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EFFECTS OF ADSORBENTS ON THE DETECTION OF THE CONTAMINANTS FROM HARD DISK DRIVE

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วิลาวัลย์ ศรีพรหม: ผลของตัวดูดซับต่อการตรวจวัดสารปนเปื้อนจากฮาร์ดดิสก์ไดรฟ์ (EFFECTS OF ADSORBENTS ON THE DETECTION OF THE CONTAMINANTS FROM HARD DISK DRIVE) อาจารย์ที่ปรึกษา: ผศ.ดร. วรินทร ชวศิริ; 89 หน้า. ISBN 974-17-3996-6

ได้ประเมินประสิทธิภาพของตัวดูดซับ 6 ชนิด สำหรับการเก็บตัวอย่างและการวิเคราะห์ปริมาณไอระเหยที่ออกมาจากส่วนประกอบของฮาร์ดดิสก์ไดรฟ์ด้วยเทคนิคการดูดซับ/การคายการดูดซับด้วยความร้อน-จีซีเอ็มเอส ตัวดูดซับที่นำมาศึกษาได้แก่ Tenax TA, Tenax GR, Carbotrap B, C, Carbopack B, C สำหรับตัวดูดซับกลุ่มพอลิเมอร์ที่มีรูพรุนนั้นจะมีความเหมาะสมในการตรวจวัดสารในช่วงกว้างตั้งแต่สารที่มีมวลโมเลกุลต่ำจนกระทั่งสารที่มีมวลโมเลกุลสูง ในขณะที่กราไฟต์คาร์บอนแบล็คจะมีความเหมาะสมกว่าในการตรวจวัดสารที่มีมวลโมเลกุลสูง นอกจากนี้ได้ศึกษาถึงผลของตัวดูดซับผสมเพื่อปรับปรุงประสิทธิภาพในการตรวจวัด พบว่า Carbopack และ Carbotrap C/B ให้ผลการตรวจวัดที่ดีกว่า Tenax TA โดยเฉพาะอย่างยิ่งสำหรับสารในช่วงคาร์บอน 10 ถึง 15 จากการศึกษาถึงปัจจัยที่เหมาะสมพบว่า เวลาที่ใช้ในการดักเก็บสารตัวอย่าง 15 นาทีที่อุณหภูมิ -60 องศาเซลเซียส อุณหภูมิและเวลาที่ใช้ในการคายการดูดซับที่เหมาะสมได้แก่ที่ 358 องศาเซลเซียส 20 วินาที และตัวดูดซับที่ใช้ในการคายการดูดซับที่เหมาะสมสำหรับสารที่มีมวลโมเลกุลต่ำได้แก่ Tenax TA และสำหรับสารที่มีมวลโมเลกุลสูงได้แก่ ใยแก้ว นอกจากนั้นได้ทดสอบปัจจัยที่ให้ค่าการตรวจวัดสูงสุดกับตัวอย่างจริงได้แก่ พิวอตคาร์ทริดจ์และสปินเดิลมอเทอร์ เพื่อหาอุณหภูมิและเวลาที่เหมาะสมในการเก็บตัวอย่างสำหรับการวิเคราะห์

สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์...ลายมือชื่อนิสิต……..……………….……………

ปีการศึกษา…………………2546………………ลายมือชื่ออาจารย์ที่ปรึกษา……...……..……...

4573412523: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEY WORD: ADSORBENT / THERMAL DESORPTION / VOLATILE ORGANIC COMPOUNDS / HARD DISK DRIVE

WILAWAN SRIPHROM: EFFECTS OF ADSORBENTS ON THE DETECTION OF THE CONTAMINANTS FROM HARD DISK DRIVE
THESIS ADVISOR: ASSISTANT PROFESSOR WARINTHORN CHAVASIRI, Ph.D.; 89 pp. ISBN 974-17-3996-6

Six adsorbents were evaluated for sampling and quantitative analysis of VOCs which released from HDD parts using adsorption/thermal desorption-GC-MS technique. The adsorbents employed were Tenax TA, Tenax GR, Carbotrap B and C, Carbopack B and C. Porous polymer adsorbents revealed higher adsorption efficiency for a wide range of molecular weight compounds whereas graphitized carbon black was more suitable for high molecular weight compounds. To improve the adsorption efficiency, dual-sorbent was examined. Carbopack and Carbotrap C/B provided better adsorption efficiency than single-sorbent; Tenax TA, especially in the range of C_{10} to C_{15}. The optimum thermal desorption conditions found for purge and trap time were 15 minutes at -60 ^{o}C trapping temperature and desorption at 358 ^{o}C for 20 seconds, and the secondary adsorption materials for low molecular weight and high molecular weight compounds wereTenax TA and glass wool, respectively. Moreover, the investigation for the optimum sampling temperature and time for pivot cartridge and spindle motor were explored.

Field of study..Petrochemistry and Polymer Science..Student’s signature…………..….
Academic year……………..….2003……..….……….Advisor’s signature…………….

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Ultimately, the author would like to express her inmost gratitude to her family and her best friends for their love, understanding, encouragement and social support throughout her entire education. Thanks are to everyone who has contributed suggestions and support during this research.

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LIST OF ABBREVIATIONS

AP	Acetophenone
CAs	Carboxylic acids
CHAP	Hydroxycyclohexylacetophenone
DMAP	2,2-Dimethoxy-2-phenylacetophenone
DOP	Di-*n*-octyl phthalate
^{o}C	Degree celsius
EHA	Ethylhexanoic acid
FE-SEM	Field Emission Scanning Electron Microscope
GACs	Granular Activated Carbons
GC-MS	Gas Chromatograph-Mass Spectrometry
HDD	Hard Disk Drive
2-HEA	2-Hydroxyethyl acrylate
HEMA	Hydroxyethyl methacrylate
HPMA	Hydroxypropyl methacrylate
IBOMA	Isobornyl methacrylate
IPA	Isopropyl alcohol
i.d.	Inside diameter
JAI	Japan Analytical Industry
Liq. N_2	Liquid Nitrogen
mmole	Millimole (s)
m/z	Mass-to-charge
o.d.	Outside diametre
ppb	Part per billion
P&T	Purge and trap
ppt	Part per trillion
TGDMA	Triethyleneglycol dimethacrylate
VOCs	Volatile organic compounds

CHAPTER I

INTRODUCTION

In electronic industries, especially Hard Disk Drive (HDD) production, the improvement of the product quality parallel with the reduction of the product size were developed. For the HDD quality and reliability, the contamination level of volatile organic (outgas), ionic and solid particulate contaminations[1] should be controlled. For this research, the volatile organic compounds (VOCs) are defined as outgas[2] released from HDD during the operations at high temperature. The trouble which originates from contamination was specified as one of important factors to obstruct the HDD reliability and caused the read/write error, head disk interference trouble and corrosive attack pole tip surface. The compounds that released from HDD component parts were detected as many types of functional groups, for example the siloxane, acrylate and methacrylate (monomers from adhesive), acetophenone (photo-initiator), dioctyl phthalate (plasticizer), *etc*. The main sources of VOCs are adhesive, solvent, grease, oil or cutting material that used in production. The detection of VOCs amount which generated from HDD parts composed of the sampling and the analysis processes. The dynamic headspace sampling device or thermal desorption was used for sampling while the analysis process mainly used gas chromatograph-mass spectrometry (GC-MS). This techniques combine the dynamic headspace (thermal desorption)[3] which is a technique that uses the temperature and a flow of inert gas to extract “volatile” components of interest from solid or liquid matrices, and transfer them to the analytical system and GC-MS[4] which is an analytical technique for identification of chemical structures, determination of a mixture, and quantitative elemental analysis, based on the application of the mass spectrometer with very sensitive/selective detector.

VOCs were purged out from the sample by inert gas and adsorbed onto an adsorption tube. After purging, adsorption tube was heated to release the VOCs for GC-MS analysis. Thus, the improvement of VOCs analysis method can also be used as an aid in detecting root cause of contamination and may assist in solving many cleanliness issues.

Aims of this research

The aims of this research are to investigate the conditions which affect on the detection of VOCs from HDD. Experimental parameters including adsorbents, sampling conditions, desorption materials, baking condition, *etc* were optimized. The evaluation of the adsorbent-adsorbate interactions in order to get a better understanding of the parameters for the correct selection of an adequate sorbent was also explored.

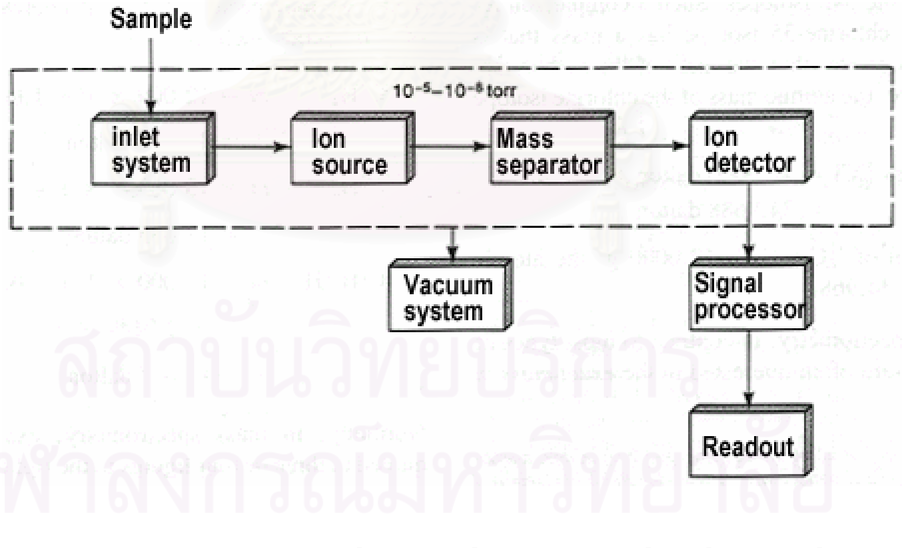
In this research, six adsorbents: Tenax TA, Tenax GR, Carbotrap B, Carbotrap C, Carbopack B and Carbopack C were selected for the investigation of detection efficiency of VOCs from HDD such as acrylates/methacrylates, acetophenones, acids, phthalates, siloxanes and hydrocarbons. To improve the efficiency, dual-sorbent trap was prepared for the analysis. After gaining the information of the best adsorbent, thermal desorption conditions such as purge and trap time, trapping temperature, desorption temperature, desorption time and secondary adsorption materials were studied. Furthermore, the sampling conditions for real samples analysis to optimize the parameter including sampling temperature and time were also examined.

CHAPTER II
THEORY

2.1 Gas Chromatograph-Mass Spectrometry (GC-MS)[5]

Mass Spectrometry (MS) is a rapid, highly sensitive technique with high spectroscopic selectivity with respect to the definition of chemical structure. Whereas some spectral techniques (*e.g.* infrared or Raman) may only yield a representative average structural composition, MS is capable of resolving individual species compositions. Moreover, with a capability to achieve this in nanogram quantities or less, the MS has a mainstream role in chemical analysis. However, when exclusively used for low molecular weight component analysis, the power of MS can be further enhanced by integration with gas chromatograph (GC). Thus, the combined GC-MS can work directly on mixtures to use the GC for separation and the MS for analysis.

The fundamental of mass spectrometry:



Mass spectrometry is a sophisticated instrumental technique that produces, separates, and detects ions in gas phase. A sample with a moderately high vapor pressure was introduced in an inlet system which operated under vacuum (10^{-5} to 10^{-8} torr) and at high temperature (up to 300 °C). It vaporized and was carried to the ionization source**.** Nonvolatile compounds may be vaporized by means of a spark or other sources. Analyte molecules are typically neutral and must be ionized. This is accomplished by various means but typically is done by bombarding the sample with high-energy electrons in an electron-impact source. The electrons produce a positive ion, for example:

$$M + e^{-} >> M^{+} + 2e^{-}$$

M is the analyte molecule and M^+ is called the molecular ion or parent ion. The M^+ ions are produced in different energy states and the internal energy (rotational, vibrational, and electronic) is dissipated by fragmentation reactions. The ions are separated in the spectrometer by being accelerated through a mass separator.

Separation is actually accomplished based on the mass-to-charge (*m/z or m/e*) ratios of the ions. Various spectrometers are based on magnetic sectors in which ions pass through a magnetic field and are deflected based on their *m/z* ratio; time-of-flight in which they traverse a long flight tube and arrive at a detector at different time based on their relative kinetic energies after being accelerated through an electrical field (the lighter ones arrive first); or quadrupoles in which the ions pass through an area with four hyperbolic magnetic poles, created by a radio frequency field, and certain ions take a “stable path” through the field and others take an “unstable path” and are not detected, the radio frequency field is scanned rapidly to detect all the ions. Figure 2.1 shows the quadrupole mass analyzer.

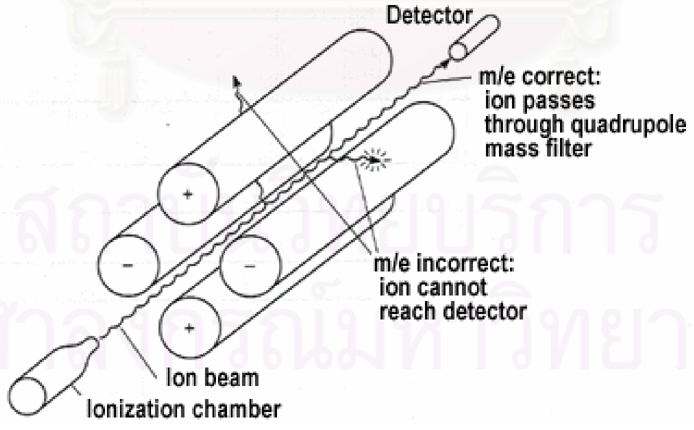


Figure 2.1 Quadrupole mass analyzer[6]

The separated ions are detected by means of an electron multiplier, which is similar in design to photomultiplier tubes. Detection sensitivities at the nanogram level are common.

The effluent from a gas chromatograph may be connected to the sample inlet system of a mass spectrometer, forming a GC-MS system. The mass spectrometer then serves as the GC detector with high sensitivity and selectivity. The mass spectrum is generally characteristic for a given compound (if only one compound is present under the GC peak), giving a certain “fingerprint” at various *m/z* ratios. The fragmentation pattern often exhibits peaks corresponding to loss of specific groups in the molecule, for example, $-CO_2$ or -NH, which lends further credence to the presence of a given molecule or which can be used to gain structural information about a molecule. The marriage of capillary gas chromatography with mass spectrometry provides an extremely powerful analytical tool. Capillary GC, with thousands of theoretical plates, can resolve hundreds of molecules into separate peaks, and mass spectrometry can provide identification.

