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Determination of VOCs in Environmental Samples by Purge and Trap-Gas Chromatography Mass Spectrometry

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Abstract

A sensitive purge and trap extraction technique was applied for determination of volatile organic compounds (VOCs). The 9 VOCs which are 1,3-butadiene, dichloromethane, chloroform, 1,2-dichloroethane, benzene, trichloroethylene, 1,2-dichloropropane and tetrachloroethylene were quantified by gas chromatography-mass spectrometry. The optimum conditions of purge and trap system were 15 min purge time at 50°C sample temperature. The analytes were trapped on VOCARB 3000 trap and desorbed at 180 °C for 0.5 min. Finally, bake step was set at 250°C for 30 min at flow rate 400 mL/min. The chromatographic conditions were DB-5MS column, helium flow rate at 1.8 mL/min, injector temperature was 220°C. Temperature program was as follow: initial of 35°C held for 4 min increase to 90°C at 6°C/min, increase to 200°C at 35°C/min, held for 1 min. This method was successfully applied for determination of 9 VOCs in environmental samples collected from Thailand industrial estate and non-contaminated area in order to compare the amount of VOCs emitted from industry.

Keyword: Volatile organic compounds, Purge and trap, GC-MS, Industrial estate

1. Introduction

Volatile organic compounds (VOCs) are a group of low molecular weight aliphatic, aromatic hydrocarbon and chlorinated hydrocarbon with low boiling point. VOCs have a wide range of industry applications. VOCs are used as fuels, solvents for paints and pesticides. VOCs are common contaminant to environmental (air, soil, water and food). VOCs are sources of air toxic, and effect to human such as acute effect and chronic effect (cancer). Human can exposure to VOCs by breathing, drinking water, eating food and beverage, adsorbing dust and soil from hazardous waste (Bloemen & Burn 1993).

The aim of this work was the development of the methods for extraction and analysis of 9 VOCs using purge and trap and gas chromatography mass spectrometric techniques. The purge-and-trap technique coupled to GC-MS has been recommended by the US Environmental Protection Agency (EPA) for determination of trace contaminated VOCs in environmental samples. The developed method was validated and applied to determination of VOCs in environmental samples. The amount of VOCs from industry area and non-contaminated area was compared in order to study the source and pathway of VOCs emission from industry to environment and community. The samples as well as water, soil and food samples were collected from industrial area and non-industrial area of eastern part of Thailand. In addition, 9 VOCs as follows: 1,3-butadiene, vinyl chloride, dichloromethane, chloroform, 1,2-dichloroethane, benzene, 1,2-dichloropropane, trichloroethylene and tetrachloroethylene were monitored due to the recommendation by the Notification of National Environmental Board of Thailand No. 30 (2007).

2. Methods and materials

2.1 Instrumentation and reagents

The purge and trap system (Stratum, Teledyne Tekmar, USA) coupled with Gas chromatography 5890 series II plus couple with 5972 series mass spectrometer (Hawlett Packard, USA) was used in this study.

Volatile organic compounds standards (1,3-butadiene, vinylchloride, dichloromethane, chloroform, 1,2-dicholoethane, benzene, 1,2-dichloropropane, trichloro-ethylene and tetrachloroethylene) and internal standard (Toluene D-8) were purchased from Supelco (USA). The 250 µg/mL standard solutions were prepared in methanol and stored in refrigerator (-2°C). Working solutions were prepared by mixing standard solutions in deionized water before analysis. Ultra high purity (UHP) helium gas was supplied from Lab solution & engineering (Thailand).

2.2 Methods

The GC-MS injection was operated in splitless mode with splitless time of 2 min. Helium carrier gas was set at 1.80ml/min. The MS condition was set detector temperature at 250 °C. The MS was operated in the electron ionization mode (EI) at 70 eV. The selected ion-monitoring (SIM) mode was used in analysis were listed in Table 1.

Environmental samples (water, soil and vegetable) were collected. The samples were collected and kept in zip bag and stored in ice box during transport and then immediately frozen at -20°C before analysis. For sample preparation for extraction of vegetable samples, vegetable sample was cut to small pieces and stored in freezer and finally blended frozen sample by blender.

