xylene (BTEX), Formaldehyde*

Introduction

Vehicle cabin can be considered as a part of living environment because people spend long periods of time inside it. Therefore, the awareness about indoor air quality inside vehicle cabin among people has increased. Pollution inside vehicle cabin may come from various sources such as smoke, particulate matter, VOCs, carbon dioxide (CO₂), carbon monoxide (CO) and many more.

VOCs such as benzene, toluene, ethylbenzene and o-xylene (BTEX) are the most dangerous pollutants inside vehicle cabin, which are associated with interior materials, gasoline loss, infiltration of outdoor air pollutants, exhaust leakage or traffic emissions in vehicular air environment [1, 2]. These harmful compounds deteriorate in-vehicle air quality and also threaten the human health. According to Faber et al. [3], inhaling BTEX compounds may lead to throat irritation and respiratory failure.

Instead of BTEX, some previous studies have been conducted to investigate the concentration of formaldehyde inside vehicle cabin. A study conducted by Xu et al. [4] found that the average concentration of formaldehyde inside vehicle cabin was 16.43µg/m³. The main source of formaldehyde was from the emissions of interior materials especially upholstery and ceiling [5]. An exposure to formaldehyde may lead to dangerous disease such as cancer [6].

According to Al-Kayiem et al.[7], when a vehicle is parked under direct sunlight, the interior temperature can increase up to 80°C. Most previous studies indicated that interior temperature is one of the main factors that contributed to BTEX and formaldehyde concentration inside vehicle cabin. A study conducted by You et al. [8] found that the concentration level of toluene increased when interior temperature was increased from 25°C to 60°C. Faber et al. [9] revealed that the concentrations of ethylbenzene and xylene drastically increased when interior temperature was increased from 20°C to 50°C. According to Xu et al. [4], the concentrations level of BTEX and formaldehyde changed significantly when a vehicle was driven in different ventilation modes.

This study was conducted to investigate the effect of indoor temperature and ventilation modes to the BTEX and formaldehyde

concentrations inside a vehicle cabin with similar vehicle used by Abd Razak et al. [10] and they only evaluated in-vehicle total VOCs. Experimental work involved two different methods which were active air sampling and direct-reading instrument. BTEX concentration was measured by active air sampling and was analysed using gas chromatograph equipment, whereas formaldehyde was measured by direct-reading instrument. This study also compared the measured concentration with the standard guideline introduced by Korea, Japan and China.

In Section 2, this paper described the detail of experimental setup, including the specification of studied vehicle and location of experiment. Subsequently, the procedures of conducting experiment using direct-reading instruments and active air sampling were presented in Section 3. Lastly, in Section 4, this study systematically discussed the dependency of BTEX and formaldehyde concentrations on the ΔT and indoor temperature during static and mobile test.

Research Methodology

Test Procedure and Vehicle

Figure 1 shows the detail of research methodology, in which this study was employed two methods which are direct-reading instrument and active air sampling. The experimental work was conducted in two condition which are static and mobile test and the conditions of tests were described in Table 1.

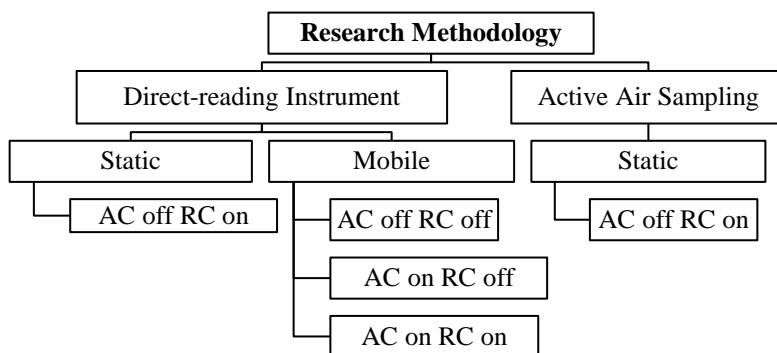


Figure 1: Flow process of research methodology

The measurement process for static test was conducted for five days on April 2017 at Padang Kawad Utama, Universiti Teknologi Mara (UiTM), Shah Alam. During this test, vehicle was parked under direct sunlight and the sun path was as shown in Figure 2.

Table 1: Conditions of Tests

No.	Test Condition	Method	Ventilation Modes	Remark
S1	Static	Direct-reading Instrument	Engine off (AC off RC on)	Air-conditioning off with recirculation without fresh air
S2				
S3				
S4				
AS1	Mobile	Direct-reading Instrument	Active Air Sampling	Air-conditioning off with circulation with outdoor air
M1			AC off RC off	Air-conditioning on with circulation with outdoor air
			AC on RC on	Air-conditioning on with recirculation without fresh air
			AC off RC off	Air-conditioning off with circulation with outdoor air
M2	Direct-reading Instrument	AC on RC off	Air-conditioning on with circulation with outdoor air	
		AC on RC on	Air-conditioning on with recirculation without fresh air	

Whereas, during mobile test, which was conducted in two different days, the driving route and the sun path was as shown in Figure 3. The ambient temperatures during the tests were also monitored. The detail specifications of vehicle chosen in this test were as shown in Table 2.