2.2 Headspace analysis[7]

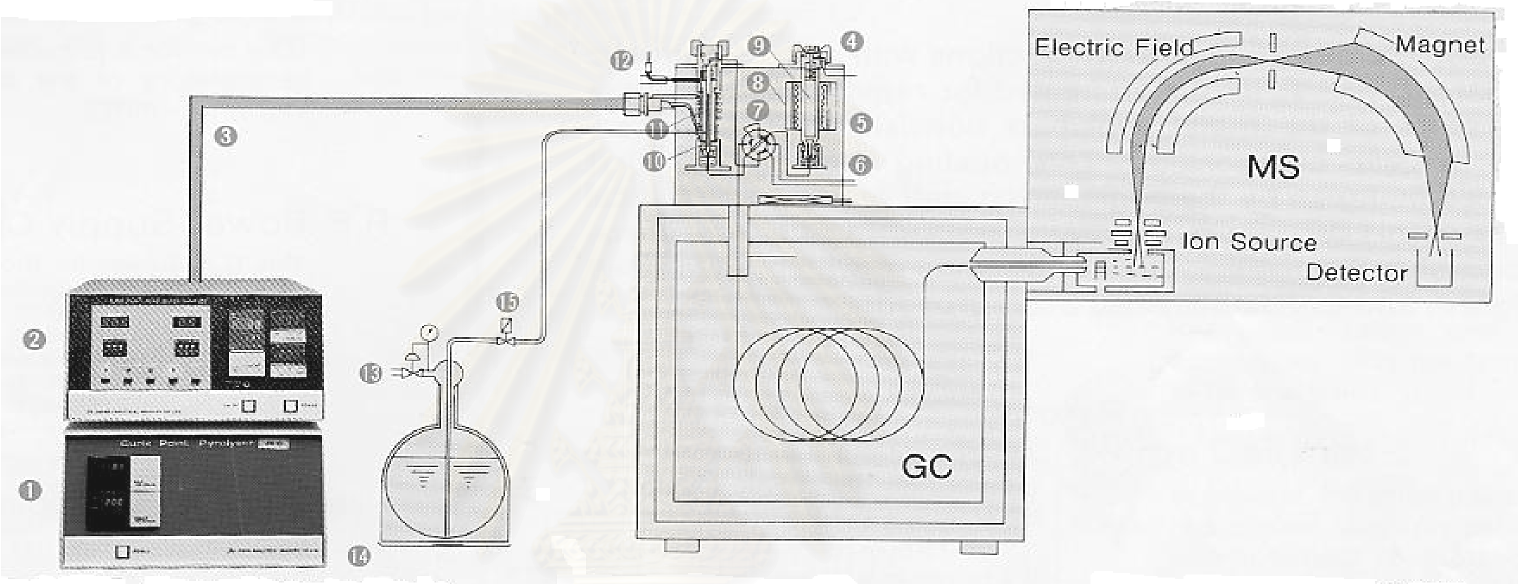
Headspace methods provide an indirect method of sample analysis suitable for the determination of organic volatiles. The gas phase in contact with the sample and not the sample matrix itself is taken for analysis. If the sample is in thermodynamic equilibrium with the gas phase in a closed thermostat vessel, this method of analysis is referred to as static headspace. If a carrier gas is passed over the sample and the sample volatiles accumulated in a cryogenic or sorbent trap, the method is generally referred to as dynamic headspace. If the carrier gas is introduced below the surface of the sample and passes through the sample in the form of a stream of small bubbles with the stripped organic volatiles accumulated in a sorbent trap, then this method is generally referred to as dynamic headspace, purge and trap, gas phase stripping, or gas phase sparging. The headspace sampling methods are used predominantly for the determination of trace concentrations of volatile substances in samples which are difficult to handle by conventional chromatographic means. Examples include dilute solutions where the matrix would obscure the components of interest, damage the column or require excessively long separation times due to the presence of late eluting peaks, inorganic or high molecular weight polymers which cannot be volatilized or solubilized under normal conditions, and inhomogeneous mixtures, such as blood, sewage, colloids, *etc*., which require extensive sample cleanup prior to analysis. In the above situations, the advantages of the headspace method are economy of effort and the attainment of a sample which is relatively free from its matrix and the problems associated with the chromatographic properties of the matrix. The main disadvantage of quantitative headspace analysis is the need for careful calibration.

2.3 Thermal desorption of gases[8]

Thermal desorption is the process by which molecules adsorbed to a substrate are released due to increasing kinetic energy. The substance which adsorbs and desorbs is referred to as the adsorbate. The substance to which the adsorbate adsorbs is called the adsorbent. Two types of adsorption to a surface are chemisorption and physisorption. Chemisorption involves the actual formation of bonds between the adsorbate and the adsorbent. Physisorption involves Van der Waals interactions such as dispersion forces or a dipolar interaction. Since these interactions are very weak, a physisorbed molecule can be easily desorbed simply by raising the temperature, thus increasing the kinetic energy and breaking the interacting forces between the adsorbate and adsorbent.

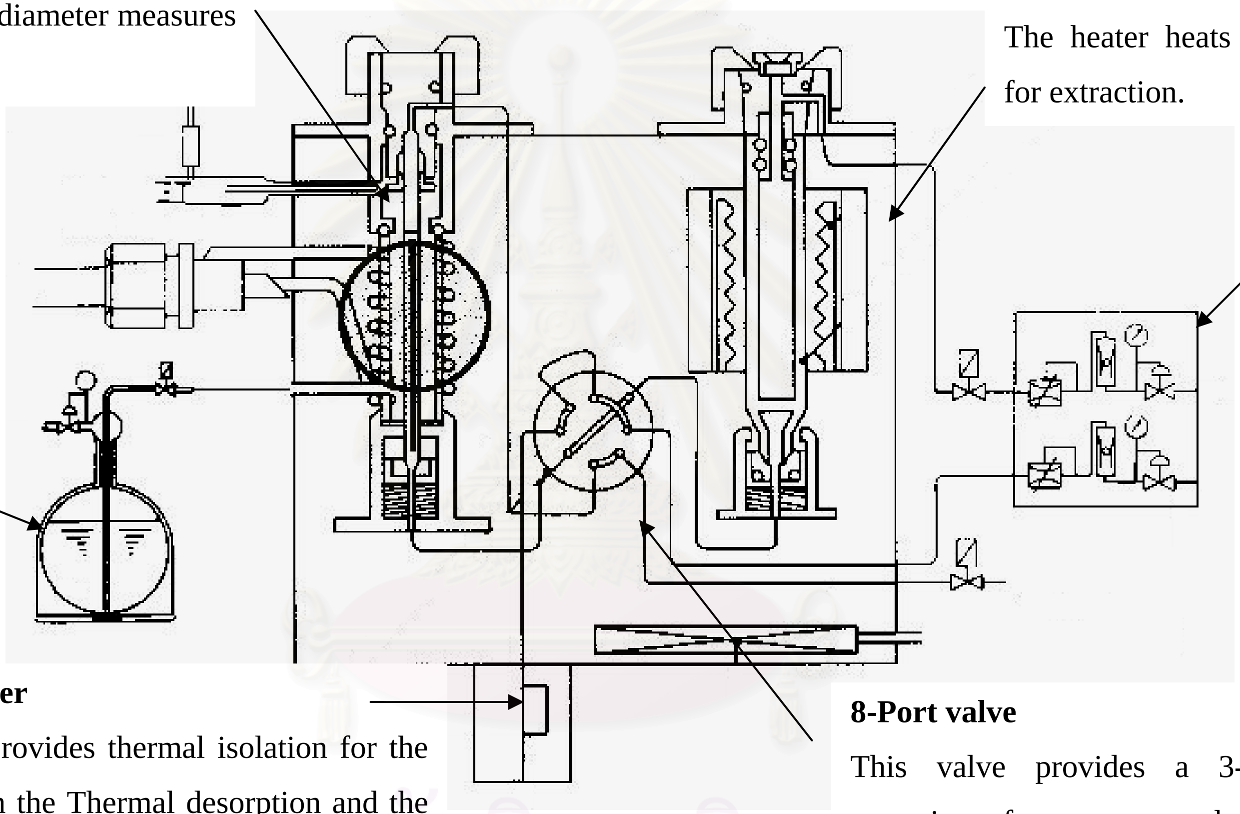
2.4 Purge and trap thermal desorption[9]

Purge and trap (P & T) thermal desorption is also a very popular technique. The P & T technique is more sensitive by at least a factor of 1000 over headspace techniques. Typical sensitivity is in the ppb range. By purging samples at higher temperatures, higher molecular weight compounds can be detected. Furthermore, the P & T technique requires more time for sample preparation and cannot normally be automated. In addition, very light volatiles and gases will not be trapped on the adsorbent resins. P & T gaves high sensitivity and the ability to eliminate water from the sample for analysis. Volatiles ranging from pentane through terpenes can readily be analyzed with this technique. Figure 2.2 illustrates dynamic headspace (thermal desorption) JAI system and Figure 2.3 displays Curie point headspace sampler model JHS-100A.



1. R.F. Power Supply (Curie Point Pyrolyzer)
2. Controller of JHS-100/100A.
3. R.F. Power Supply Cable
4. Device of JHS-100/100A.
5. Carrier gas inlet
6. Purge gas inlet
7. 8-Port valve
8. Sample Heater Coil
9. Sample tube
10. Adsorption tube
11. Induction heating coil
12. Adsorption temperature controller sensor
13. Pressurizing gas inlet
14. Liquid nitrogen dewar vessel
15. Refrigerator carrier solenoid valve

Figure 2.2 Dynamic headspace (thermal desorption) JAI System[10]



Adsorption tube

This tube is made of quartz. Its inside diameter measures 2.5 mm.

Sample Heater

The heater heats a sample for extraction.

Liquid Nitrogen Dewar Vessel

The Dewar vessel supplied as standard accessory to cool the system.

Flow controller

This controller is designed for independent controlling of the carrier gas and the purge gas.

Needle Heater

The heater provides thermal isolation for the pipe between the Thermal desorption and the Gas chromatograph.

8-Port valve

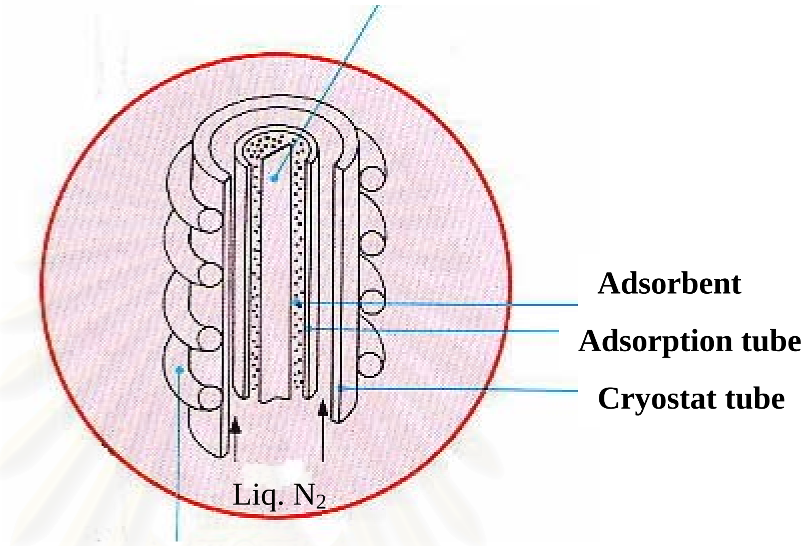
This valve provides a 3-stage operation for purge and trap, defrost and analysis.

Figure 2.3 Curie point headspace sampler model JHS-100A[10]

2.5 Curie point pyrolyzer[11]

Pyrolysis-GC analytical method has been used extensively for developing pyrolyzers using the Curie point method of heating. Curie point headspace sampler model JHS-100A is a powerful concentrator in gas chromatographic accessories to increase a concentration of low contents in samples. The low level volatile in a sample matrix was purged out from the matrix by heating and gas purge in a long period (minutes or hours). The purged volatile was trapped on a small amount adsorbent which is cooled from room temperature to -150 ^{o}C according to the characteristic of adsorbent. The sample is enclosed in a ferromagnetic metal, pyrofoil, or deposited on ferromagnetic wire, pyrowire, which is placed in a flow path of a GC carrier gas and in a RF field. The foil or the wire is rapidly heated to the Curie point of the ferromagnetic metal with the induction of radio frequency. Temperature is reached instantaneously, less than 0.2 seconds. The trapped samples on adsorbents were rapidly heated to Curie point of center pyrofoil in a second and desorbed very thin band and carried to chromatographic column by the flow of carrier gas. Curie-point-pyrolysis is a well proven method for the analysis of complex non-volatile chemical materials, polymers and co-polymers, paints, additives, adhesives, rubber materials and also support for environmental analysis and pharmaceutical industries.

2.5.1 Curie point heating system[10]



Pyrofoil

Pyrofoil is made of ferromagnetic materials which can control desorption temperature in a sample gas.

Induction Heating Coil

This coil induction-heats the pyrofoil provided as a core to heat the adsorbent located around the pyrofoil. When heated, the adsorbent instantly desorb any adsorbed sample gas.

The sample is enclosed in a pyrofoil of ferromagnetic metal or deposited on a wire of ferromagnetic metal which is placed in the flow line of carrier gas. The foil or wire is rapidly heated to the Curie point of the ferromagnetic metal with the induction of radio frequency.[12] At this temperature, the ferromagnetism of the pyrofoil or wire changes to the paramagnetism. Then the sample is pyrolyzed and the pyrolysis products are released instantly from the foil or wire. The products formed are carried to the gas chromatographic column by the flow of carrier gas.

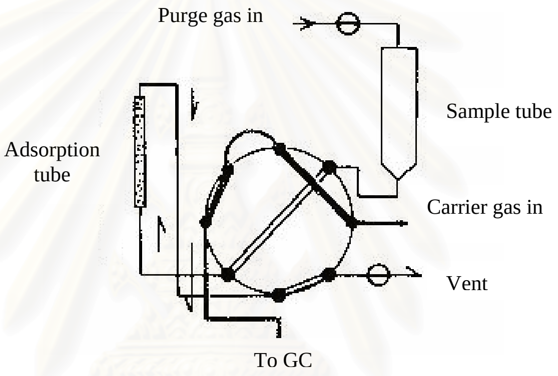
2.5.2 Ferromagnets[13]

Ferromagnets will tend to stay magnetized to some extent after being subjected to an external magnetic field. All ferromagnets have a maximum temperature where the ferromagnetic property disappears as a result of thermal agitation. This temperature is called the Curie temperature. Ferromagntic materials will respond mechanically to an impressed magnetic field, changing length slightly in the direction of the applied field. Ferromagnetism is a phenomenon by which a material can exhibit a spontaneous magnetization, and is one of the strongest forms of magnetism and is the basis for all permanent magnets.

2.5.3 Eight-port valve operation[10]

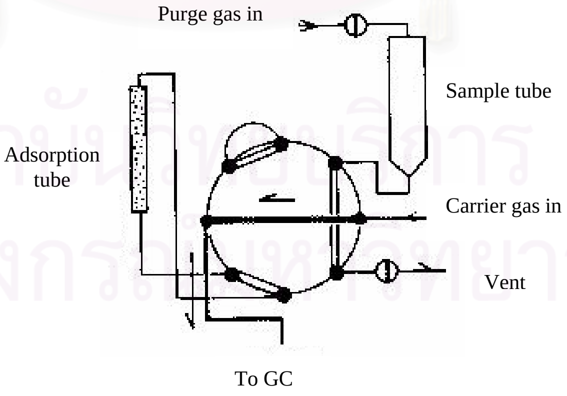
For thermal desorption analysis, the operation of eight-port valve to control the VOCs to get into the GC column was separated to three steps; purge and trap, defrost and analysis. The details were shown as follows:

2.5.3.1 Purge and trap stage



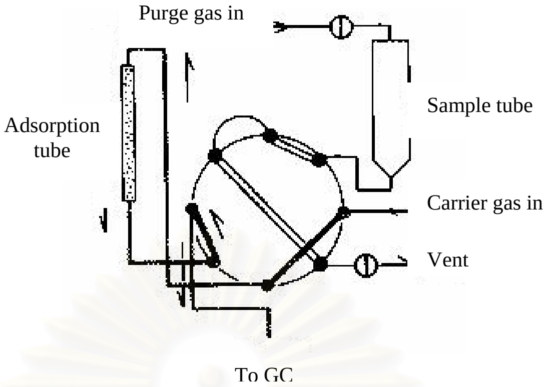
Volatile components extracted by the sampling heater is led to the adsorption tube which is cooled below 0 °C, and trapped.

