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Determination of Volatile Organic Compounds in Ambient Air of Pasir Gudang by using Gas Chromatogrpahy-Mass Spectrometry

Aina Syahira Rosli and Faizuan Abdullah*

[a]*Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia*
**Corresponding Author: faizuan@utm.my*

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GRAPHICAL ABSTRACT

ABSTRACT

Accumulation of VOCs in ambient air affects air quality through the secondary organic aerosol and generation of surface level ozone. Hence, the study of determination of VOCs in ambient air was conducted to monitor the VOCs content in Pasir Gudang industrial area. The study was performed at the affected school during Sungai Kim Kim illegal chemical waste dumping tragedy, Sekolah Kebangsaan Taman Pasir Puteh, Pasir Gudang in January 2020. Gas chromatography–mass spectrometry (GC/MS) was employed to measure the VOCs content especially benzene, toluene, ethylbenzene and xylene. Sorbent cartridge was used to sampled the VOCs in the ambient air via active and passive sampling method. Both quantitative and qualitative analysis of VOCs showed low level of VOCs concentration with 96.36 ± 2.52 percent of recovery. The concentration of VOCs at all sampling point were below limit of range (LOR), it shows that the compounds are below the instrument sensitivity. Limits of detection (LOD) for benzene, toluene, ethylbenzene and o-xylene was 0.05 $\mu g/m^3$ meanwhile for m,p-xylene is 0.1 $\mu g/m^3$. Meanwhile, limit of quantification (LOQ) for benzene, toluene, ethylbenzene and o-xylene is 0.64 $\mu g/m^3$ meanwhile for m,p-xylene is 1.3 $\mu g/m^3$. This study concludes that the VOCs especially BTEX were not detected using the active and passive sampling technique using sorbent cartridge.

Keywords: Volatile Organic Compound (VOCs), BTEX, Gas Chromatography-Mass Spectrometry (GC-MS), Thermal desorption (TD), Pasir Gudang

1. INTRODUCTION

Many sites across Malaysia are being mandated to measure the level of volatile organic compounds (VOCs) to understand fully their impact on environment. VOCs are compounds that easily become gases or vapor and often released from burning fuel or consumer products. VOCs are one of the most hazardous group of air pollutants. Exposing to VOCs may cause severe health problem and high risk to chronic disease, such as cancer [1]. Some of VOCs compound such as BTEX group which consist of benzene, toluene, ethyl benzene and toluene are very hazardous and according to World Health Organization (WHO), benzene are classified as toxic to human, though no safe level of exposure is recommended yet. Each of the compounds has a different ozone reactivity or ozone fonning potential. Therefore, the concentration of benzene, toluene, ethyl benzene and xylenes from the ambient air should be determined accurately and must be monitored continuously because there is no study about VOCs standard in ambient air in Malaysia yet. A specific list of compounds (see Table 1) to be determined by using their respective response factors was intended to provide for more precise quantification of the major fraction of VOC typically occurring in ambient air.

Our study took place in industrial area of Pasir Gudang where there are several industries that may have discharge VOCs through air or water. In a chemical pollution case in March 2019, it is reported that an illegal tyre recycling factory had allegedly dumped chemical waste in Sungai Kim Kim in Pasir Gudang causing several students, teachers and canteen workers from several schools had experienced nausea, dizziness and vomiting. The chemical that are analyze from this case are compounds such as acrylonitrile and acrolein, in addition to methane, hydrogen cyanide, toluene, xylene and limonene. Thus, sampling strategies vary according to the objectives of the studies, type of sample, expected concentration range, required sensitivity, accuracy, and precision, selectivity, presence of interferences, portability, and cost [3]. Monitoring their concentration levels has been conducted routinely to help establish the proper maintenance of air quality in urban/rural area. VOCs are considered as contributors to global warming by Intergovernmental Panel for Climate Change (IPCC) because of their chemical reactivity and their potential to produce tropospheric ozone and another photochemical oxidant. Thus, the present study aims to analyse samples the VOCs especially BTEX in the ambient air of Pasir Gudang using sorbent cartridge, to analyze the VOCs captured in the sorbent cartridge using GC-MS with thermal desorption technique and to compare the result of VOCs in active and passive sampling method.