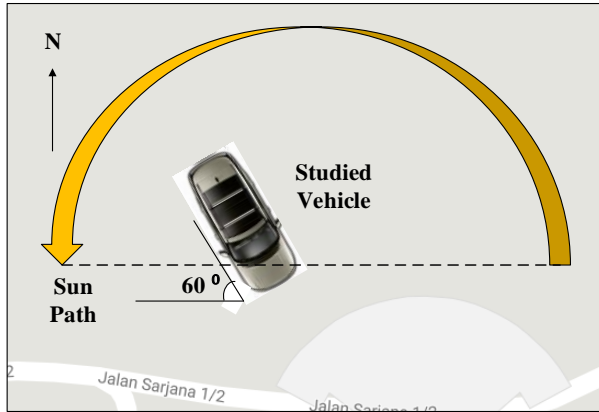


Figure 2: Position of vehicle during static test

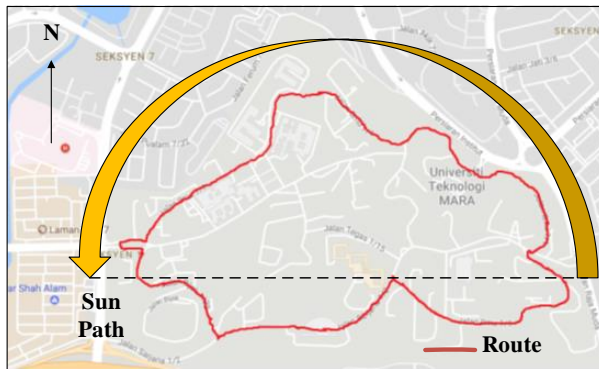


Figure 3: Driving route during mobile test

Table 2: Specification of Studied Vehicle

Model	Dimension	Year of Manufacture
Nationally Made Sedan Car complete with Leather Seat	Length, 4.257 m Width, 1.680 m Height, 1.502 m Cabin Volume, 10.742 m ³	2011

Measurements took place between 10.00 a.m. until 4.00 p.m. as the sun load within this period was at the highest point. During the mobile condition, the test vehicle was driven at a constant speed of 30 ± 5 km/h on the selected route. Ventilation conditions for mobile condition were set as

follows: (i) Air Conditioning and Recirculation off (AC off RC off); (ii) Air Conditioning on and Recirculation off (AC on RC off); and (iii) Air Conditioning and Recirculation on (AC on RC on). It took 20 min for the measurement under each ventilation condition before switching it to another.

Field Measurement and Active Air Sampling

Figure 4 shows the experimental setup for equipment included Environmental Monitoring Instrument (EVM 7), Aeroquol S500 and Questemp QT36. EVM 7 and Aeroquol S500 were used to measure indoor temperature and formaldehyde inside vehicle cabin. Meanwhile, the outdoor temperature was measured using Questemp QT36. All equipment was placed at the driver's breathing zone. Interior temperature, ambient temperature and formaldehyde were measured with 5 minutes time interval for static test and 1 minute time intervals for mobile test. The specified VOCs of BTEX were sampled by the tedlar bag and analyzed latterly using gas chromatograph.

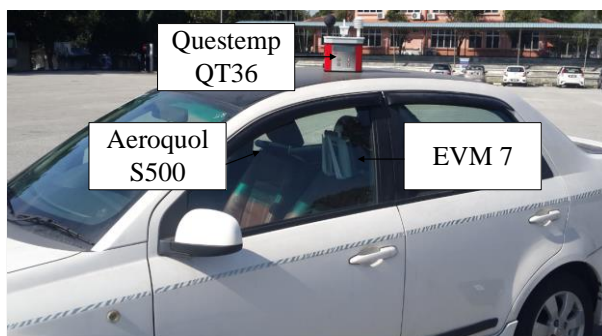


Figure 4: Experimental setup for instrument method

Measurement of BTEX using active air sampling process was divided into two steps which were sampling and analysis and was conducted under the requirement of the EPA Method 18 [11]. Figure 5 shows the test schematic diagram of air sampling setup inside vehicle cabin, where the gas chromatograph with flame ionization detector (FID) as shown in Figure 6 was employed to analyse the air sample.