2.5.3.2 Defrost stage



After trapping, defrost stage, the sample is defrosted for preparation to send it, in a narrow band for improvement of peak resolution, to the GC.

2.5.3.3 Analysis stage



The sample trapped on the adsorption tube is desorbed by rapid heating due to the Curie point principle, and is brought to the column in the GC.

2.6 Adsorbents

2.6.1 Classification[14]

Adsorbents can be classified by structure type and water adsorption characteristics. Structured adsorbents take advantage of their crystalline structure and/or their molecular sieving properties. The hydrophobic (nonpolar surface) or hydrophilic (polar surface) character may vary depending on the competing adsorbate. A large number of zeolites have been identified, and these include both synthetic and naturally occurring varieties. Table 2.1 displays the classification of adsorbents.

Table 2.1 Classification of common adsorbents

Classification	Amorphous	Structure
Hydrophobic	Activated carbon Polymer	Carbon molecular sieves Silicalite
Hydrophilic	Silica gel Activated alumina	Common zeolites: 3A (KA), 4A (NaA), 5A (CaA), 13X (NaX), Mordenite, Chabazite, *etc*

2.6.2 Types of adsorbent[15]

Adsorbent resins were utilized by purge and trap and other thermal desorption applications. A wide variety of adsorbent resins are available from many suppliers and manufacturers. In order to properly select an adsorbent resin for a particular application the user must have knowledge of the types of analytes that one wishes to analyze as well as an understanding of the physical properties of the adsorbent resins available. Six adsorbents including Tenax TA, Tenax GR, Carbotrap B and C, Carbopack B and C were selected to explore in this research. The physical property of Tenax TA, Tenax GR and Carbotrap are shown in Appendices A.1, A.2 and A.3, respectively.

2.6.2.1 Tenax TA is a porous polymer resin based on 2,6-diphenylene oxide. It has been specifically designed for the trapping of volatiles and semi-volatiles from air or which have been purged from liquid or solid sample matrices. Tenax TA is a low bleeding material with a low level of impurities and has replaced Tenax GC, which was distributed in the past. Using thermal desorption techniques, detection of volatile organics in the ppb and ppt level is feasible. Due to its low affinity for water, Tenax TA is especially useful for the purging and trapping of volatiles from high moisture content samples. Tenax TA is designed primarily as a trapping agent, and has very low levels of impurities. Tenax TA is suitable for the separation of high boiling polar compounds such as alcohols, polyethylene glycol compounds, diols, phenols, mono and diamines, amides, aldehydes and ketones.

2.6.2.2 Tenax GR is a composite material of Tenax TA and 30% graphite. It maintains the high temperature stability to 350 ^{o}C. These properties make Tenax GR an ideal adsorbent for the trapping of volatiles from air, water and solid samples. Since its density is twice of that of Tenax TA, this enables a larger amount of the Tenax GR resin to be placed inside the desorption tube, thereby increasing the ability to retain volatiles on a small resin bed.

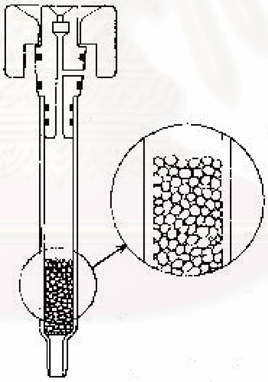
2.6.2.3 Carbotrap B and Carbotrap C are graphitized carbon blacks that are ideal adsorbent resins for the trapping of a wide range of organic analytes from C_4/C_5 through the medium boilers. They have a coarse mesh size (20/40) which prevents high backpressures in the desorption tubes.

2.6.2.4 Carbopack B and Carbopack C are graphitized carbon blacks used as an adsorbent and it suitable to adsorb for airborne contaminants which similar to Carbotrap.

The ideal adsorbent[16] shoud be chemically inert, thermally stable, have a low background, quantitatively adsorb and desorb both very volatile and semi-volatile organic compounds, quantitatively adsorb and desorb both polar and non-polar compounds, stable on storage, able to sample very low levels and adsorption should be uninfluenced by the humidity of the air.

2.6.3 Preparation and conditioning solid sample tubes[17]

Clean tube before packing then insert a small silanized glass wool plug in one end of the sample tube, weigh the required amount of adsorbent. A small funnel will aid in inserting the adsorbent resin, then insert another glass wool plug into the other end of the sample tube to hold the resin in place. The solid sample tube with volume of 10 mL was shown below.



The sample tubes must be conditioned before use by continuous flow of a high purity carrier gas. Heating the sample tube while continuing to purge gas through the adsorbent resin inside, recommend the temperature program of 4 to 10 ^{o}C/min from room temperature up to the maximum temperature and continue for 4 to 6 hours. Continuous flow must be maintained through the sample tube and resin at all time. The sample tube should be conditioned 25 to 50 degrees higher than the temperature at which it will be desorbed. After the heating cycle time is complete, the sample tubes should be removed and gas flow must be maintained through the adsorbent.

2.7 Literature review on the detection of the contaminants from VOCs

For the determination of VOCs, the most important factor for the analysis was adsorbent. Several papers which concerned with the adsorbent selection have been reported. In 1995, Sunesson and colleagues[18] evaluated eight adsorbents for sampling and quantitative analysis of microbially produced volatiles using thermal desorption-gas chromatograph. The adsorbents studied were Tenax TA, Tenax GR, Chromosorb 102, Carbotrap C, Carbopack B, Anasorb 727, Anasorb 747 and Porasil C/*n*-octane (Durapak). The study was performed using a tested atmosphere consisting of ten compounds differing in polarity and volatility: 2-propanol, dimethyl disulfide, toluene, furfural, 1-octen-3-ol, 3-octanone, 3-octanol, 2-isopropyl-3-methoxy pyrazine, 2-methylisoborneol and geosmin. The adsorbents were tested in low $\mu g/m^3$ levels and varying humidity. Tenax TA proved to have the best properties considering from the volatiles amount obtained, breakthrough and standard deviation during sampling/analysis.

Wartelle and colleagues[19] reported the investigation of granular activated carbons (GACs) made from agricultural by-products as adsorbents for short path thermal desorption gas chromatographic analysis of selected polar and nonpolar organic compounds in 2000. GACs made from macadamia nut, black walnut and hazelnut shells were compared to four commercially available adsorbents, namely, Tenax TA, Carboxen 569, Carbosieve SIII and coconut charcoal for their properties in purge-and-trap analysis. Adsorption values and breakthrough volumes were calculated for compounds from C_3 and C_6 to C_{10}. GACs derived from macadamia nut shells were found to adsorb and desorb between 80% (benzene) and 227% (ethylbenzene) more acetone (C_3), benzene (C_6), toluene (C_7), ethyl- (C_8), *n*-propyl- (C_9), or *sec*-butylbenzenes (C_{10}) purged from water at the 100 ppb level than the commercial adsorbents tested.

In 2000, Clement and colleagues[20] developed the determination method for the pesticides: alachlor, atrazine, captan, formothion, lindane and phosalane in atmospheric samples to evaluate the atmospheric contamination by pesticides during treatments and by post-application. Atmospheric samples were collected by using stainless steel sampling tubes containing different types of adsorbents: Tenax TA, Carbopack Y, Carbopack B, Carbotrap, Carboxen, Chromosorb 106 and XAD-4 to test for their ability of efficiently trap pesticides. The result showed that Tenax gave the best results for all the pesticides used.

In 2002, Hollender and colleagues[21] reported a simple method using active trapping on adsorbents and thermal desorption followed by GC-MS analysis for the indoor air monitoring of monoterpenes. The study was carried out using a dynamically generated atmosphere consisting of 11 monoterpenes: camphene, camphore, Δ^3-carene, 1,8-cineol, limonene, linalool, α-pinene, β-pinene, α-terpinene, γ-terpinene and fenchyl alcohol. The influence of the different adsorbents: Tenax TA, Tenax GR, Carbosieve SIII, Chromosorb 106 on the yield of six selected monoterpenes at indoor air concentrations was studied. Tenax GR gave relatively the best yields followed by Tenax TA. Detection limits of approximately 1 $\mu g/m^3$ were determined with Tenax GR for most of monoterpenes.

Several papers have been reported on the optimum thermal desorption condition for VOCs. In 1993, Esteban and colleagues[22] studied the isolation of volatile compounds from plants by gas chromatographic technique such as solvent extraction, steam distillation. The reproducibility of the method was evaluated for several operating conditions, the results of Automatic Thermal Desorption (ATD) method was better than those obtained with other sample preparation methods. Some applications of the ATD method in the gas chromatographic determination of volatile components of umbelliferae seeds are also presented, including the determination of the enantiomeric forms of limonene.

In 1998, Holdren and colleagues[23] developed the identification and quantification methods for VOCs in ambient air that preconcentrate sufficient amounts by thermal desorption technique present at very low level parts per billion (ppb). The studied parameters were adsorption and desorption temperature. In 2002, Yamamoto and colleagues[24] studied VOCs in ambient air analysis technique, the sample collection technique such as temperature and time was evaluated.

The developed thermal desorption method for the analysis of workplace air to the analysis of polar compounds has been reported by Hallama and colleagues[25] in 1998. The method was validated for both pumped and diffusive sampling of test gases containing polar volatile organic compounds (esters, alcohols, ketones or aldehydes) on adsorption tubes and subsequent analysis of these tubes. Carbosieve SIII, Carboxen 569, Carbopack B and Tenax TA were used as solid adsorbents. Analysis was performed by thermal desorption of the analytes from the adsorbent tubes followed by GC-FID. It could be demonstrated that thermal desorption-GC-FID is feasible also for the analysis of polar compounds.

The application of thermal desorption-GC-MS for the analysis of carboxylic acids (CAs) have been discussed. In 2000, Ehara and Sakamoto[26] determined the optimum analytical condition based on the esterification recoveries using 10 mmole L^{-1} of CAs methanol solution. Purge and trap sampling was carried out with a Curie point headspace. The optimum instrument conditions were: purging, 150 ^{o}C for 10 minutes; trap temperature, -10 ^{o}C; desorption, 358 ^{o}C for 20 seconds. A comparison of pyrolysis (Py)-GC-MS, P&T-GC-MS, and solvent extraction-GC-MS was made based on conversions of the CAs into the corresponding CA methylesters. The merits of the P&T method for the other two methods were validated according to quantitative data, the coefficient of variation, and the lower limit of the determination calculated from the standard deviation. As a result, the P&T method is more useful than the pyrolysis and solvent extraction methods.

From the previous research, it was found that there was no report about the determination of VOCs from HDD components. Thus, in this research the study of the adsorbent selection and optimum the thermal desorption will be done for improving the best efficiency of the VOCs in HDD analysis especially in trace amount.

CHAPTER III
EXPERIMENTAL

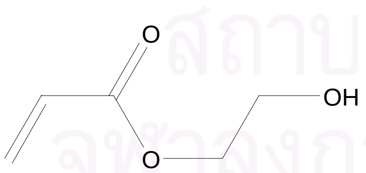
3.1 Instrument and equipment

Gas Chromatograph-Mass Spectrometry (GC-MS) was carried out on a Hewlette Packard model HP6890/5973 with helium as a carrier gas. The column used for chromatography was a fused-capillary column type of HP-5MS (30 m length, 0.25 mm i.d.) coated with immobilized poly(dimethylsilicone) of 0.25 μm thickness from J&W Scientific company. Thermal desorption or dynamic headspace connected to GC-MS was conducted on Curie point headspace sampler model JHS-100/100A. Outgas collector was carried out on a Japan Analytical Industry (JAI) model HM-04. Surface analysis was performed by Field Emission Scanning Electron Microscope (FE-SEM) model JSM 6330F.

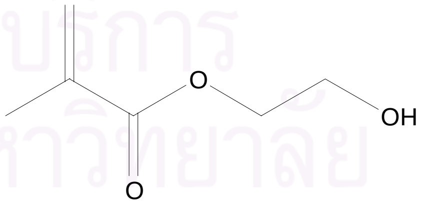
3.2 Chemicals

The standard solutions used in this research were classified into six groups.

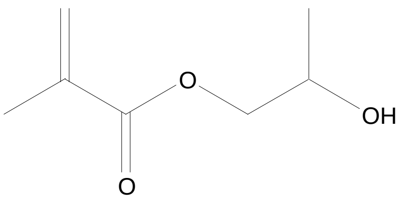
3.2.1 Acrylate/Methacrylate group: 2-hydroxyethyl acrylate (2-HEA), hydroxyethyl methacrylate (HEMA), hydroxypropyl methacrylate (HPMA), isobornyl methacrylate (IBOMA), triethyleneglycol dimethacrylate (TGDMA) were purchased from Aldrich chemical company.



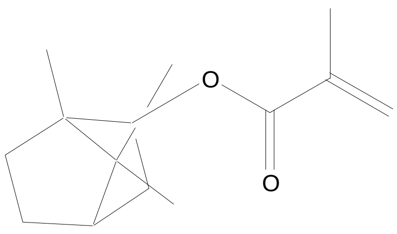
2-HEA



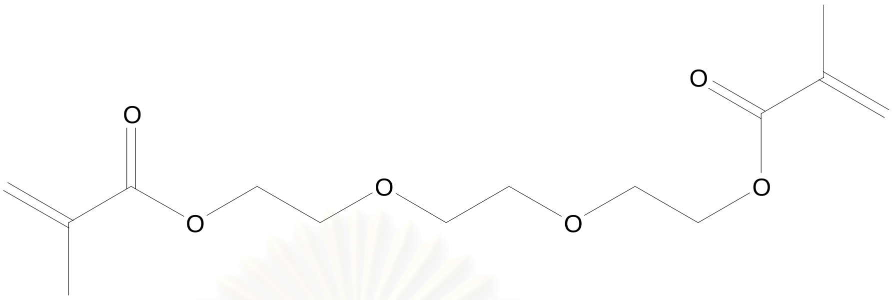
HEMA



HPMA

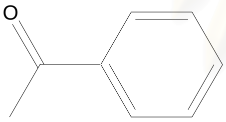


IBOMA

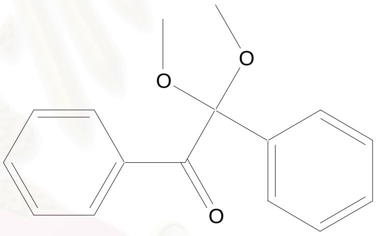


TGDMA

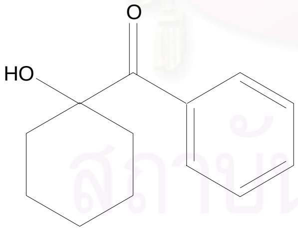
3.2.2 Acetophenone group: acetophenone (AP), 2,2-dimethoxy-2-phenylacetophenone (DMAP), hydroxycyclohexylacetophenone (CHAP) were purchased from Aldrich chemical company.