Table 1. Four substances at least to be quantified using their own response factors, according. Boiling points (°C) and m/z values for integration and calibration/quantification.

Compounds	Boiling point (°C)	m/z value	Allowed maximum contamination level (ppm)
Benzene	80.1	78	0.005
Toluene	110.6	91	1
Ethylbenzene	136	91	0.7
Xylene	144.4	91	10

2. EXPERIMENTAL

2.1 Sampling site

Pasir Gudang is an urbanised area located in the Johor, an administrative and industrial center of Malaysia. High traffic density as well as construction activities might contribute to the level of VOCs in this area as well as chemical and petrochemical industries. Sampling was carried out at SK Taman Pasir Putih, which is a school that has the highest victim of the Sungai Kim Kim pollution in 2019. Figure 1 below shows the location site of the sampling area. Any pollution event from that direction can influence the concentration of VOCs at the sampling locations.

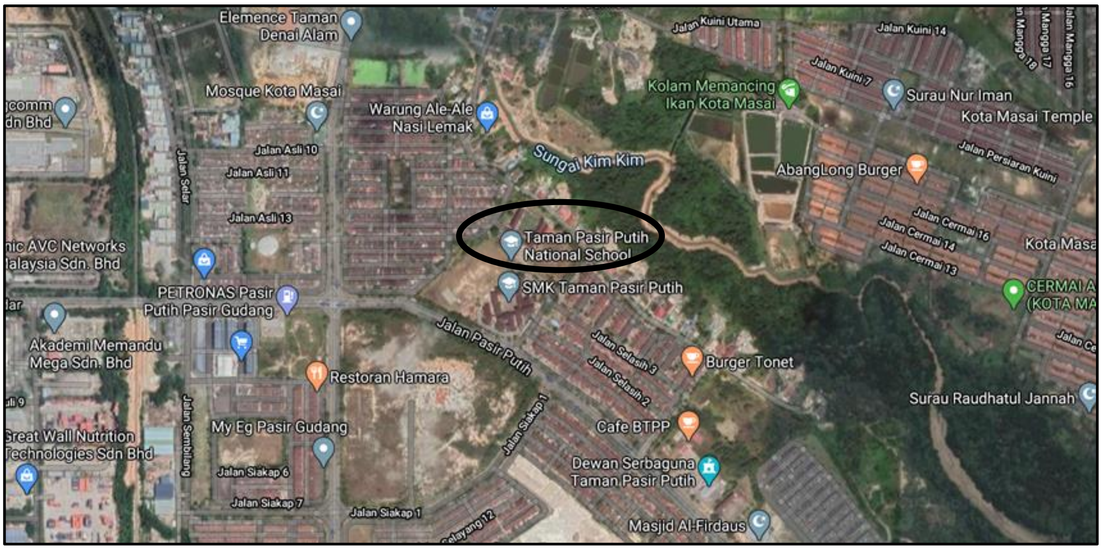


Figure 1: Map showing sampling site with high emission of VOCs, Taman Pasir Putih (near to Sungai Kim Kim)

2.2 Sampling Process

Both active and passive sampling are followed as United State Environment Protection Agency (USEPA) method. The location of sampling site is in urbanized area of Pasir Gudang which is elementary school because the emission of VOCs is high and the school was the most effected during the case. Before the sampling process, sorbent cartridges (Tenax, Markes), were vacuumed with high pure nitrogen gas to remove air, water vapor, and any organic compounds. For active sampling, the ambient air sample was collected around 9a.m to 9p.m on weekday. The ambient air samples were pumped into a sorbent cartridge for about 12 hours at a flow rate of 0.1L min^{-1} by using portable air sampler (Buck Libra Pump L-4). Figure 2 below shows the active sampling process at SK Taman Pasir Puteh and Figure 3 shows the pump used for active sampling. For passive sampling, samples were left for two weeks. Four active sampling and four passive sampling which total of eight samples were collected from SK Taman Pasir Puteh at four different school's building level. The cartridges were kept prior to the analysis, which was carried out 48 hours after the sampling. All cartridges were kept in room temperature for maximum two weeks before analysis.