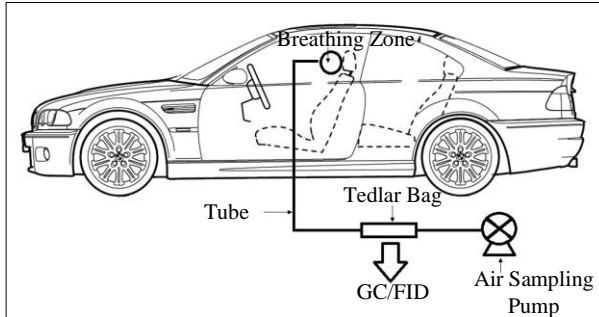


Figure 5: Test schematic of air sampling and analysis

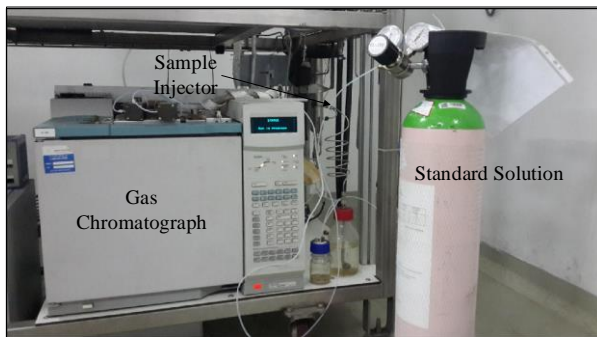


Figure 6: Gas chromatograph

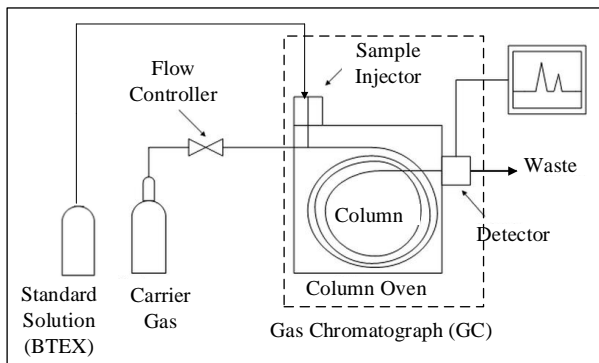


Figure 7: Schematic diagram of calibration setup

Figure 7 shows the schematic diagram to setup the equipment for calibration process. The detail process of analyzing air sample was illustrated in Figure 8. The process started with the calibration process, where the purpose of this process is to identify the setting parameter for gas

chromatograph. After that, a standard solution consisted of BTEX with 5 ppm concentration of each compound was analyzed based on parameters provided by gas chromatograph manufacturer.

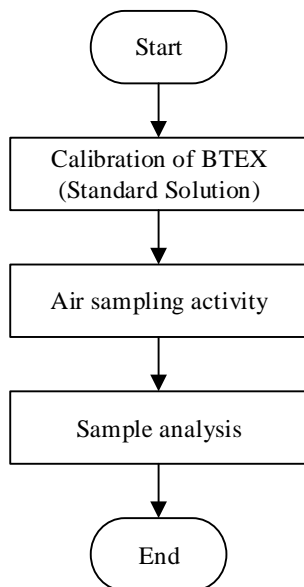


Figure 8: Flow process of active air sampling

After several trials, the final parameters that suit to the standard solution were defined and summarized in Table 3. Figure 9 shows the chromatogram for BTEX (standard solution) together with the peaks of retention times (RT). These RTs were used as the reference to identify the BTEX compounds inside the air sample. The retention time (RT) for BTEX were 3.363 minutes, 5.433 minutes, 8.548 minutes and 9.823 minutes respectively.

Table 3: Summary of Gas Chromatograph Parameter

Cappillary Column	Carrier Gas	Inlet Split Ration	Oven Temperature Program
DB-5MS (30m × 250µm × 0.25µm nominal)	Argon 1.5 ml/min	1:50	From 40°C (2 min), at 3°C/min to 90°C and at 5°C/min to 160°C

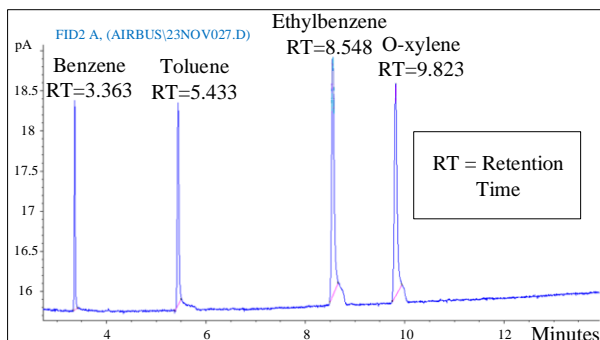


Figure 9: Chromatogram for BTEX (standard solution)

A calibrated air sampling pump (Gilair 3) was set at a rate of 2.0 L/min for 20 seconds. Sampling process was performed using tedlar bag after the vehicle was parked 2 hours under direct sunlight. Indoor temperature was recorded before starting the sampling process. Sampling volume was calibrated using the following equation (1):

$$V_s = Q_a \cdot t \cdot \frac{293.15}{273.15 + T} \cdot \frac{P}{101.325} \quad (1)$$

where V_s is standard sampling volume (L); Q_a is actual flow rate ($L^3 \text{ min}^{-1}$) measured by the volume meter; t is sampling time (min); T and P are ambient temperature ($^{\circ}\text{C}$) and barometric pressure (kPa). Figure 10 shows the experimental setup for active air sampling.