AP

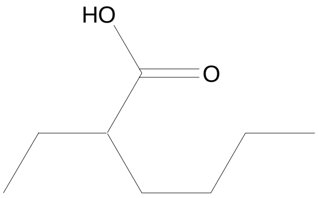


DMAP



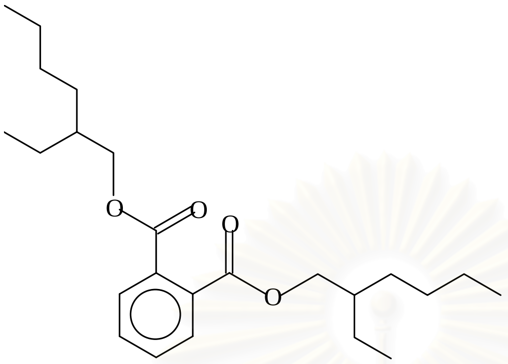
CHAP

3.2.3 Acid group: ethylhexanoic acid (EHA) was purchased from Aldrich chemical company.



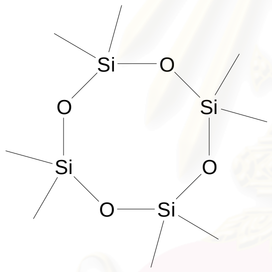
EHA

3.2.4. Phthalate group: di-*n*-octyl phthalate (DOP) was purchased from Aldrich Chemical Company.

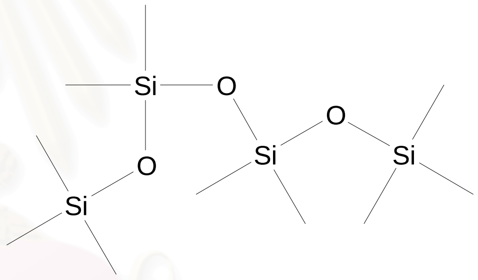


DOP

3.2.5 Siloxane group: octamethylcyclotetrasiloxane was purchased from Aldrich chemical company while decamethyltetrasiloxane was purchased from Tokyo Kasei company.



octamethylcyclotetrasiloxane



decamethyltetrasiloxane

3.2.6. Mixed alkanes standard (C_{10} to C_{25}) solutions were purchased from Ultra Scientific company.

Remarks: The internal standard used in this research consisted of two chemicals: decane was purchased from Merck and naphthalene-d8 was purchased from Ultra Scientific company.

3.3 Preparation of standard solution

3.3.1 Preparation of stock solutions

Prepare a 10 μg/μL solution by weighing 0.25 ± 0.005 g of each compound into an empty vial. Then rinsing the material out of the vial by isopropyl alcohol (IPA) and transfer to 25 mL volumetric flask. Repeat rinsing until the volume is nearly 25 mL. Carefully adjust the final volume of volumetric flask by syringe or dropper.

3.3.2 Preparation of mixed monomers (acrylate/methacrylate, acetophenone, acid and phthalate groups)

Transfer each stock solution (3.2.1 - 3.2.4) 500 μL into 10 mL volumetric flask, adjust the final volume to 10 mL by syringe or dropper. The low concentration of each compound is 500 ng/μL. For the analysis, the concentration 1,000 ng was prepared by injecting 2 μL of 500 ng/μL of mixed monomers for each analysis.

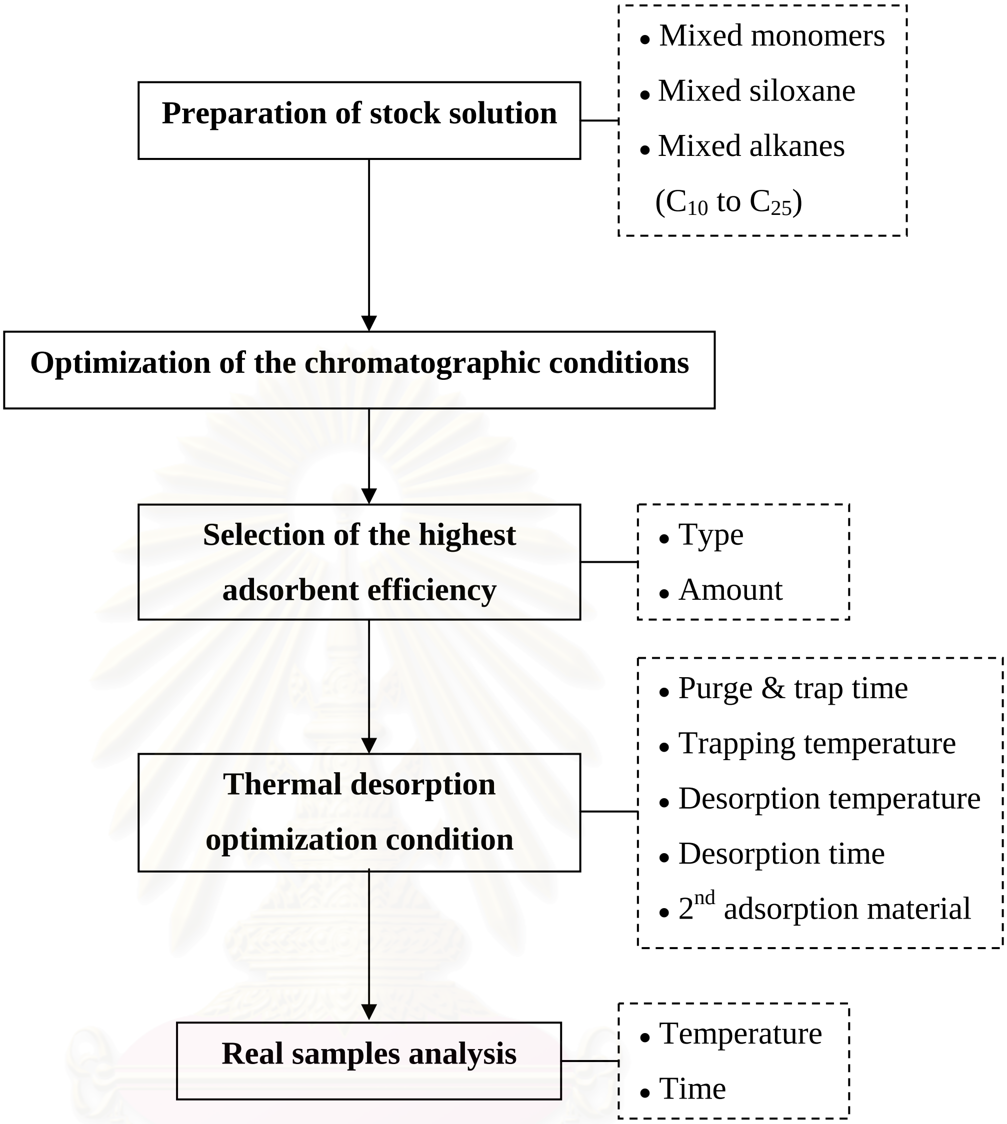
3.3.3 Preparation of mixed siloxanes

Transfer each stock solution (siloxane group: 3.2.5) 50 μL into 10 mL volumetric flask, adjust the final volume to 10 mL by syringe or dropper. The low concentration of each compound is 50 ng/μL. For the concentration 50 ng, inject 1 μL for each analysis.

3.3.4 Mixed alkanes standard (C_{10} to C_{25})

Transfer mixed alkanes (C_{10} to C_{25}) solution 1,000 μg/mL into 10 mL volumetric flask and then dilute the solution with methylene chloride. The final concentration is 100 ng/μL.

After preparation of all solutions, chromatographic conditions were optimized to examine for the best resolution. The important factor which affects on the determination of VOCs is an adsorbent type, thus the best adsorbent was evaluated. After that, thermal desorption condition was optimized including purge and trap time, trapping temperature, desorption temperature, desorption time and secondary adsorption materials. Furthermore, the optimum sampling condition of real samples analysis was studied. Scheme 3.1 shows the VOCs in HDD component analysis step.



Scheme 3.1 The analysis of VOCs in HDD components

3.4 Materials and methods for analysis of VOCs in HDD components

3.4.1 Adsorbent tubes

The adsorbent tubes were custom-made of quartz, 16 mm o.d., a wall thickness of 1 mm and 120 mm long. They were filled with solid adsorbents, silanized glass wool plugs were used to hold the adsorbents and also plugged at the ends with the same material. Before sampling, all tubes were conditioned at 260 ^{o}C for more than six hours at a flow rate of 100 mL/min helium (purity 99.999%) and tested before use. The blank chromatograms obtained by thermally desorbing the traps under the same conditions of analysis and at maximum sensitivity confirmed that no peak of impurity which could disturb the gas chromatographic analysis was present.

3.4.2 Adsorbents

The following adsorbents were purchased from Supelco: Tenax TA, Tenax GR, Carbopack B and C, Carbotrap B and C. The former four adsorbents were of a particle size ranging between 60 and 80 mesh. The specific surface area of these adsorbents were determined for 35, 24, 100 and 10 m^2g^{-1}, respectively.[27] The corresponding bulk densities were 0.25, not specified, 0.36 and 0.72 gmL^{-1}, respectively. The others had properties similar to those of Carbopack B and C except for the particle size ranging between 20 and 40 mesh.

Tenax TA[28] is a porous polymer based on 2,6-diphenylene oxide and Tenax GR is the result of coprecipitation of graphitized carbon with Tenax TA polymer. It contains 30% graphitized carbon. Carbopack B and C, Carbotrap B and C are graphitized carbon blacks that are ideal adsorbent resins for the trapping of a wide range of organic analytes.[29]

3.4.3 Optimization of chromatographic conditions

In order to optimize the chromatographic condition, a mixture of ten monomers was directly injected at a split ratio of 50 : 1. The best capillary column, suitable oven temperature program, optimum carrier gas flow rate, injector temperature and mass detector condition were determined on the basis of peak resolutions and reproducibility of the retention times. The GC and MS conditions are listed in Table 3.1.

Table 3.1 GC-MS parameter for the analysis of VOCs

Parameter	Value
GC/MS Instrument	Hewlett Packard HP6890/5973
Column type	HP-5MS (30 m x 0.25 mm x 0.25 mm)
Column flow	1 mL/min
Carrier gas	Helium (purity 99.999%)
Inlet system	Split 50 : 1
GC Condition	
Injector temperature	250 ^{o}C
Oven program	
Initial temperature	40 ^{o}C
Initial time	5.00 min
Ramp	8 ^{o}C/min
Final temperature	280 ^{o}C
Final time	5.00 min
Interface temperature	280 ^{o}C
MS Condition	
Mass range	33-550
Threshold	150
Scan (/sec)	2.85 scans/sec

3.4.4 Thermal desorption

The JHS-100/100A[10] is a thermal desorption system developed for the introduction of samples into GC-MS system. VOCs purged from sample matrix by heating were trapped on an adsorbent and then desorbed by Curie-point heating with pyrofoil, while introducing into the gas chromatography column. The thermal desorption unit was mounted in the supply gas line of the GC-MS system. Thus, the GC carrier gas line was routed to the thermal desorption unit, passed through its eight-port-valve and was then redirected to the split injector. The analytes were desorbed from the adsorption tube onto a focusing trap which was at room temperature. After the focusing step, the analytes were desorbed from the trap by rapid heating into the injector of the GC-MS. The parameters for thermal desorption are listed in Table 3.2.

Table 3.2 Thermal desorption parameter for the analysis of VOCs

Parameter	Value
Thermal-extraction temperature	250 ^{o}C
Temperature of desorption for the trap	200 ^{o}C
Temperature of transfer line	250 ^{o}C
Purge and trap time	Optimization
Adsorbent for sample tube	Optimization
Secondary adsorption material	Optimization

3.5 Analytical procedure for the determination and quantification of VOCs in HDD components

After three sets of standard solutions (mixed monomers, mixed siloxanes and mixed alkanes standard (C_{10} to C_{25})) were prepared, inject the standard to thermal desorption system model JHS-100/100A which connected to GC-MS for each analysis. With thermal desorption system, VOCs released by heating the traps at 250 ^{o}C were cryofocused kept at -60^{o}C. Samples and standards were run in triplicate, peak areas were calculated by Chemstation software (Hewlette Packard). Peak areas obtained by thermal desorption were compared with internal standard.

For quantitative analysis by thermal desorption-GC-MS, the internal standard method was used. This approach is less attentive and offers better precision than other calibration methods. For mixed ten monomers, decane aqueous solution containing 1,000 ng/μL was added in the same volumetric flask as internal standard. For mixed alkanes standard (C_{10} to C_{25}), naphthalene-d8 aqueous solution containing 100 ng/μL was added as an internal standard.

3.6 Effect of the parameters on adsorptivity of VOCs in HDD components

3.6.1 Effect of adsorbents

The determination of VOCs by thermal desorption-GC-MS was studied for the effect of adsorbents by comparing between six adsorbents: Tenax TA, Tenax GR, Carbopack B, Carbopack C, Carbotrap B and Carbotrap C. The standard solution for testing was classified into two groups: mixed ten monomers and mixed alkanes standard (C_{10} to C_{25}). For improving the adsorbent efficiency, dual-sorbent was also studied.

3.6.2 Effect of the amount of adsorbent

The analysis was carried out and the amount of adsorbent was varied: 350, 1,700, 500 and 2,000 milligrams for two adsorbents; Tenax TA and Tenax GR, respectively.

3.6.3 Effect of the purge and trap time

The analytical conditions were as follows: thermal-extraction temperature, 250 ^{o}C; trapping temperature, -60 ^{o}C and desorption, 358 ^{o}C for 20 seconds. Purge and trap time was varied: 5, 10, 15, 20 and 25 minutes

3.6.4 Effect of trapping temperature

Thermal desorption conditions were carried out and trapping temperature was varied: 20, 0, -20, -40 and -60 ^{o}C.

3.6.5 Effect of desorption temperature

Thermal desorption conditions were carried out and desorption temperature was varied: 255, 315 and 358 ^{o}C.

3.6.6 Effect of desorption time

Thermal desorption conditions were carried out and desorption time was varied: 5, 10, 20 and 25 seconds.

3.6.7 Effect of secondary adsorption material

Thermal desorption conditions were carried out and secondary adsorption material was varied: Tenax TA, Glass wool and Carbopack C.

3.6.8 Trace VOCs analysis

Low amount of siloxane 50 ng was selected to verify the preceding developed method whether it was suited for the investigation of trace components from HDD.

3.6.9 Effect of the sampling condition for real samples analysis

The outgas collector model HM-04 was applied for the sample collection by putting the sample into the gold-plating chamber volume ~ 200 mL and then heated up, the VOCs released from samples will be trapped by the adsorbents which connect to the chamber holder. The outgas collector was displayed below.

The optimization parameters were trapping temperature and trapping time which varied from 85, 110 and 150 ^{o}C and 1, 3, 5 and 7 hours for real samples: pivot cartridge and spindle motor.

CHAPTER IV
RESULTS AND DISCUSSION

In this research, the detection of the contaminants from HDD using adsorption/thermal desorption - gas chromatograph-mass spectrometry (GC-MS) was explored. Six adsorbents were evaluated for their efficiency in quantitative analysis of VOCs such as monomers derived from adhesives and hydrocarbons. Not only single-sorbent but also dual-sorbent were employed to observe the adsorbent efficiency. After the most appropriate adsorbent was disclosed, thermal desorption conditions including purge and trap time, trapping temperature, desorption temperature, desorption time and secondary adsorption materials were investigated. Real samples, *e.g.* pivot cartridge and spindle motor were selected to examine for the optimum sampling conditions: temperature and time at the fixed flow rate of 50 mL/min.