Table 2. GC-MS parameters

Parameter	**Description**
Initial oven temperature	40°C
Final oven temperature	220°C
Oven ramp rate	30°C/sec
Carrier gas	Helium
Method	Split

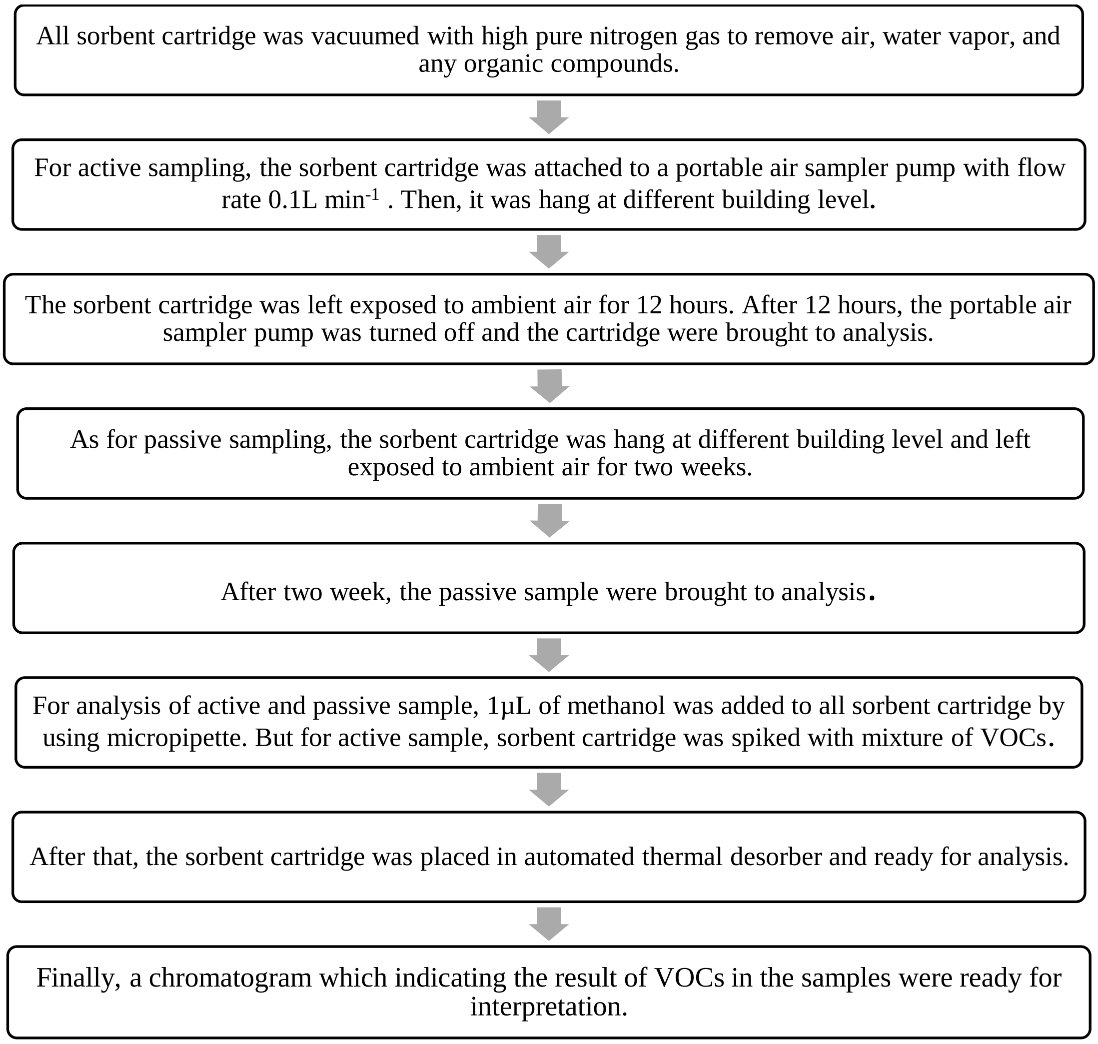
Figure 2. Active sampling process at Taman Pasir Puteh

Figure 3. Portable air sampler pump (Bulk Libra pump L-4) used for active sampling

2.3 Analysis of VOCs using TD-GC-MS

The sorbent cartridge was brought to ALS Technichem in Shah Alam, Malaysia for analysis. The instrument that were used was automated thermal desorber (TD-100XR, Markes) and GC-MS (Agilent Technologies) as can be seen in Figure 4 below. The GC-MS parameter are shown in table 2 above. All standard used was provided by ALS Technichem. Internal standard that was use is 0.25ppb of methanol. 1µL of methanol was added to all sample cartridge by using micropipette. One blank sorbent cartridge and one sorbent cartridge with surrogate was used for calibration prior to analyzing all samples to ensure that the TD-GC-MS system produces a clean chromatographic background. Figure 5 below shows the flow chart of analysis (from sampling to final result).