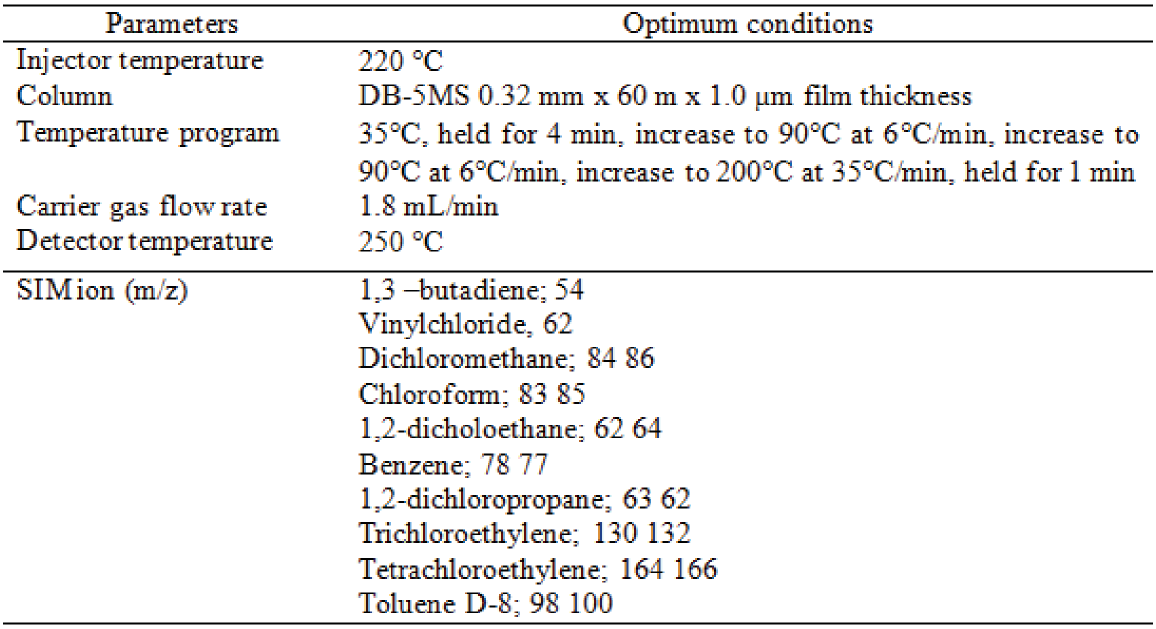
In order to study the emission of VOCs from industry, 2 industrial estates in the eastern part of Thailand were chosen as the contaminated area. The 4 areas in the same city that without industrial estate were chosen as non-contaminated area (controlled area).

3. Results and Discussion

3.1 The optimization of gas chromatography-mass spectrometry.

In this work, GC-MS was used to separate 9 VOCs, 1,3-butadiene, vinyl chloride, dichloromethane, chloroform, 1,2-dichloroethane, benzene, trichloroethylene, 1,2-dichloropropane and tetrachloroethylene. Firstly, 9 VOCs separations were performed on a 30 m and 0.25µm film thickness HP5-MS capillary column. Unfortunately, this column could not be separated all VOCs peaks. The longer column with more film thickness of 60 m with 1 µm film thickness HP5-MS column was chosen in order to increase separation performance. The temperature program, initial of 35°C held for 4 min, increase to 60°C at 25°C/min, increase to 90°C at 6°C/min, increase to 200°C at 35°C/min, held for 1 min and carrier gas flow rate of 1.8 mL/min were the optimum conditions. The 9 VOCs were completely separated within 13.75 min. In addition, injector temperature of 220°C was optimum condition because it provided the higher peak area of most compounds. The GC-MS optimum conditions were summarized in Table 1.