4.1 Selection of adsorbent

The analysis of VOCs present in HDD is important to control the cleanliness of product. The use of thermal desorption trapping to concentrate VOCs prior to the analysis has been established as a proven technique for VOCs analysis,[30] this method involves collecting the sample. After collection, the trap is rapidly heated, the VOCs are desorbed, and typically the compounds are analyzed using a gas chromatographic system. An alternative trapping method involves the use of adsorbents to collect the VOCs. The choice of a suitable adsorbent is critical and requires a good knowledge of adsorbent properties.[31] The preferred adsorbent must be considered since they are of a wide range of physical and chemical properties of both the adsorbents as well as the analytes to be trapped and analyzed. A proper choice of adsorbent-adsorbate couple will help in proceeding smoothly in further steps such as selection of technology, good separation efficiency, *etc*. The preceeding analysis gave an indication of the identification of the compounds from a mixture. This may be possible by several means, such as condensation (exploiting the substantial difference in boiling points), absorption (exploiting the solubility in different solvents) or adsorption (exploiting the adsorptivity on different adsorbents).[32] When adsorption is concerned, it is very crucial to decide the adsorbent to be used. In this study, the determination of the trapping efficiency of the analytes on the adsorbents was investigated by thermal desorption-GC-MS technique. At first, chromatographic conditions were explored and then adsorbent types and amount of adsorbents were evaluated.

4.1.1 Effect of adsorbents

4.1.1.1 Effect of adsorbents on the adsorption efficiency of mixed monomers

The adsorption of mixed ten monomers released from HDD components: 2-HEA, HEMA, HPMA, IBOMA, TGDMA, AP, DMAP, CHAP, EHA and DOP, mixed alkanes (C_{10} to C_{25}) on six different adsorbents was first examined. Two types of adsorbents: porous polymer such as Tenax TA, Tenax GR and graphitized carbon black such as Carbopack B, Carbopack C, Carbotrap B and Carbotrap C were compared using thermal desorption/GC-MS technique. Some physical properties of each adsorbent are shown in Table 4.1.

Table 4.1 Physical properties of six selected adsorbents[27]

Adsorbent	Mesh size	Composition	Surface area (m^2/g)	Density (g/mL)
Porous polymers				
Tenax TA	60/80	Poly (2,6-diphenylene oxide)	35	0.25
Tenax GR	60/80	Graphite carbon 30% and Tenax TA 70%	24	-
Graphitized Carbon Blacks				
Carbopack B	60/80	Graphite carbon	100	0.36
Carbopack C	60/80	Graphite carbon	10	0.72
Carbotrap B	20/40	Graphite carbon	100	0.36
Carbotrap C	20/40	Graphite carbon	10	0.72

The amount in nanogram of mixed monomers was calculated based on the peak area of decane as an internal standard and that of mixed alkanes (C_{10} to C_{25}) was based on an internal standard naphthalene-d8. Selected chromatograms of mixed monomers and mixed alkanes (C_{10} to C_{25}) are shown in Appendices B.1 and B.2. The concentration of each monomer was 1,000 ng per analysis while the concentration of mixed alkanes (C_{10} to C_{25}) was 500 ng. Each analysis was performed in triplicate for reproducibility assurance and then the correction factor was adjusted for calculation (Appendix B.3). In Figure 4.1, the quantitative analysis of mixed monomers was determined using six different adsorbents.

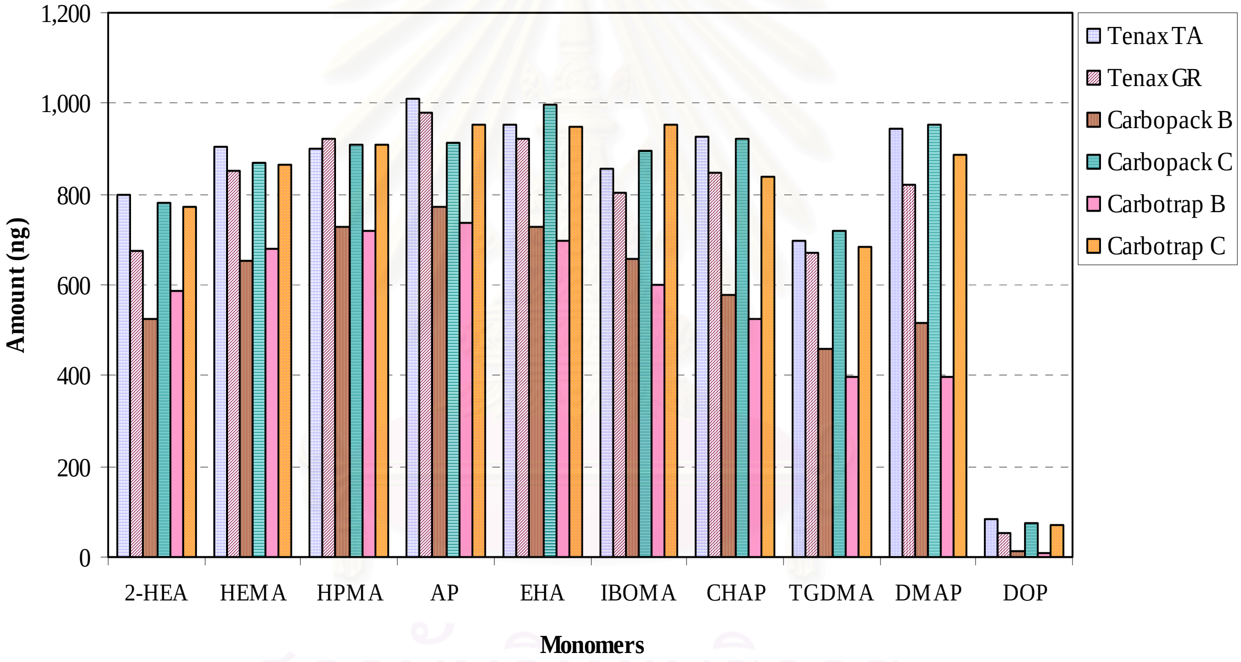


Figure 4.1 Adsorption efficiency of six selected adsorbents upon the analysis of mixed monomers

From Figure 4.1, the best results were reached with Tenax TA and Carbopack C followed by Tenax GR and Carbotrap C. Nevertheless, for Carbopack B and Carbotrap B, it gave low adsorptivity especially for high molecular weight samples such as TGDMA, DMAP and DOP. For the highest molecular weight as DOP, all adsorbents gave low adsorptivity. For porous polymer adsorbent, Tenax TA gave the better efficiency than Tenax GR due to graphite carbon content.

For 2-HEA, HEMA, AP, CHAP and DOP compounds, Tenax TA gave the highest adsorptivity and for HPMA Tenax GR gave the highest adsorptivity. Thus, porous polymer adsorbent was suitable for lower molecular weight samples: 2-HEA (116), HEMA (130), HPMA (144), AP (120) and CHAP (204). For EHA, TGDMA and DMAP, Carbopack C gave the highest adsorptivity while Carbotrap C gave the higher adsorptivity for IBOMA. Graphitized carbon black with higher density, high molecular weight samples TGDMA (286) and DMAP (256) gave the better result except EHA (144) which had a low molecular weight. The polarity of compound could also have an effect on adsorption efficiency. However, for DOP (390) which had a very high molecular weight, both types of adsorbent were not suitable for analysis. Based upon these results, it could be assumed that for low molecular weight compounds, porous polymer adsorbent revealed higher efficiency. For high molecular weight samples, graphitized carbon black was more suitable. For graphitized carbon black, the lower density adsorbent (Carbotrap B and Carbopack B) exhibited lower efficiency.

4.1.1.2 Effect of adsorbents on the adsorption efficiency of mixed alkanes (C_{10} to C_{25})

Figure 4.2 displays the amount of mixed alkanes (C_{10} to C_{25}) detected from six different adsorbents. The best results were visualized from the use of Tenax TA followed by Tenax GR. However when the number of carbon in the mixed alkanes was more than 20, the efficiency was suddenly decreased especially for the number of carbon as 24 and 25, the amount decreased is about 1/25 of prepared amount which showed the same manner for all adsorbents. On the other hand, Carbopack C and Carbotrap C gave good efficiency in the range of C_{10} to C_{17}, while for Carbopack B and Carbotrap B, the results gave very low adsorptivity. For hydrocarbons, porous polymer still gave better adsorption efficiency for low molecular weight than graphitized carbon black. Thus, for single-sorbent, Tenax TA was suitable for low molecular weight alkanes in the range of C_{10} to C_{20}.

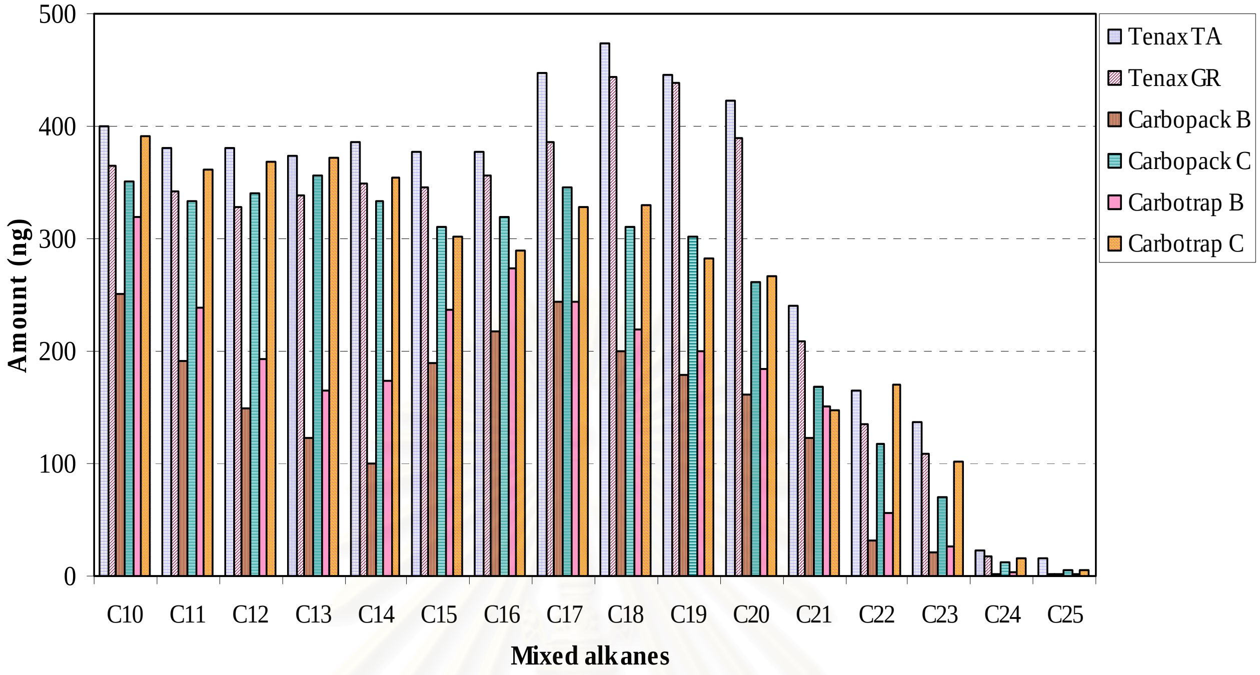


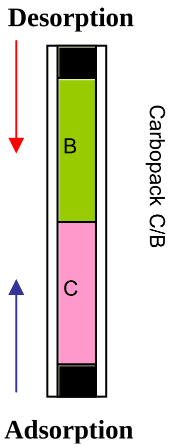
Figure 4.2 Adsorption efficiency of six adsorbents upon the analysis of mixed alkanes (C_{10} to C_{25})

Previously, thermal desorption-GC-MS technique was developed to evaluate the atmospheric contamination of pesticides during treatments and by post-application by Clement and colleagues in 2000.[20] Different types of adsorbents were tested for their ability to efficiently trap pesticides. Tenax gave the best results among all the pesticides used. The use of thermal-desorption method, especially for pesticides with low volatility and/or poor thermal stability presented some difficulties. In 2002, Hollender and colleagues[21] reported that the analysis of a dynamically generated atmosphere consisting of 11 monoterpenes using Tenax GR gave relatively good results followed by Tenax TA.

From the above data, the adsorption efficiency of hydrocarbon should be improved especially for high molecular weight compounds when the number of carbon was more than 20. Dual-sorbent which composes of two adsorbents would be explored whether it could increase the adsorption efficiency.

4.1.1.3 Effect of dual-sorbent on the adsorption efficiency of mixed alkanes (C_{10} to C_{25})

An example for dual-sorbent packing and the VOCs direction flow of dual-sorbent trap displays below.



For Carbopack C/B packing (ratio 1:1), the first layer is Carbopack C and the second layer is Carbopack B. VOCs were adsorbed from the first layer through the second layer (bottom to top) and desorption direction was desorbed from the second layer through the first layer (top to bottom). For other dual-sorbents, the same performance was conducted.

Four types of dual-sorbent Carbopack C/B, Carbotrap C/B, Carbopack B/C and Carbotrap B/C were evaluated compared with Tenax TA. The analysis results were displayed in Figure 4.3.

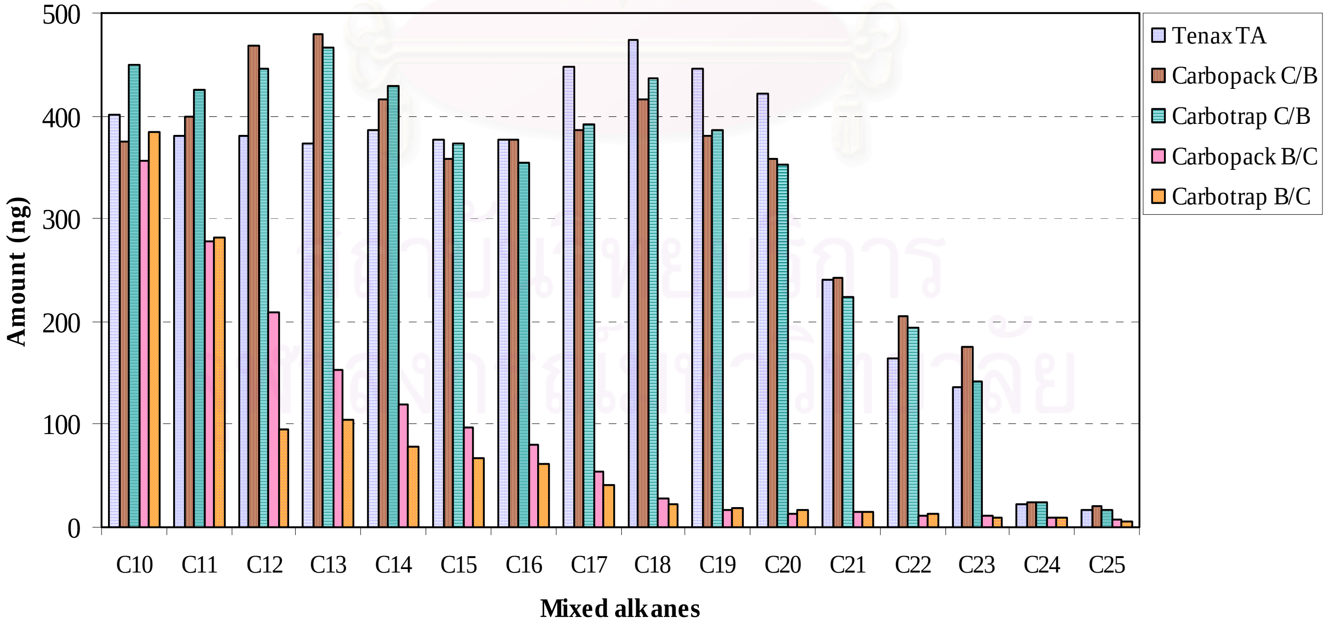


Figure 4.3 Adsorption efficiency of dual-sorbent upon the analysis of mixed alkanes (C_{10} to C_{25}) compared with Tenax TA

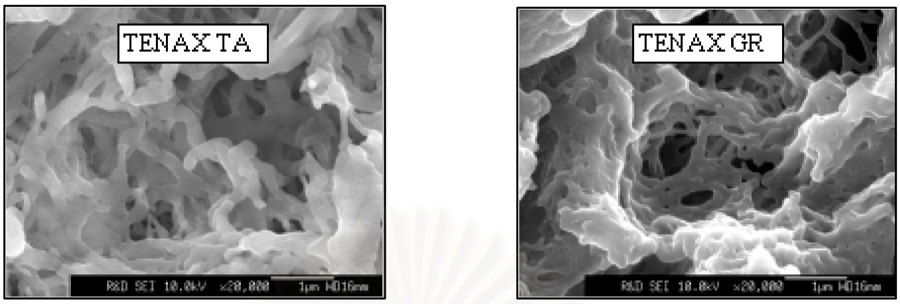
Comparing between single-sorbent Carbopack C, Carbotrap C and dual-sorbent Carbopack C/B, Carbotrap C/B, the result showed that for all ranges of hydrocarbons C_{10} to C_{25}, dual-sorbent provided better adsorption efficiency than single-sorbent. From Figure 4.3, dual-sorbent Carbopack C/B and Carbotrap C/B displayed higher efficiency especially in the range of C_{10} to C_{15}, they gave better adsorption efficiency than Tenax TA. For higher molecular weight alkanes (C_{21} to C_{25}), the adsorption efficiency was increased for all dual-sorbent types comparing with single-sorbent.