Figure 4. TD-GC-MS instrument that was used for analysis of VOCs



All sorbent cartridge was vacuumed with high pure nitrogen gas to remove air, water vapor, and any organic compounds.

For active sampling, the sorbent cartridge was attached to a portable air sampler pump with flow rate 0.1L min^{-1} . Then, it was hang at different building level.

The sorbent cartridge was left exposed to ambient air for 12 hours. After 12 hours, the portable air sampler pump was turned off and the cartridge were brought to analysis.

As for passive sampling, the sorbent cartridge was hang at different building level and left exposed to ambient air for two weeks.

After two week, the passive sample were brought to analysis.

For analysis of active and passive sample, 1µL of methanol was added to all sorbent cartridge by using micropipette. But for active sample, sorbent cartridge was spiked with mixture of VOCs.

After that, the sorbent cartridge was placed in automated thermal desorber and ready for analysis.

Finally, a chromatogram which indicating the result of VOCs in the samples were ready for interpretation.

Figure 6. Flow chart of analysis (from sampling to final result)

3. RESULTS AND DISCUSSION

3.1. Result of active sampling of VOCs

Table 3 shown below are the result of VOCs for active sampling. From the result shown, the level of BTEX was below the limit of range. It was reported that benzene has 100% recovery meanwhile toluene show 95.2 % recovery, ethylbenzene with 97.2%, m,p-xylene with 93.2% and o-xylene with 96.2%. The average recovery of BTEX compound are (96.36±2.52) percent of recovery. It is reported that the LOD of benzene, toluene, ethylbenzene and o-xylene is 0.05 µg/m^3 meanwhile for m,p-xylene is 0.1 µg/m^3. Even though BTEX compound was below detection limit in that area, it is important to measure the concentration of each compound to monitor the VOCs level as well as to avoid adverse impact on human and ecology.

Table 3. Result of active sampling of VOCs compound in ambient air of Pasir Gudang in January 2020

Compound	LOR ($\mu g/m^3$)	Result	Recovery (%)
Benzene	0.05	<0.05	100
Toluene	0.05	<0.05	95.2
Ethylbenzene	0.05	<0.05	97.2
Xylene (m,p)	0.1	<0.1	93.2
Xylene (o)	0.05	<0.05	96.2

The results indicated that the average of four sorbent cartridge used, shows that the compound was not detected in the area. In addition, there is not a constant amount of residues dumped to Sungai Kim Kim, so VOC concentration levels in the air are rather changeable with time. The quality control term Laboratory Control Spike (LCS) refers to a certified reference material, or a known interference free matrix spiked with target analytes. The purpose of this QC parameter is to monitor method precision and accuracy independent of sample matrix. In total, 64 VOC species were identified in this study, including 25 alkanes, four alkenes, 13 aromatics, 13 carbonyls and nine other compounds. Aromatic hydrocarbons were among the main VOCs released into the atmosphere as result of many factors such as vehicle combustion and chemical factories. Many aromatic hydrocarbon VOC monomers were harmful to humans and the environment because of their toxicity. For example, benzene can damage the hematopoietic system and the nervous system. In addition, benzene has been identified as a carcinogen by the World Health Organization International Cancer Research Center.