Table 1: The optimum condition of the GC-MS and SIM ions for VOCs



Parameters	Optimum conditions
Injector temperature	220 °C
Column	DB-5MS 0.32 mm x 60 m x 1.0 µm film thickness
Temperature program	35°C, held for 4 min, increase to 90°C at 6°C/min, increase to 90°C at 6°C/min, increase to 200°C at 35°C/min, held for 1 min
Carrier gas flow rate	1.8 mL/min
Detector temperature	250 °C
SIM ion (m/z)	1,3 –butadiene; 54 Vinylchloride, 62 Dichloromethane; 84 86 Chloroform; 83 85 1,2-dicholoethane; 62 64 Benzene; 78 77 1,2-dichloropropane; 63 62 Trichloroethylene; 130 132 Tetrachloroethylene; 164 166 Toluene D-8; 98 100

3.2 The optimization of purge and trap.

The purge and trap conditions were varied to obtain the highest sensitivity and the best repeatability for the analysis. Firstly, helium gas purging flow rate was set at 40 mL/min in accordance with the manufacturer's recommendation (Meloan, 1999, Teledyne Tekmar, 2009). For the type of trap, VOCARB 3000 and VOCARB 4000, were the recommendation traps for determination of VOCs (United States Environmental Protection Agency, 1996). However, the higher peak areas were obtained from VOCARB 3000. Type of sparger was the next study. The more efficient extraction was obtained from frit sparger when it was compared with fritless sparger because the dispersion of fine bubbles provides more efficient than that of large bubbles (Meloan, 1999). However, frit sparger could not suitable with vegetable samples or sediment samples because sample was clogging up of the gas flow routes. Therefore, 25 mL fritless with 15 mL sample solution was chosen in this study.

The sample temperature was the next parameter, the increasing in temperature always increase in purge efficiency (Meloan, 1999). The sample temperature was varied 30-70°C. The sample temperature of 50°C was chosen as the optimum condition because low boiling point of some compounds such as vinyl chloride and 1,3-butadiene were instable when high temperature performed. It was due to its stability and reactivity properties. In the purge time study, the increasing in the peak area was found when the purge time increased from 5 to 11 min. However, the purge time more than 15 min led to a slightly decreasing in the peak area in almost of the compounds. The longer purge time decreased the peak area because the helium itself causes stripping of the trapped analytes (Campillo, Vinas, Lopez-Garcia, Aguinaga, & Hernandez-Cordaba, 2004). Therefore, 15 min was chosen as the optimum condition. The dry purge time was varied between 1-5 min. When the dry purge time more than 1 min performed, the peak areas of almost all compounds were decreased. Due to the VOCs compounds were removed from trapped together with moisture to waste. Therefore, 1 min was the optimum condition of the dry purge time.

In desorption temperature study, the compounds were desorbed and transferred to GC-MS instrument. The highest peak area was achieved at 180°C. When the temperature was more than 200°C, the decreasing in peak area was found. Desorption time was studied between 0.5-4 min. The highest peak areas were obtained at desorption time between 0.5-1 min. The decreasing in peak area was found when desorption time was more than 1 min. Thus, the optimum desorption time was 0.5 min, which provided the high peak area for almost of the compound. Transfer line temperature also effects on the vaporization of VOCs and prevents the condensation of VOCs in the injection port of GC instrument.

The transfer line temperatures of 180-240°C were varied. The decreasing in peak areas of VOCs was found when the temperature was increased. It was found that 180°C was the optimum transfer line temperature because at high temperature, inconstant of peak area was monitored. Finally, bake was the step that cleans up the trapping material prior to next analysis and removed any contamination of tailing compounds (Teledyne Tekmar, 2009). After the desorption step, the trap temperature was raised to 260°C at 400 mL/min He flow rate. Bake time of 10-30 min was varied. The decreasing in peak area of residue peak was found when the bake time increased from 10-30 min. Thus, 30 min was optimum condition for bake time. The optimization of purge and trap were summarized in Table 2

Table 2: The optimum conditions of purge and trap system.

Parameters	Optimum Conditions
1. Trap	VOCARB 3000
2. Sparger	Sparger 25 mL fritless
3. Sample temperature	50°C
4. The purge time	15 min
5. The dry purge time	1 min
6. The desorption time	0.5 min
7. The desorption temperature	180°C
8. The transfer line temperature	180°C
9. Bake time	30 min