The packing adsorbent direction for dual-sorbent also had a profound effect on the adsorption efficiency. Carbopack and Carbotrap C/B displayed better adsorption efficiency than Carbopack and Carbotrap B/C direction. From Figure 4.3, the adsorption direction which gave better performance was Carbopack C (high molecular weight) on the first layer and Carbopack B (low molecular weight) on the second layer. The reason for packing by Carbopack C/B having an effect on adsorption and desorption because the high molecular weight compounds were desorbed before the low molecular weight ones. The disadvantage of the packing by B/C direction is that some molecules may lost during the desorption process. In order to improve the packing by B/C direction, purge and trap time should be adjusted for higher adsorption efficiency.

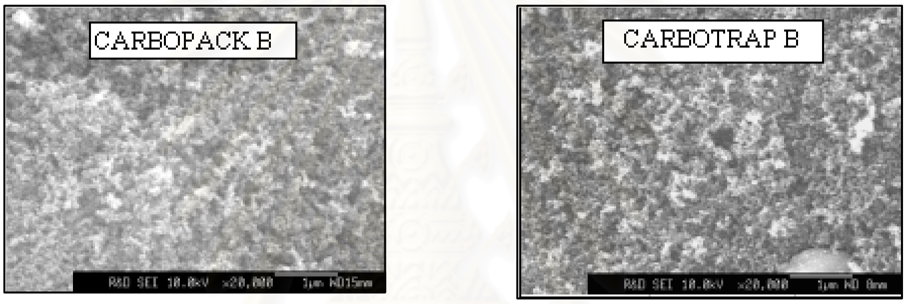
Tenax TA is widely used in sampling VOCs in indoor air and material emissions.[37] This is because Tenax had low affinity for water: it was easy to clean up after sampling, has low background emissions and is thermally stable. It has also proven to be suitable for enriching VOCs (boiling point 50 to 100 to 240 to 260 ^{o}C) from air. However, not all VOCs of interest can be retained on Tenax TA. Increasing polarity of the adsorbate also decreased the efficiency of adsorption. Certain individual VOCs have also been shown not to give reproducible results.

The surface analysis of six selected adsorbents by FE-SEM analysis was performed. They could be separated according to different pore size distribution: group 1 (Tenax TA and Tenax GR), group 2 (Carbopack B and Carbotrap B) and group 3 (Carbopack C and Carbotrap C) as shown in FE-SEM micrograph in Figure 4.4.

Group 1



Group 2



Group 3

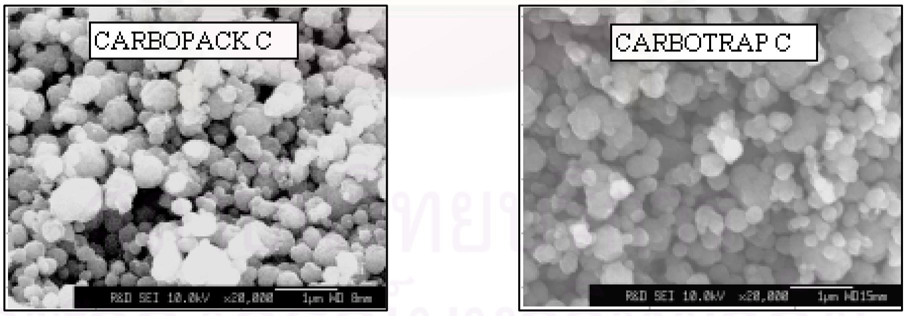


Figure 4.4 FE-SEM photograph of six selected adsorbents

FE-SEM photographs of six selected adsorbents showed that adsorbents in group 2 had the smallest pore size and the shape of adsorbent was difficult to observe, whereas those in group 3 had a larger pore size with spherical shape. For the adsorbents in group 3, the adsorption efficiency for high molecular weight samples should be better than adsorbents in group 2 because of a larger hole size structure. It could thus assume that adsorbents in group 3 could adsorb higher molecular weight compounds while those in group 2 were not able to adsorb a large molecule. The adsorbents in group 1 had the biggest pore size with the shape being network. Furthermore, for desorption process, the structures of the adsorbents in group 1 were not so packed, therefore the molecular releasing process was easier.

According to these results, porous polymers: Tenax TA and Tenax GR were the best adsorbents for a wide range of hydrocarbon compounds. For low molecular weight compounds such as C_{10} to C_{15}, the utilization of dual-sorbent Carbopack C/B or Carbotrap C/B was superior to that of single-sorbent. For monomers, Tenax TA and Carbopack C were the best.

4.1.1.4 Effect of the amount of adsorbents on the adsorption efficiency of mixed monomers

The amount of adsorbents could have an effect on the adsorption efficiency due to the limit of adsorbed volume and the amount of adsorbents. The analysis results are shown in Figure 4.5.

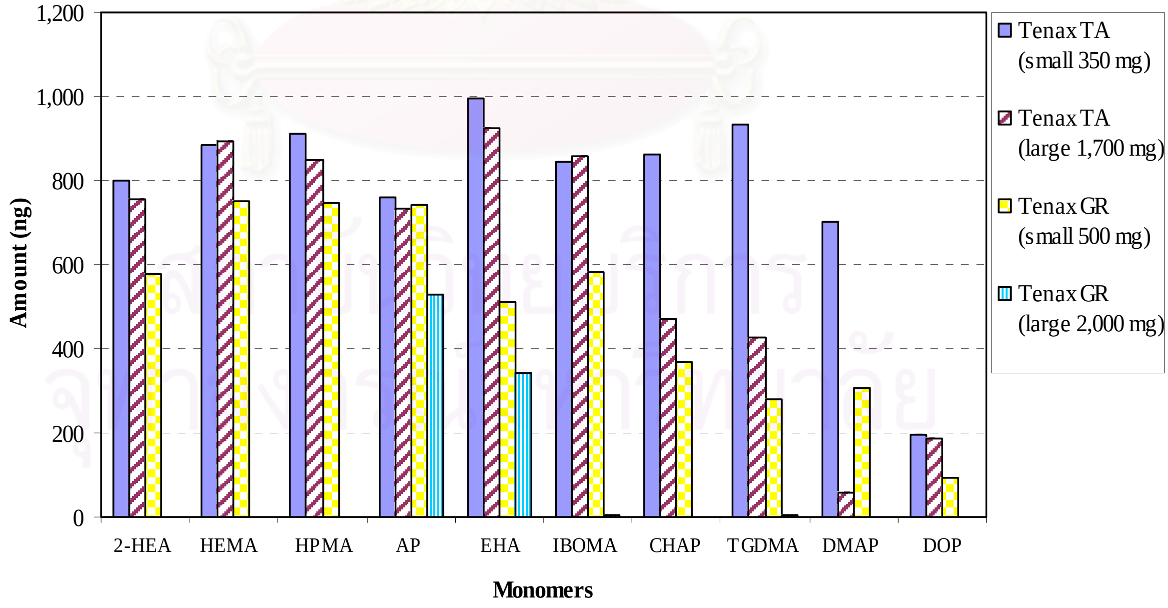


Figure 4.5 The effect of the amount of adsorbents on adsorption efficiency upon the analysis of mixed monomers

The adsorption efficiency test for the amount of adsorbent was performed by varying the amount of adsorbents: Tenax TA and Tenax GR. Adsorbents were packed into two sample tube sizes: small tube volume 1.6 mL and large tube volume 10 mL. The amount of adsorbent was packed into sample tube as follows:

Tenax TA: Small tube-350 mg and Large tube-1,700 mg
Tenax GR: Small tube-500 mg and Large tube-2,000 mg

From Figure 4.5, Tenax TA with less amount of adsorbent exhibited the higher efficiency than the tube containing higher amount upon the analysis of mixed monomers except HEMA and IBOMA. Tenax TA with higher amount also provided the better efficiency. Whereas Tenax GR gave better performance for less amount of adsorbent for all monomers examined. Tenax GR with large amount found that for 2-HEA, HEMA and HPMA compound were not detected.

4.1.1.5 Effect of the amount of adsorbents on the adsorption efficiency of mixed alkanes (C_{10} to C_{25})

From Figure 4.6, with the less amount of Tenax TA, it gave better adsorption efficiency for the analysis of C_{16} to C_{25}. The results were similar to those using Tenax GR with less amount of adsorbent. The use of Tenax TA in higher amount gave better adsorption efficiency from C_{10} to C_{15}. Using large amount of Tenax GR, the low efficiency was observed for all alkanes in the range of C_{10} to C_{25}. For alkanes with the number of carbon more than 20, there was no effect of the amount of adsorbent on adsorptivity.

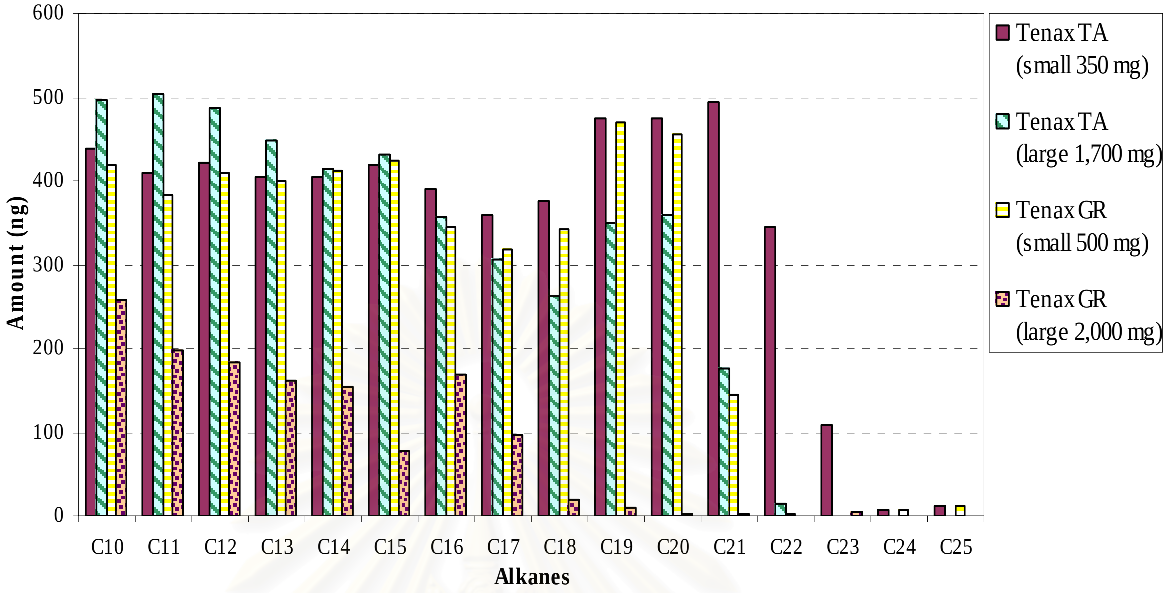


Figure 4.6 The effect of the amount of adsorbents on adsorption efficiency upon the analysis of mixed alkanes (C_{10} to C_{25})

From the above data, more amount of adsorbent revealed lower adsorptivity, especially for higher molecular weight samples. Whereas Tenax TA less and more amount of adsorbent were displayed similar adsorption efficiency especially for low molecular weight compounds.

Generally, the less amount of adsorbent gave the less adsorption efficiency due to the limit of the volume capacity. From the result, more amount of adsorbent detected the lower adsorption efficiency that may cause from the desorption process ability. More amount of adsorbent need more time for desorption process. For Tenax GR, more amount of adsorbent showed the low efficiency that may cause from the poor desorption ability. Thus, the better performance for adsorption and desorption ability was less adsorbent amount. To improve the adsorption efficiency of Tenax GR, more desorption process time should be explored.

4.2 Study on the optimum thermal desorption conditions for the determination of VOCs

Thermal desorption is a good and reliable method for rapid and direct analysis of thermally volatile compounds. The optimization of thermal desorption conditions including purge and trap time, trapping temperature, desorption temperature and time and secondary adsorption materials would be explored for better adsorption efficiency. Thermal desorption or purge and trap system used was a JHS-100/100A Curie point headspace sampler (Japan Analytical Industry Co., Ltd.), which was directly attached to GC-MS. Thermal desorption parameters are presented in Table 3.2 (Chapter III).

4.2.1 Effect of purge and trap time on the adsorption efficiency of mixed monomers

In order to optimize the analytical conditions for better adsorption efficiency of VOCs analysis, purge and trap time is the first parameter of thermal desorption unit to be considered. Purge and trap time is the time using for transferring the collected VOCs in sample tube to the secondary adsorption tube. The process for this is as follows: for mixed monomers, purge and trap time was varied from 5, 10 minutes and so on until reaching the highest amount of VOCs using Tenax TA 350 mg as an adsorbent. The analytical conditions were: thermal-extraction temperature, 250 ^{o}C; trapping temperature, -60 ^{o}C and desorption temperature, 358 ^{o}C.

Figure 4.7 shows that purge and trap time intensely affected on the determination of mixed monomers. To illustrate this, the optimum purge and trap time which provided the highest VOCs amount for all monomers except DMAP and DOP was 20 minutes. For DMAP, the optimum purge and trap time was 25 minutes and that for DOP was 15 minutes. For certain compounds such as 2-HEA, HEMA, HPMA, AP, EHA, IBOMA and CHAP, the purge and trap time was found to be 15 minutes. The same adsorption efficiency was gained as that observed at 20 and 25 minutes (the variation within 20%). Thus, to save time for the analysis, the purge and trap time of 15 minutes should be chosen. For TGDMA, DMAP and DOP, the observed results revealed in different tendency from other monomers, especially DOP. This may cause from its high molecular weight.