Accuracy is usually measured as a percent recovery. QC analyses used to measure accuracy include standard recoveries, laboratory control samples, spiked samples, and surrogates. Accuracy represent how close a measurement comes to its true value. Thus, it is important to validate the experiment because bad equipment, human error or poor data processing can lead to inaccurate result. Major sources of errors can be breakthrough of compounds during sampling and inappropriate calibration. Air quality is dependent on weather condition and is therefore sensitive to climate change. This type of strong seasonality may also be explained in part by temperature inversion during raining. In ambient air, VOC concentrations generally reach a maximum in winter due to higher atmospheric stability. Moreover, chemical removal of VOC by OH radicals is faster in summer than in winter, as higher radiation and temperature of the former generally facilitate their removal reaction rate. In contrast, a study reported that temperature and wind speed can exert important influences on the observed VOC levels [4]. Thus, during the sampling time, it was reported that it is raining which have greatly affect on VOCs concentration. According to Ibrahim et. al (2019), high level of humidity affects VOCs. Decrease in ambient temperature and relative humidity will decrease the release of VOCs, which will affect its peak concentration and stable concentration.

3.2 Result of passive sampling of VOCs

Result of passive sampling of VOCs in ambient air of Pasir Gudang in January 2020 were shown in table 4 below. Among the most abundant VOCs, benzene, toluene, ethylbenzene, m,p-xylene were our main concern and need to be identified and quantified in the sampling sites. In all sites, the qualitative distribution of VOCs is similar. Most of the analytes are not detectable in air since it is lower than limit of range (LOR). Benzene, toluene, ethylbenzene and o-xylene shows concentration of lower than 0.64 $\mu g/m^3$ meanwhile m,p-xylene shows concentration of lower than 1.3 $\mu g/m^3$. As reported, the LOQ for benzene, toluene, ethylbenzene and o-xylene is 0.64 $\mu g/m^3$ meanwhile for m,p-xylene is 1.3 $\mu g/m^3$.

Table 4. Result of passive sampling of VOCs in ambient air of Pasir Gudang in January 2020

Compound	LOR ($\mu g/m^3$)	Sample 1 (Ground floor)	Sample 2 (First level)	Sample 3 (Second level)	Sample 4 (Third level)
Benzene	0.64	<0.64	<0.64	<0.64	<0.64
Toluene	0.64	<0.64	<0.64	<0.64	<0.64
Ethylbenzene	0.64	<0.64	<0.64	<0.64	<0.64
m,p-xylene	1.3	<1.3	<1.3	<1.3	<1.3
o-xylene	0.64	<0.64	<0.64	<0.64	<0.64

All samples were spikes with 1µL of internal standard before analysis. An internal standard is an analyte or group of analytes added to a sample at a constant concentration, for calibration and quantitation. The internal standard is an analyte chemically similar to those being evaluated. It is typically added in GC/MS methods to correct analyte concentrations during analysis. The recoveries of the spiked analytes are evaluated to determine accuracy in a given matrix. Before analysis, a surrogate is added into a blank sorbent cartridge to perform continuing calibration verification (CCV). Surrogate consist of 3 chemicals which are 1,2-dichloromethane-d4, toluene-d8 and n-bromofluorobenze which concentration of 10ppmv each, is used because each surrogate represents a group of analytes. Samples that fail surrogate recovery criteria are re-spiked and re-analyzed to determine if poor recovery is due to laboratory spiking error or matrix interference.

BTEX compound can be harmful to both human and environment. Thus, several precaution should be taken care of while doing the study. Working in a ventilated area and using rubber gloves is highly recommended. Another way to reduce exposure to volatile organic chemicals, is to properly dispose of partially full containers of chemicals that are old or no longer needed. Gases can leak from sealed containers, so this step alone may contribute greatly to reducing your exposure. While handling sorbent cartridge, it is recommended to wear gloves to prevent direct exposure to VOCs. Other than that, we need to wear face masks when sampling and analysis process to avoid inhaling VOCs as it can cause shortness of breath.

3.3 Source appointment of VOCs

In general, VOCs are harmful to both health and environment, so management of the risks associated with VOCs necessitates accurate and reliable monitoring. Due to the extreme variety of VOCs sources and the complexity of their emissions, understanding the proportion of major VOCs emission and proportion of each pollutant source in the ambient air seem to be a great importance. One of the major contributors to VOCs emission around the study area was illegal dumping that happened in the river, or a gasoline-related material such as petroleum. Since the case was a year before this study was conducted, it is possible that the VOCs are loss in the time being and thus, it is difficult to detect VOCs during this study. Even though there is slightly detectable VOCs content in the area, it is mainly caused by the factory and petrol station nearby of the study area.