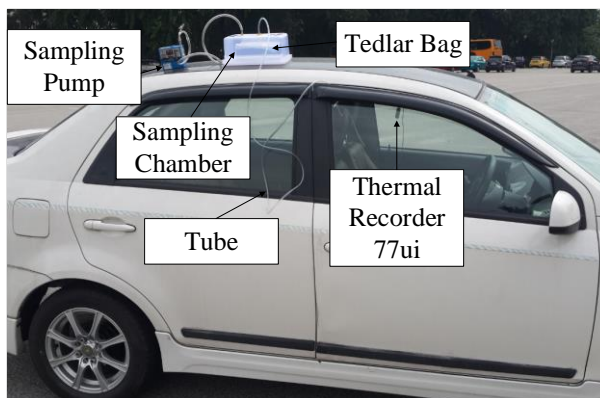


Figure 10: Experimental setup for active air sampling method

Tedlar bag is a non-sorbing properties and is used by this study to collect air sample. However, there has been some evidence proven by previous studies that losses occur in tedlar bags [12, 13]. Lipari [12] found that o-xylene and ethylbenzene inside tedlar bag lost 10.7 % and 13.3 % in 48 hours, respectively. Meanwhile, the study conducted by Yan Wang et al. [13] revealed that within 24 hours, approximately 25.6 % of the toluene was lost. Therefore, to avoid or reduce any losses in the tedlar bag, the process of analysing air sample was performed within 24 hours.

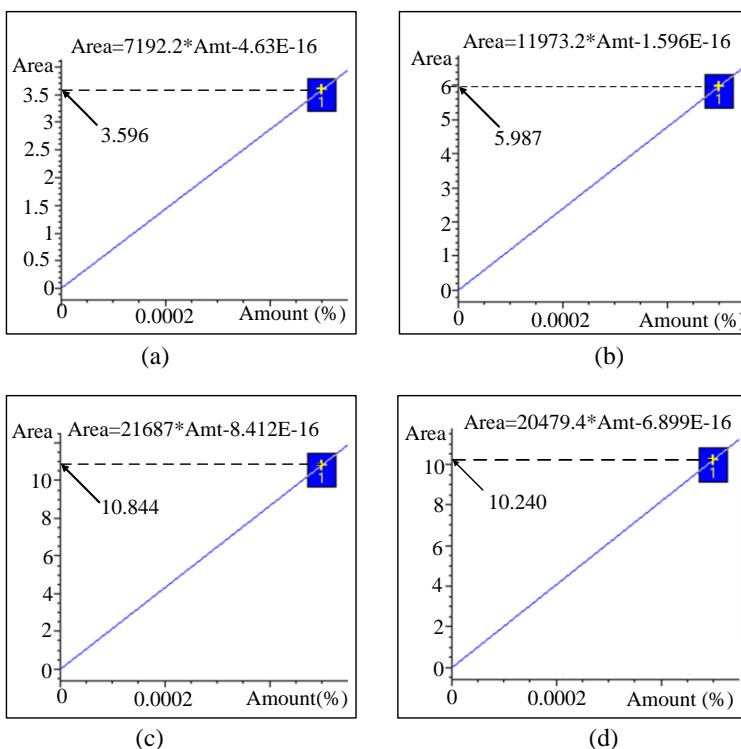


Figure 11: Calibration curve for (a) Benzene, (b) Toluene, (c) Ethylbenzene, and (d) O-xylene

Firstly, the air sample in the tedlar bag was transferred to the sample injector. The air sample then underwent rapid heating to volatize the compounds into the GC capillary column. Quantification analyses were performed by gas chromatograph-flammable ionization detector (GC/FID, Agilent 5890). The oven temperature was programmed from 40 °C (holding time 2 min) to 90 °C at 3 °C/min to 160 °C at 5 °C/min. Identification of

compounds was based on analysis of retention times of four VOCs which were BTEX, and the National Institute of Standards and Technology (NIST) library. The concentrations of compounds were calculated based on calibration curve as shown in Figure 11.

Result and Discussion

Table 4 summarizes the types and concentration of measured VOCs inside the test vehicle in different conditions and methods. Compared to the standard established by Korea, Japan and China, all concentrations of formaldehyde inside vehicle cabin exceeded the permissible exposure limits (PEL).