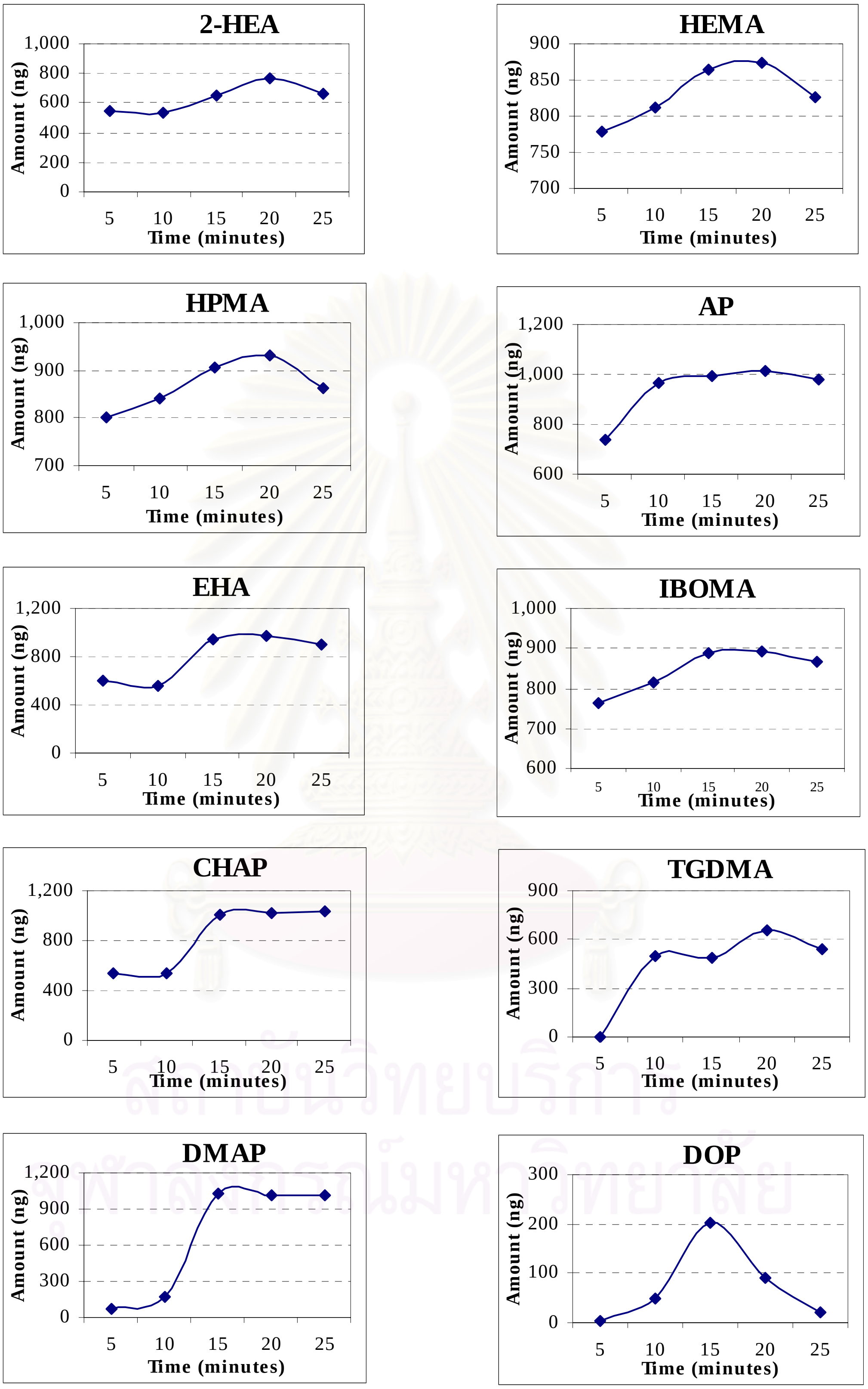


Figure 4.7 The effect of purge and trap time on adsorption efficiency upon the analysis of mixed monomers

4.2.2 Effect of purge and trap time on the adsorption efficiency of mixed alkanes (C_{10} to C_{25})

Figure 4.8 presents the effect of purge and trap time on the analysis of mixed alkanes (C_{10} to C_{25}). For mixed alkanes in the range of C_{10} to C_{15}, the optimum purge and trap time was 25 minutes. However, at purge and trap time 20, 25 and 30 minutes, the adsorption efficiency of mixed alkanes in the range of C_{10} to C_{15} was similar. For higher molecular weight alkanes from the number of carbon 16 to 22, the optimum purge and trap time was decreased to 10 minutes. For the number of carbon more than 22, the low adsorption efficiency was detected.

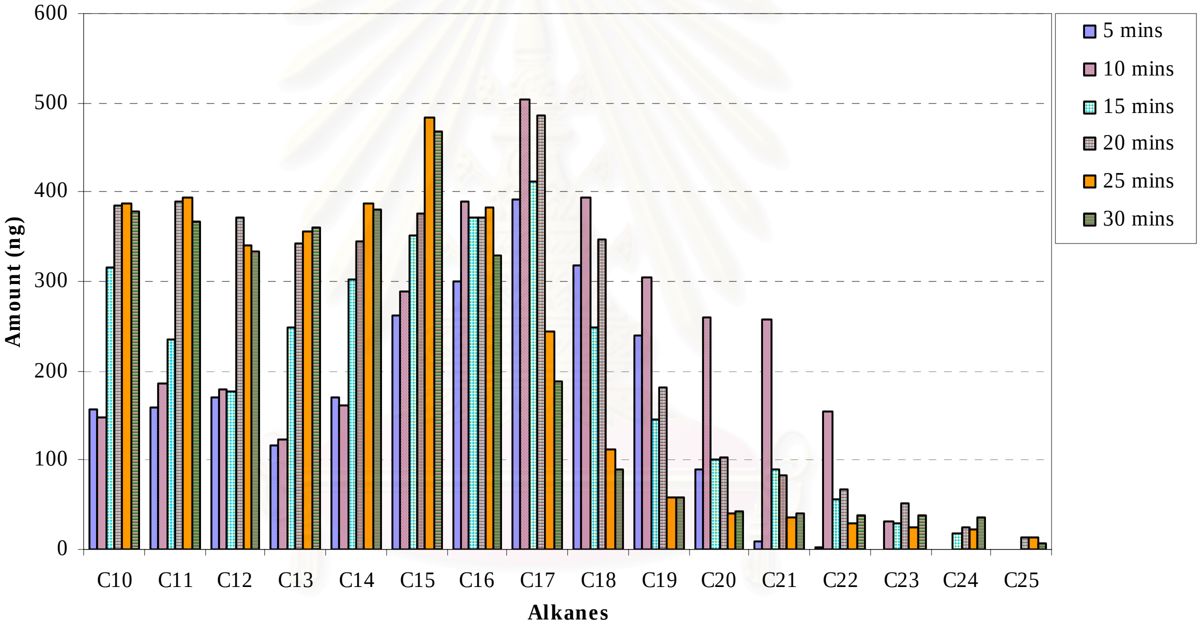


Figure 4.8 The effect of purge and trap time on adsorption efficiency upon the analysis of mixed alkanes (C_{10} to C_{25})

Thus, for low molecular weight compounds, the optimum purge and trap time could be 20 minutes while for medium molecular weight compounds, this time could be 10 minutes. For high molecular weight compounds, the analysis method however should be further developed.

4.2.3 Effect of trapping temperature on the adsorption efficiency of mixed monomers

Trapping temperature is the temperature which trapped VOCs transferred from sample tube being desorbed and trapped by the secondary adsorption tube. The variations of trapping temperature in thermal desorption-GC-MS for this study were 20, 0, -20, -40 and -60 °C. The analytical conditions were: thermal-extraction temperature, 250 °C and desorption temperature, 358 °C. The trapping temperature was determined in consideration of the rapidity of cooling and the variations of the amount of VOCs.

Mixed monomers were first examined. The results display in Figure 4.9.

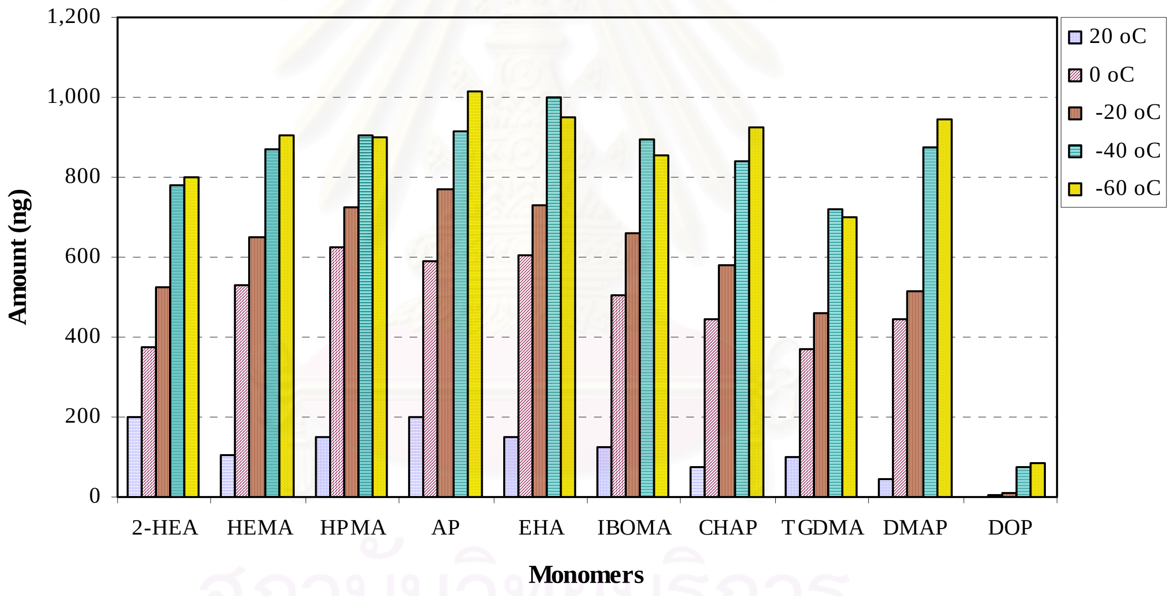


Figure 4.9 The effect of trapping temperature on adsorption efficiency upon the analysis of mixed monomers

Figure 4.9 exhibits the effect of trapping temperature on the determination of VOCs for all monomers. The optimum trapping temperature was -60 °C. The lowest amount of all monomers was found at trapping temperature of 20 °C. The lower temperature, the better adsorption efficiency.

4.2.4 Effect of trapping temperature on the adsorption efficiency of mixed alkanes (C_{10} to C_{25})

The effect of trapping temperature for mixed alkanes (C_{10} to C_{25}), the results are expressed as shown in Figure 4.10.

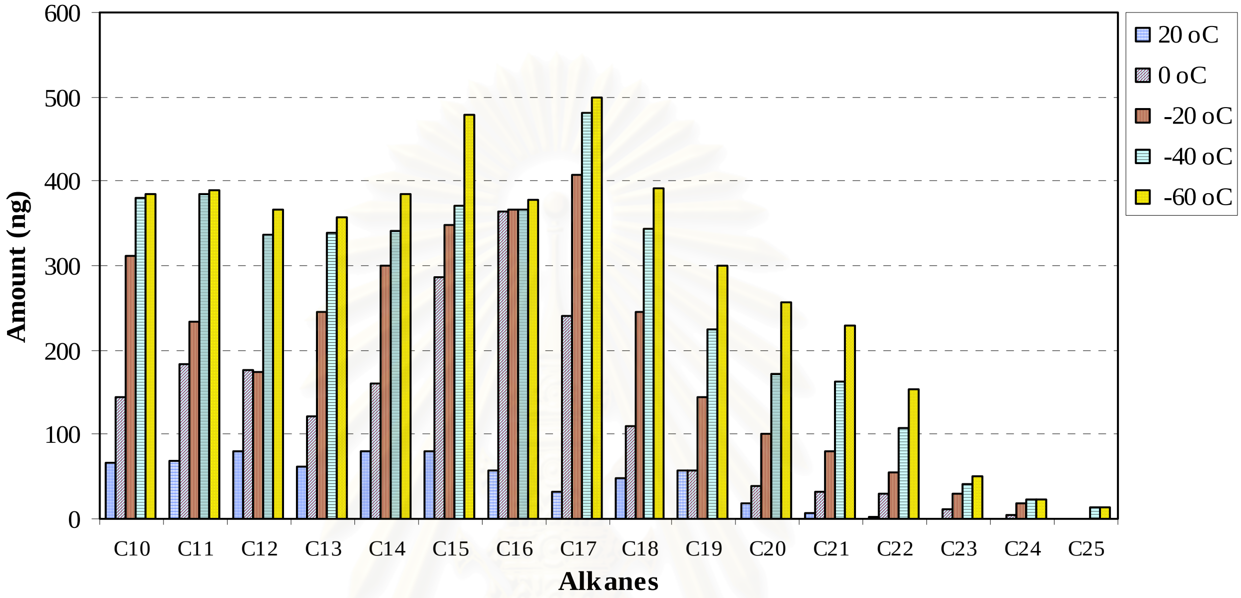


Figure 4.10 The effect of trapping temperature on adsorption efficiency upon the analysis of mixed alkanes (C_{10} to C_{25})

Figure 4.10 shows the amount of mixed alkanes detected with various trapping temperatures studied (20, 0, -20, -40 and -60 ^{o}C) in thermal desorption-GC-MS using mixed alkanes (C_{10} to C_{25}). The results revealed the same tendency. The optimum trapping temperature was -60 ^{o}C and the lowest amount of mixed alkanes was found at trapping temperature 20 ^{o}C.

From this experiment, the lower trapping temperature generally exhibited better adsorption efficiency for both mixed monomers and mixed alkanes. At lower trapping temperature, high molecular weight VOCs could be trapped more efficiently than at higher trapping temperature. At high temperature, all low molecular weight VOCs may be lost because of their facile volatility. Even though, the efficiency of the trapping process was appreciated at very low temperature (-60°C), liquid nitrogen that normally used to cool the trapped samples was mandatorily required. This will however cost the process. Seeking for another efficient trapping temperature, it was observed from the experimental results that the trapping temperature at -40 °C could be also utilized. This is because the adsorption efficiency at trapping temperature -40 °C was less than trapping temperature at -60 °C 5 to 10 % for mixed monomers, mixed alkanes in the range of C_{10} to C_{17} and 15 to 20 % for mixed alkanes in the range of C_{18} to C_{25}.

4.2.5 Effect of desorption temperature on the adsorption efficiency of mixed monomers

Desorption temperature is the heated temperature to the center of pyrofoil and then desorbed very thin band and carried VOCs to chromatographic column. The optimum desorption temperature for thermal desorption condition was used as follows: thermal-extraction temperature, 250 °C; trapping temperature, -60 °C and desorption time, 20 seconds. The desorption temperature was varied for 255, 315 and 358 °C for mixed monomers as presented in Figure 4.11.