3.3 The optimization of extraction conditions

The parameters that affect the extraction efficiency were evaluated in this study. The parameters such as, the salting out effect, step of antifoam adding, concentration of antifoam, extraction time, extraction temperature, centrifuge rate, centrifuge time and filtered solution were studied. Firstly, 5 g of sample was used in optimization of extraction condition. And then 9 VOCs standard solutions were spiked into sample vial. In the salting out effect, the effect of salting out was increased to extraction efficiency in analytical procedures. The salting out effect was the decreased of solubility of analyte in water when salt was added to the solution. Therefore, molecules of analyte will be removed of solution and into headspace by gas flow (Satoshi, Andrea, & Kai-Uwe, 2012, Alonso, Castellanos, Besalu & Sanchez, 2012). In this research, the extraction efficiency of all compounds was improved with addition of 3%w/v NaCl. The antifoam was also effect extraction efficiency. No addition of antifoam, the VOCs could analyzed in vegetable samples. Since, the matrix of the samples causes serious foaming during purge step (Campillo, Vinas, Lopez-Garcia, Aguinaga, & Hernandez-Cordaba, 2004). Sample foaming can be reduced by decreasing the purge flow rate or adding antifoam agent (Roose & Brinkman, 1998). The 0.005 %v/v of antifoam was used during sample extraction process in order to eliminate of foam bubbles.

The extraction time was soaking the sample in DI-water and storage in 40mL vial. For 1-5 hour of extraction time, increasing in peak area for mostly compounds was monitored. In addition, 10-15 hour of extraction time, decreasing in peak area and poor standard deviation were obtained. Thus, 10-15 hour was not suitable in this extraction. Therefore, 5 hour of extraction time was chosen as the optimum condition. The extraction temperature was the next parameter. In general, higher temperature will cause an increase of liquid extraction efficiency due to enhance sample wetting, better of the extraction solvent, and desorption rate of analyte from matrix to the solvent (Koning, Janssen & Brinkman, 2009). However, VOCs was inapplicable in extraction of higher temperature because analyte was low boiling point and instable in high temperature. No significant difference in peak area was found when increasing temperature. Therefore, 0°C was chosen for extraction temperature as an optimum condition because low boiling point of some compounds such as vinyl chloride and 1,3-butadiene were instable when high temperature performed. The centrifuge rate was performed due to fully separate the clear extracted solution and residue vegetable fiber. The centrifuged rate of 1500 rpm was optimum condition because good separated between precipitate and solution. It was performed to supernatant and easy to suction with syringe before injection to PT system. In addition, the higher centrifuge speed could not effect to extraction efficiency because the purpose of centrifuge was separated the clear extracted solution. The centrifuge time was the next parameter, increasing in peak area of most VOCs was found in centrifuge time of 2-4 min. However, decreasing in peak area with centrifuge time more than 4 min was monitored. Thus, centrifuged time 4 min was optimum condition.

The filtered and non-filtered of samples before injection into PT were compared. The increasing peak area of most VOCs was monitored when non-filtered performed. Finally, sample preparation was 5g of vegetable weighed into a 40 mL vial, 30 mL DI-water, 3%w/v

NaCl were then added into vial. Temperature of 0°C and time for extraction of 5 hour were used as the optimum extraction condition. After extraction, 0.005% antifoam was added into vial, centrifuge rate at 1500 rpm for 4 min and non-filtered before injected to PT system were the optimum condition. The optimum conditions of extraction are summarized in table 3.

Table 3: The optimum conditions for extraction of sample.

Parameters	optimum conditions
1. The salting out	3% w/v
2. Added antifoam step	after extraction
3. Antifoam Concentration	0.005 %v/v
4. The extraction time	5 hour
5. The extraction temperature	0°C
6. The centrifuge rate	1500 rpm
7. The centrifuge time	4 min
8. Filtered	Non-filtered

3.4 The validation method.

The optimum conditions of purge and trap coupled with gas chromatography mass spectrometry were used for validation method. The linearity, limit of detection, limit of quantification, precision and accuracy were studied. The linearity of 9 VOCs was of 0.05-500 µg/L. The LOD and LOQ were 0.20 ng/L-0.22 µg/L and 1.0 ng/L-0.74 µg/L, respectively. The repeatability (%RSD, n=10) and intermediate precision (%RSD, n=9) at second level concentration were 8-22% and 7-19%. The precision at this level are acceptable followed by AOAC manual (AOAC International, 1993), (not over 30% at 1 µg/L level). The accuracy was evaluated by spiking 9 VOCs in the vegetable sample. The %recovery was in the range of 89-165%. The %recovery was acceptable followed by AOAC manual (not over 40-120% at 1 µg/L level). The validation characteristics were summarized in table 4.