Effect of Temperature to Formaldehyde Concentration during Static Test using Direct-reading Instrument

During the test, all measurements including outdoor temperature, indoor temperature and formaldehyde were monitored and recorded at every 5 minutes. In order to ensure the data were reliable and acceptable, this study was conducted in four different days. Average outdoor temperature recorded from day 1 until day 4 was 32 °C to 34 °C. As shown in Figure 12, the indoor temperature increased when the vehicle was parked under direct sunlight and this contributed to high temperature difference (ΔT) between outdoor and indoor temperature. ΔT can be described by Equation 2 as follow.

$$\Delta T = T_i - T_o \quad (2)$$

where, T_i is indoor temperature and T_o is outdoor temperature. Figure 13 (a) shows the graph of ΔT for S1, S2, S3, and S4, in which ΔT increased proportionally with indoor temperature. The highest indoor temperatures recorded for S1, S2, S3, and S4 were 58.4 °C, 57.9 °C, 55.8 °C, and 51.3 °C, respectively. This finding was supported by the study conducted by Al-Kayiem et al. [7].

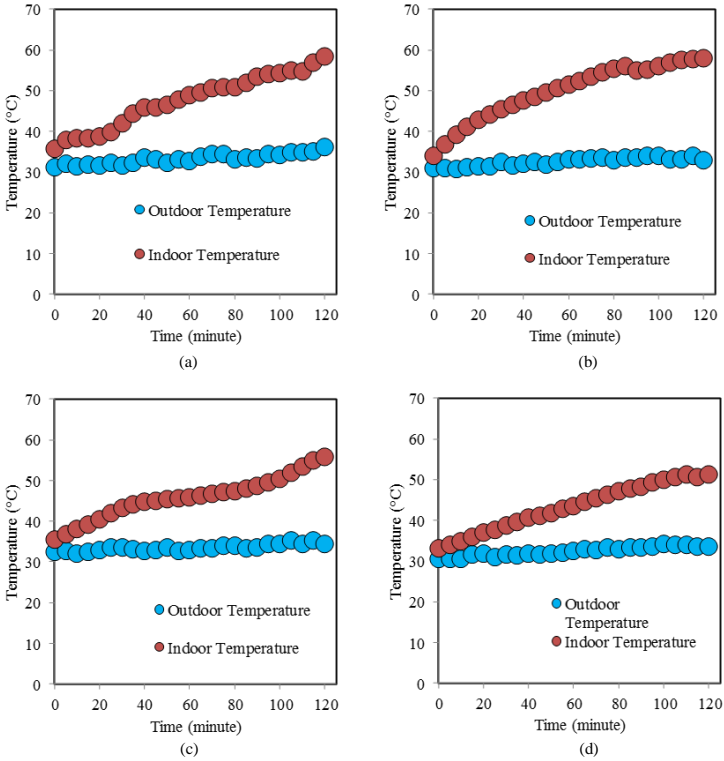


Figure 12: Temperature condition during static test at (a) S1, (b) S2, (c) S3, and (d) S4

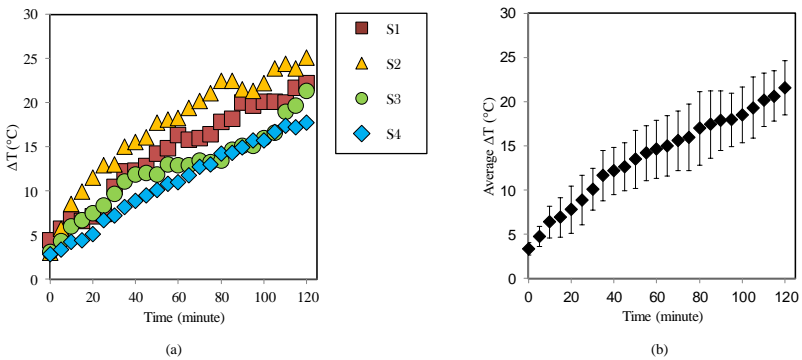


Figure 13: (a) Temperature difference (ΔT) and (b) Average of Δt with standard deviation error bars

Average ΔT and standard deviation were calculated and presented in Figure 13 (b). The purpose of calculating these two values was to evaluate the reliability of the data (T_i and T_o) that was measured in experimental work. The small standard deviation bar as shown in Figure 13 (b) indicated that the effect of outdoor temperature to the indoor temperature was less dominant and this condition occurred possibly due to the vehicle window glasses that blocked the solar radiation from entering the vehicle cabin.