4. CONCLUSION

In this study, a TD-GC-MS methodology was successfully developed for trace analysis well below 0.64µg/m^3 of 64 VOC standards in air samples. In conclusion, the mean recovery of the method uses for passive sampling reported to be 96.36±2.52%. Five VOCs samples were negatively reported which is benzene (<0.64 µg/m^3), toluene (<0.64 µg/m^3), ethylbenzene (<0.64 µg/m^3), m,p-xylene (<1.3 µg/m^3) and o-xylene(<0.64 µg/m^3). The LOD for benzene, toluene, ethylbenzene and o-xylene is 0.05 µg/m^3 meanwhile for m,p-xylene is 0.1 µg/m^3. In addition, the LOQ for for benzene, toluene, ethylbenzene and o-xylene is 0.64 µg/m^3 meanwhile for m,p-xylene is 1.3 µg/m^3. The proposed methodology enables reliable characterization of chemical composition of the ambient air in Pasir Gudang, collected during January 2020 by both active and passive sampling. All samples were negatively identified and quantified. Benzene, toluene and ethylbenzene showed lowest concentration with below than 0.64 µg/m^3 while xylene reported to be below 1.3 µg/m^3.

Overall, benzene, toluene, xylene and ethylbenzene were reported to be below LOR, as per say its concentration is low at the time of sampling due to several reason which are temperature and humidity factor. It is desirable to find the precise determination of VOCs typically occurring in ambient air. Thermally desorbable passive samplers have many advantages. They offer increased sensitivity since essentially the whole sample is available for analysis; huge dynamic range; freedom from solvent use and contamination issues associated with chemical desorption; and more rapid sample turnaround. In addition, the devise itself is reusable and can be used in either active or passive mode. Adsorbents can be easily replaced for customized applications. Once collected, adsorbent samples have been shown to have good linearity, excellent stability in long-term storage tests, high recovery, and good precision. New approach in this direction can be induced from the technique described in literature such as Ghidotti *et. al* (2018) and Ribes *et. al* (2007). More studies need to be carried out in order to evaluate seasonal effects in emissions of VOCs in the study area. This would help to thoroughly describe VOCs behaviors, since statistical models may vary between different seasons.

REFERENCES

[1] Caselli, M., Gennaro, G. D., Marzocca, A., Trizio, L., & Tutino, M. (2010). Assessment of the impact of the vehicular traffic on BTEX concentration in ring roads in urban areas of Bari (Italy). Chemosphere, 81(3), 306–311.

[2] Cetin E. Odabasi M. Seyfioglu R.(2003). Ambient volatile organic compound (VOC) concentrations around a petrochemical complex and a petroleum refinery. Sci. Total Environ. 312:103.

[3] De Koning, S., Janssen, H.-G., & Brinkman, U. A. T. (2009). Modern Methods of Sample Preparation for GC Analysis. Chromatographia, 69(S1), 33–78.

[4] Ibrahim, I. Z., Chong, W. T., Yusoff, S., Wang, C., Xiang, X., & Muzammil, W. K. (2019). Evaluation of common indoor air pollutant reduction by a botanical indoor air biofilter system. Indoor and Built Environment.

[5] Pankow, James F., et al. “Determination of a Wide Range of Volatile Organic Compounds in Ambient Air Using Multisorbent

Adsorption/Thermal Desorption and Gas Chromatography/Mass Spectrometry.” Analytical Chemistry, vol. 70, no. 24, 1998, pp. 5213–5221.

[6] Rabaud, N. E., Ebeler, S. E., Ashbaugh, L. L., & Flocchini, R. G. (2002). The Application of Thermal Desorption GC/MS with Simultaneous Olfactory Evaluation for the Characterization and Quantification of Odor Compounds from a Dairy. Journal of Agricultural and Food Chemistry, 50(18), 5139–5145.

[7] Ramírez N., Marcé R. M., & Borrull F. (2011). Determination of volatile organic compounds in industrial wastewater plant air emissions by multi-sorbent adsorption and thermal desorption-gas chromatography-mass spectrometry. International Journal of Environmental Analytical Chemistry, 91(10), 911–928.