Table 4: The validation characteristics

Characteristics	Value
Linearity	0.05-500 µg/L ($R^2 > 0.995$)
LOD	0.20 ng/L - 0.22 µg/L
LOQ	1.0 ng/L – 0.74 µg/L
Reatability (%RSD, n=10)	8-22 %
Intermediate (%RSD, n=10)	7-19%
%Recovery	89-165%

3.5 Determination of VOCs in samples.

The proposed method was applied for determinations of 9 VOCs in environmental samples. The 53 water samples and 24 soil samples were collected from 6 areas in the Rayong province, Thailand. The VOCs of 12.5 µg/L chloroform and 2.5 µg/L benzene were found in tap sample collected from area near the first industrial estate. The VOCs of 5.2 µg/kg dichloromethane, 1.6 µg/kg chloroform and 2.4 µg/kg benzene were found in one soil sample collected from the area near the first industrial estate. In addition, 1.2-5.0 µg/kg dichloromethane and 0.1-0.9 µg/kg benzene were found in the second industrial estate. Whereas, no VOCs was found from samples collected from non-contaminated areas. The amount of VOCs found in the environmental samples from six site of study was shown in table 5. The samples that contaminated with VOCs in area near industrial estate were not significant difference with non-contaminated area. It was indicated that the source of VOCs in environment was not only industry but also other reasons such as transportation or household used.

Table 5: Number of sample that VOCs contaminated in difference study area

Study area	Number of sample		
	dichloromethane	benzene	chloroform
Industrial estate 1	19	16	4
Industrial estate 2	26	4	0
Non-contaminated area 1	19	17	0
Non-contaminated area 2	18	16	0
Non-contaminated area 3	4	2	2
Non-contaminated area 4 (control area)	2	0	0

For vegetable samples, 4 types of vegetable (ivy gourd, chinese cabbage, kale, and swamp morning glory) were collected from area near the industrial estate 1. Vegetables samples were classified into 2 groups. i) Vegetables sell in the market near industrial estate. These vegetable samples could not be identified the origin but generally imported from other cities. ii) Vegetables growing in the area near industrial estate. The amount of VOCs in vegetable obtained from market and grown by agriculturist near industrial estate was compared in this work in order to study the sources and pathway of VOCs from industry to environment as well as the food chain.

The results of analysis, dichloromethane, chloroform, 1,2-dichloroethane, benzene and tetrachloroethylene were found in vegetable samples as shown in table 6. In addition, the higher amount of benzene, dichloromethane and chloroform were found in vegetable grown in industrial area when compare with the vegetable samples collected from the market. Whereas, no significant difference in the amount of 1,2-dichloroethane and tetrachloroethylene were found in both groups of vegetable samples. It was indicated that the trend of VOCs founded in vegetables grown in the industry area were higher than collected from the market. Since, vegetable grown in the industrial area was effected by VOCs in the environment. The water for agriculture contaminated from the industry could be the possible reason. In addition, the adsorption of VOCs in air and dust particles by the vegetable could also the pathway of VOCs from industry to the vegetables.

Table 6: VOCs found in vegetable samples collected from industrial estate area

Sample	group	Concentration (µg/kg)				
		Dichloro-methane	Chloroform	1,2-dichloro-ethane	Benzene	Tetrachloro-etylene
Swamp morning glory	i*	n.d***.	n.d.	n.d.	52±19	187±45
	ii**	387±88	n.d.	188±35	212±53	220±52
Chinese cabbage	i	41±10	56±22	n.d.	94±8	185±28
	ii	229±49	124±18	n.d.	112±3	183±12
Kale	i	n.d.	38±5	n.d.	65±11	139±12
	ii	51±24	58±8	n.d.	252±12	140±6

*i =Market, ** ii = Grown in industry area, ***n.d. = Not Detected

4. Conclusion

The method for the determination of nine VOCs in environmental samples by purge and trap-GC-MS techniques was developed. This method can be used for the quantitative measurement of VOCs at very low concentrations (ng/L). In addition, the low level contamination of VOCs was found in environmental samples collected from industrial area of Thailand. However, the contamination was below the maximum concentration levels accepted from the Notification of National Environmental Board of Thailand. In addition, the sources of VOCs emission to environment were not only industry but also other ways such as transportation.

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