Figure 14 (a) shows the formaldehyde concentrations for S1, S2, S3, and S4, in which the concentrations increased proportionally with the time taken during the experimental works. The highest concentration recorded for S1, S2, S3, and S4 were 1.09 mg/m^3 , 1.11 mg/m^3 , 0.93 mg/m^3 , and 1.27 mg/m^3 , respectively. Average formaldehyde concentration and standard deviation were calculated and presented in Figure 14 (b). The small standard deviation bar indicated that the data of formaldehyde concentrations obtained from this study were spread around the mean value, even the experimental works were conducted in different Ss.

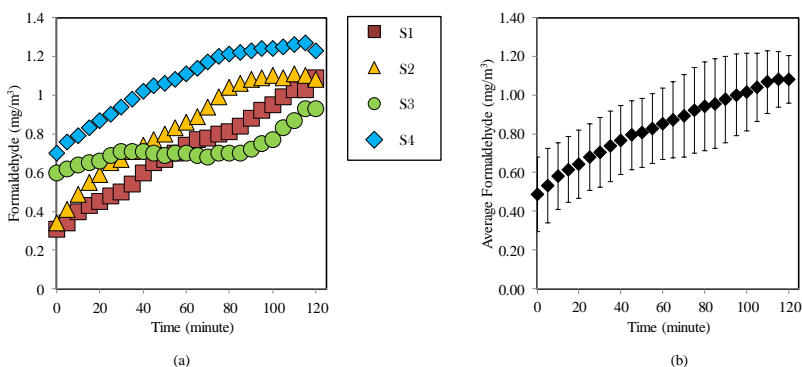


Figure 14: (a) Formaldehyde concentration (b) Average formaldehyde concentration with standard deviation error bars

Most previous studies revealed that VOCs concentration inside vehicle cabin was influenced by indoor temperature, in which the indoor temperature was related to ΔT . Positive correlation with R^2 equal to 0.9685, 0.9724, 0.7860, and 0.9598 as depicted in Figure 15 (a) indicates that the concentration of formaldehyde increases when ΔT rises. The R^2 that is close to one indicates that the correlation between these two variables is significantly strong. This finding was similar to those presented by previous studies [8–10]. The high temperature inside vehicle cabin accelerates the melting process of interior material; thus, causing the emission of formaldehyde concentration.

Validation of experimental result with theoretical model as shown in Figure 15 (b) indicates that the logarithm of $C_a/T^{0.75}$ in this study is in a good

linear relationship with $1000/T$, with R^2 equal to 0.9734, 0.9864, 0.7966, and 0.9307 for all formaldehydes in the four days as they are close to one. Xiong et al. [14] performed this validation process to their experimental result and reported a similar finding.

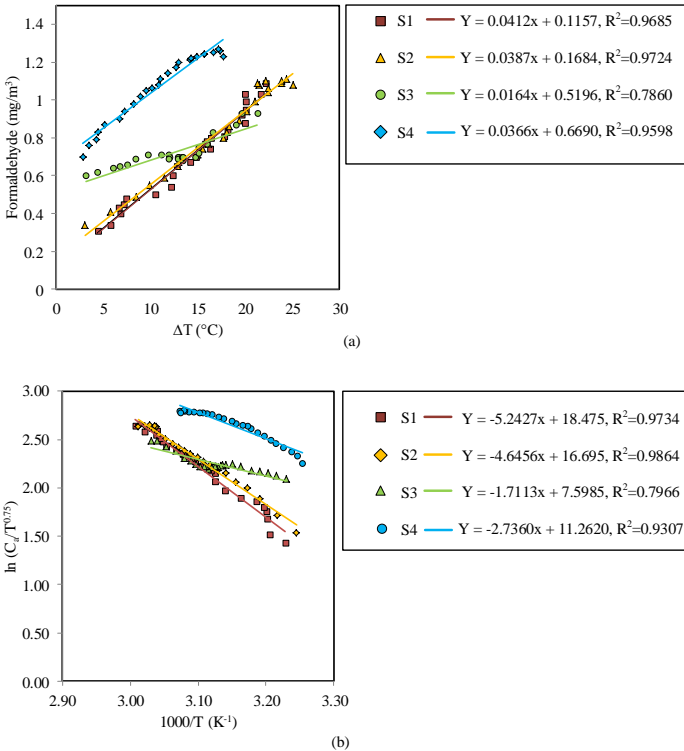


Figure 15: (a) Correlation between formaldehyde and Δt and (b) Validation of experimental data with theoretical correlation

Figure 16 shows the comparison of formaldehyde concentration with standard guideline introduced by Korea, Japan and China. The allowable limits were 0.25 mg/m^3 for Korea and 0.10 mg/m^3 for Japan and China. Comparing with the Korea guideline, the minimum concentration for S 1, 2, 3 and 4 which were 0.31 mg/m^3 , 0.34 mg/m^3 , 0.60 mg/m^3 and 0.70 mg/m^3 , exceeded about 1 to 3 times from the allowable limit and exceeded about 3 to 7 times from the allowable limit introduced by Japan and China. This indicates a poor air quality level inside the studied vehicle.

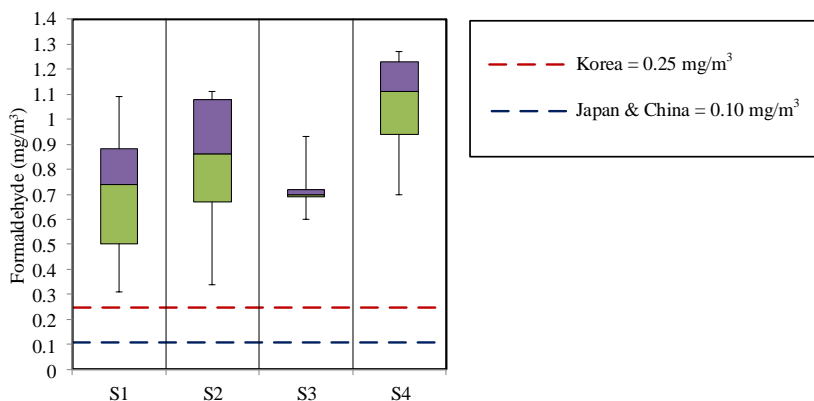


Figure 16: Comparison of formaldehyde concentration with standard guideline

Concentration of Benzene, Toluene, Ethylbenzene and O-xylene (BTEX) during Static Test using Active Air Sampling

The concentrations of BTEX were measured under static test, in which the vehicle was parked under direct sunlight for 2 hours. The outdoor and indoor temperature recorded during the sampling process before analyzing using gas chromatograph were 34.6 °C and 61.0 °C, respectively. The high indoor temperature inside studied vehicle accelerated the emission process of BTEX from the leather material, even in a low concentrations. This finding was supported by a study conducted by Chen et al. [1], where they reported that the concentrations of BTEX were influenced by the emission of coating, paints and adhesives from the leather material.

The results obtained from the air sample shows a low concentration of BTEX which are 0.17 ppm, 0.13 ppm, 0.08 ppm and 0.05 ppm, respectively. This might be due to the age of vehicle that was used in this study, which was more than 5 years. As revealed by You et al. [8], VOCs concentration inside vehicle cabin decreases significantly as time goes on, and a used vehicle will have less VOCs than a new one, because of the ventilation after delivering it to the customer from the production line. Figure 18 shows the percentage of BTEX molecule obtained from this study.

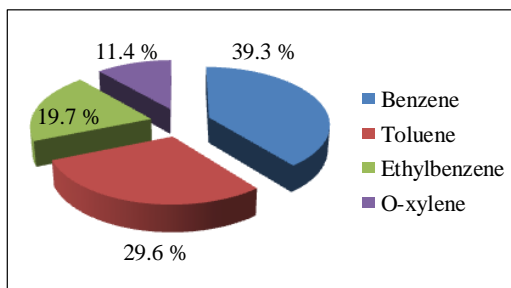


Figure 18: Percentage of BTEX molecule

Effect of Temperature to Formaldehyde Concentration During Mobile Test using Direct-reading Instrument

Figure 17 (a) shows the distribution of formaldehyde concentration during mobile test using three different ventilation modes. Under ventilation mode (i), without operating air-conditioning system and little external air was brought into the vehicle cabin environment, indoor temperature increased drastically from the initial temperature. The concentrations of formaldehyde increased linearly to 0.59 mg/m^3 and 0.62 mg/m^3 on M1 and M2, respectively. Under ventilation mode (ii), by operating air-conditioning system and air that enters from the outside of vehicle cabin, indoor temperature slightly decreased and it can be seen that the formaldehyde concentrations were inconsistent. This indicates that at certain time, the concentration level is influenced by the surrounding area. Under ventilation mode (iii), air-conditioning system was operated with an air recirculation, indoor temperature continued to decrease from previous ventilation mode. It can be seen that formaldehyde concentrations slightly increased for both M1 and M2 and remained constant towards the end of the test, even when the indoor temperature was low in this ventilation mode. This condition occurred due to the air that contained formaldehyde was trapped inside the vehicle cabin, and some of the concentrations penetrated out through the gap of vehicle part such as the door. Xu et al. [4] conducted a similar study to measure TVOCs concentration, and the result showed the same pattern of concentration with this study. Therefore, it can be concluded that the role of ventilation mode is more dominant in determining formaldehyde concentration compared to indoor temperature.

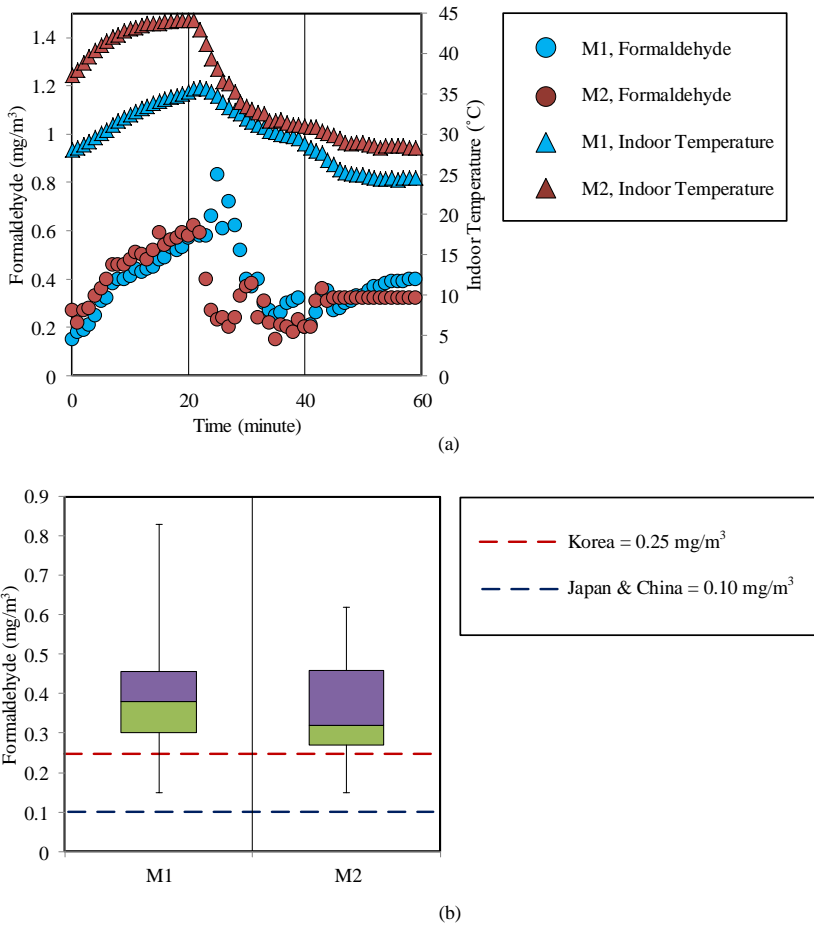


Figure 17: (a) Formaldehyde concentration and indoor temperature during mobile condition and (b) Comparison of formaldehyde concentration with standard guideline

Figure 17 (b) depicts the comparison between formaldehyde concentration during mobile test with allowable limit introduced by Korea, Japan and China. Overall, formaldehyde concentrations for both M1 and M2 during mobile test were much better compared to static test. The minimum concentrations recorded were almost 2 times lower than the maximum limit set by Korea. However, the concentrations exceeded about 1.5 times from the maximum limit set by Japan and China.

Table 4: Summary of in-vehicle Pollutants Concentrations

Con.	Method	S/Period	Minimum (mg/m ³)	Maximum (mg/m ³)	Average (mg/m ³)	VOCs
St	DRI	S1	0.31	1.09	0.71	FD
		S2	0.34	1.11	0.84	
		S3	0.60	0.93	0.72	
		S4	0.70	1.27	1.07	
Mo		M1	0.15	0.83	0.39	
		M2	0.15	0.62	0.35	
St	AAS		0.17 ppm			BN
			0.13 ppm			TL
			0.08 ppm			EN
			0.05 ppm			OX

Legends:

- Con.:** Condition
- St:** Stationary
- Mo:** Mobile
- DRI:** Direct Reading Instrument
- AAS:** Active Air Sampling
- FD:** Formaldehyde
- BN:** Benzene
- TL:** Toluene
- EN:** Ethylbenzene
- OX:** O-xylene

Conclusion

As a conclusion, formaldehyde concentration inside vehicle cabin strongly depends on the indoor temperature during static test. In contrast with mobile test, the role of ventilation modes is more dominant compared to indoor temperature, in which the concentration levels are inconsistent and slightly increase even when the indoor temperature decreases under ventilation mode (AC on RC off) and (AC on RC on), respectively.

With the rising of temperature, total emission of formaldehyde during stationary test also increases and exceeds the allowable limit introduced by

Korea, Japan and China. This illustrates a poor air quality level inside the studied vehicle. However, formaldehyde concentrations are much better during mobile test, in which the concentrations are lower than the maximum allowable set by Korea, even when the concentrations are slightly higher than the maximum limit allowed by Japan and China.

Meanwhile, the concentrations of BTEX that were measured in this study are low, which possibly occurred due to the influences of vehicle age. The age of vehicle used in this study was more than 5 years and possibly it had less BTEX concentrations.

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