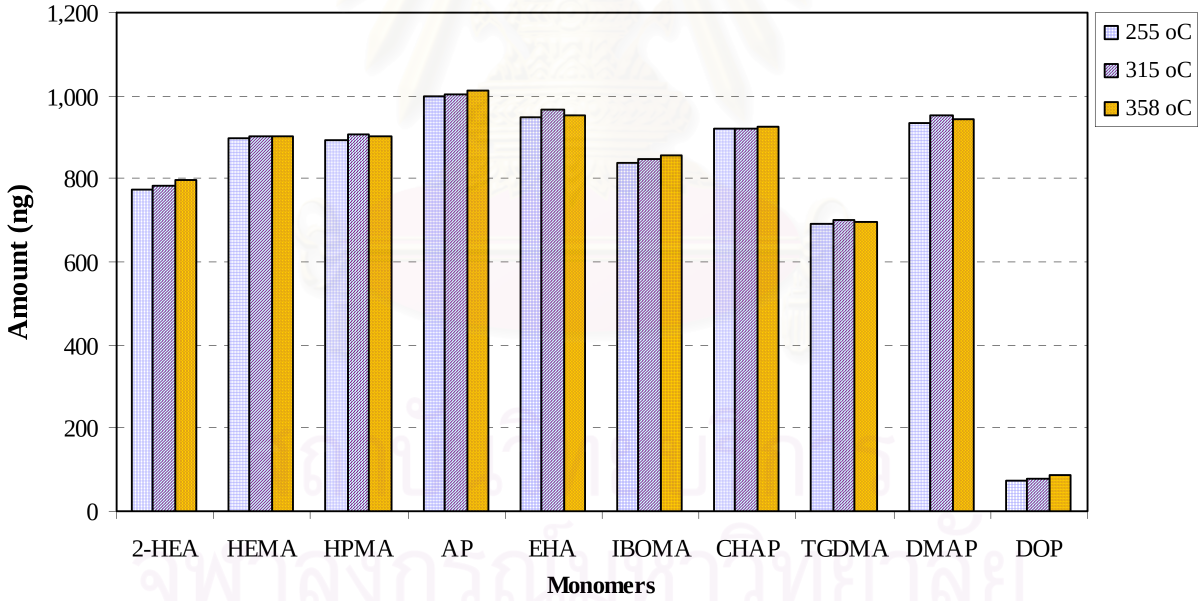


Figure 4.11 The effect of desorption temperature on adsorption efficiency upon the analysis of mixed monomers

From Figure 4.11, there was no significant variation of the amount of monomer detected at any desorption temperature of 255, 315 and 358 °C. At the desorption temperature 255 °C, the lowest amount of VOCs was found while at the desorption temperature 315 °C, the high amount of some compounds such as HPMA, EHA and DMAP were observed. At 358 °C, the highest amount of VOCs could be determined for 2-HEA, HEMA, AP, IBOMA, CHAP, TGDMA and DOP. However, overall results exhibited that the optimum desorption temperature should be 358 °C.

4.2.6 Effect of desorption temperature on the adsorption efficiency of mixed alkanes (C_{10} to C_{25})

The results of the effect of desorption temperature for mixed alkanes (C_{10} to C_{25}) are displayed in Figure 4.12.

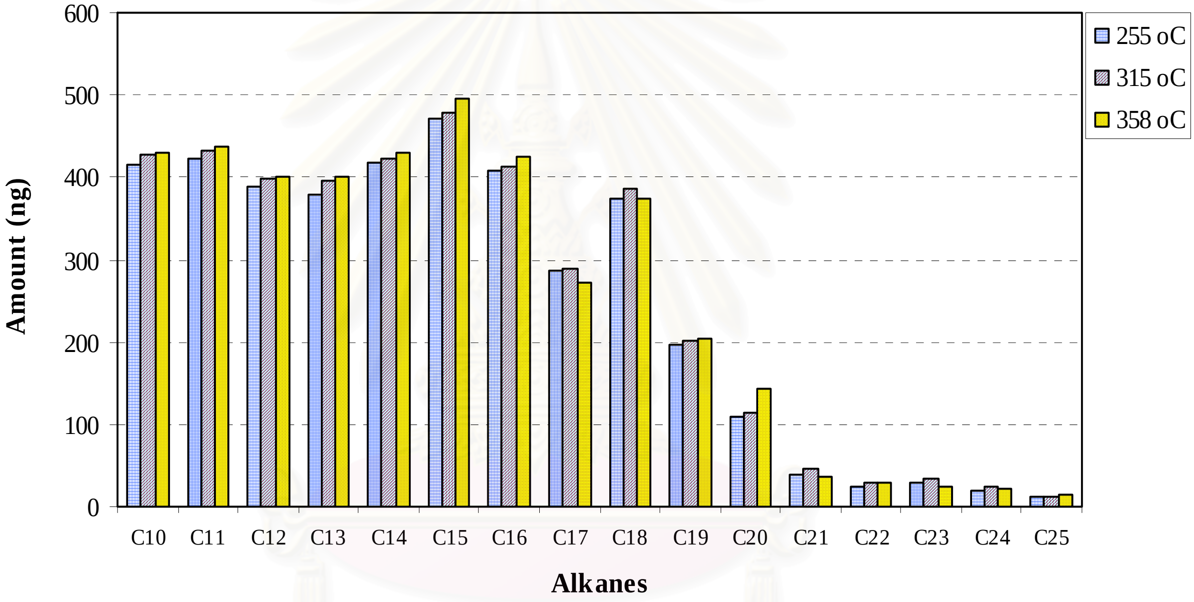


Figure 4.12 The effect of desorption temperature on adsorption efficiency upon the analysis of mixed alkanes (C_{10} to C_{25})

From Figure 4.12, the same performance was found as that observed for mixed monomers. The highest desorption temperature at 358 °C revealed the highest adsorption efficiency comparing with other temperatures for all ranges of mixed alkanes (C_{10} to C_{25}).

At the lowest desorption temperature 225 °C, some low molecular weight compounds may be lost due to the volatility. Thus, the higher desorption temperature should be better for trapping all molecular mass ranges.

4.2.7 Effect of desorption time on the adsorption efficiency of mixed monomers

Desorption time of pyrolysis timer is the heating time of pyrofoil for desorped VOCs before transferring to GC column. The short time pyrolysis was not enough to desorb VOCs from the adsorption tube, thus the optimum time could be adjusted to get the complete desorption of VOCs. The optimum desorption time was examined exploiting the thermal desorption conditions as follows: thermal-extraction temperature, 250 ^{o}C; trapping temperature, -60 ^{o}C and desorption temperature, 358 ^{o}C. The desorption time was varied for 5, 10, 20 and 25 seconds.

Mixed monomer was first examined and the results display in Figure 4.13.

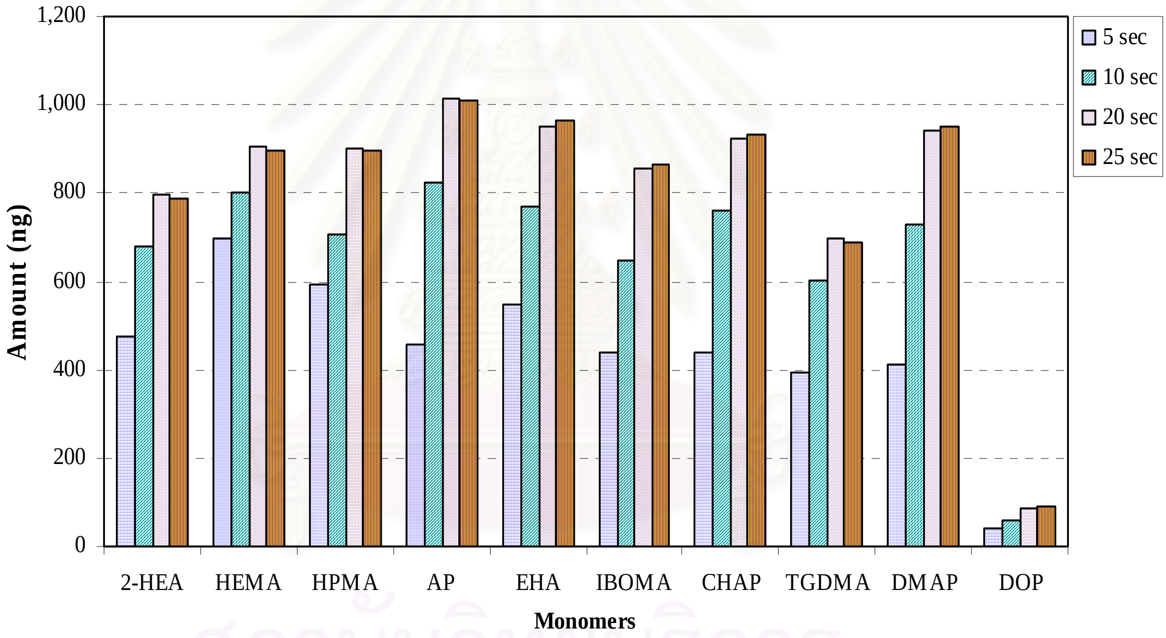


Figure 4.13 The effect of desorption time on adsorption efficiency upon the analysis of mixed monomers

From Figure 4.13, the desorption time for all monomers displayed the similar tendency. Employing less desorption time gave lower amount of VOCs whereas using more desorption time provided higher amount of VOCs. At desorption time of 20 and 25 seconds, no difference in the amount of VOCs was detected while at higher desorption time made the broad peak on GC chromatogam. Thus, the optimum desorption time was adjusted for 20 seconds.

4.2.8 Effect of desorption time on the adsorption efficiency of mixed alkanes (C_{10} to C_{25})

From Figure 4.14, the same performance was found as that visualized for mixed monomers. All mixed alkanes with the number of carbon in the range of C_{10} to C_{25}, desorption time of 20 and 25 seconds provided similar results concerning the amount of VOCs detected. Thus, the optimum desorption time for mixed alkanes was 20 seconds.

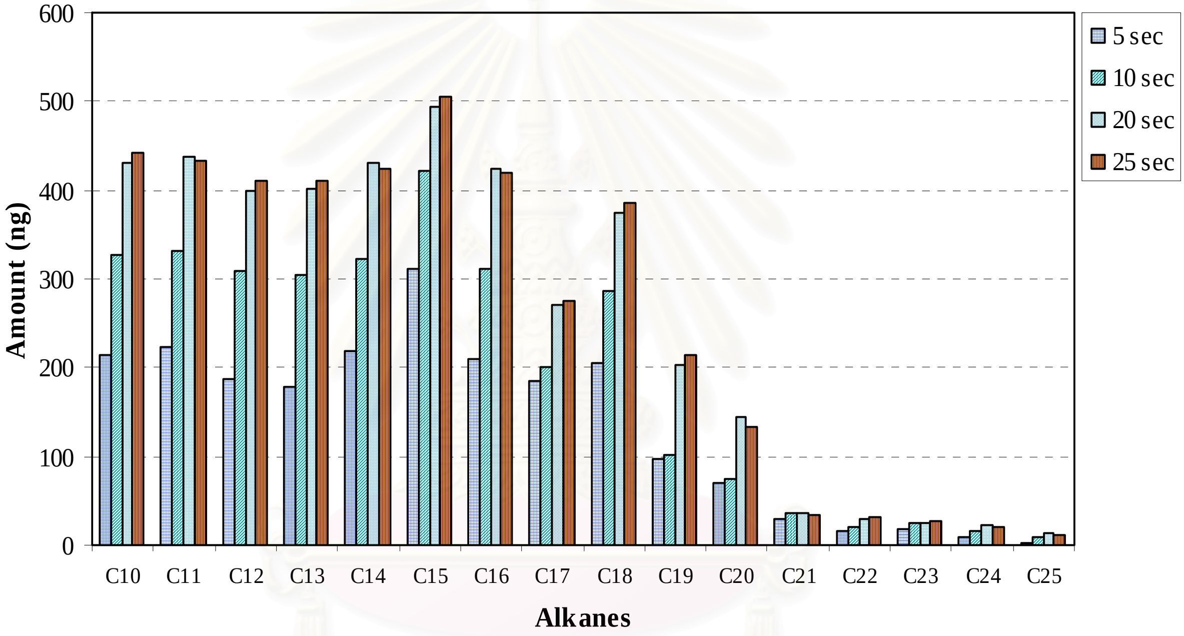


Figure 4.14 The effect of desorption time on adsorption efficiency upon the analysis of mixed alkanes (C_{10} to C_{25})

4.2.9 Effect of secondary adsorption material on the adsorption efficiency of mixed monomers

For good adsorption efficiency of VOCs analysis, a desorption process is the important process and the adsorbent type should also necessary to be matched. Secondary adsorption material is the adsorbent which used for trapping the desorbed VOCs from sample tube before the VOCs being transferred to GC column. Three types of secondary adsorption materials were selected to compare the adsorption efficiency: Tenax TA, glass wool and Carbopack C. Mixed monomers were first tested and the results display in Figure 4.15.

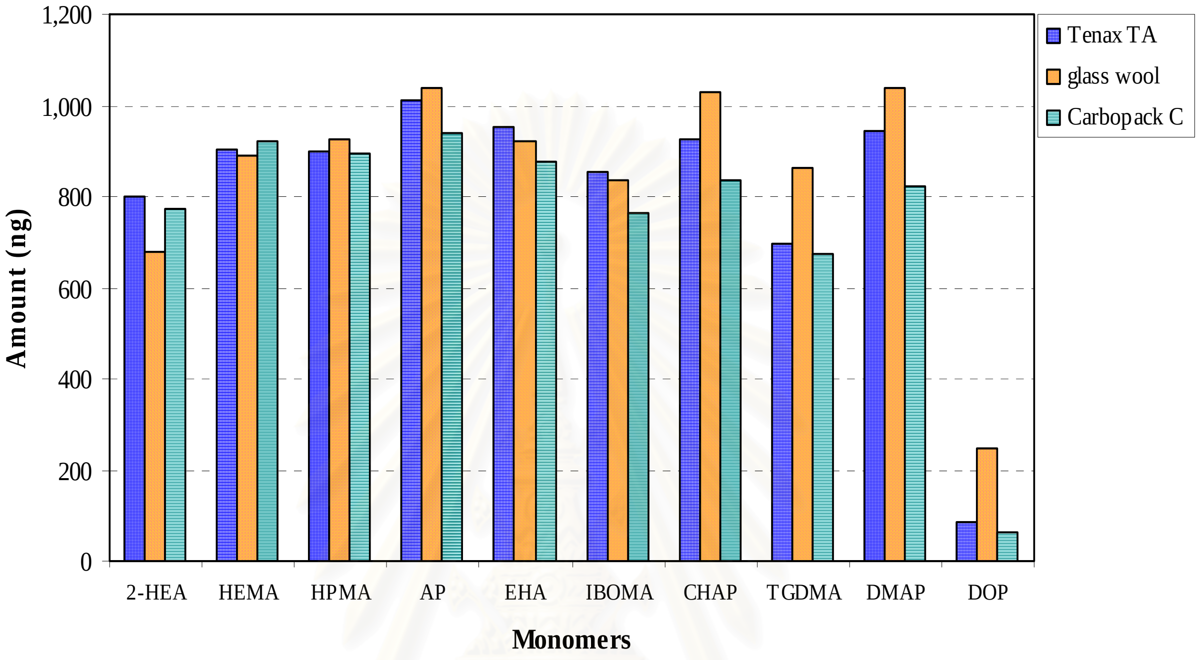


Figure 4.15 The effect of secondary adsorption material on adsorption efficiency upon the analysis of mixed monomers

With different adsorption efficiency of secondary adsorption material, glass wool gave the highest amount of VOCs for some monomers such as HPMA, AP, CHAP, TGDMA, DMAP and DOP compared with Tenax TA and Carbopack C. Whereas for some monomers such as 2-HEA, EHA and IBOMA, Tenax TA gave the best adsorption efficiency. For low molecular weight compounds, not much difference among three secondary adsorption materials while for high molecular weight compounds, CHAP, TGDMA, DMAP and DOP, glass wool was the best.

4.2.10 Effect of secondary adsorption material on the adsorption efficiency of mixed alkanes (C_{10} to C_{25})

Figure 4.16 shows the comparison of the adsorption efficiency of secondary adsorption material for mixed alkanes (C_{10} to C_{25}). Tenax TA exhibited its good efficiency especially for mixed alkanes in the range of C_{10} to C_{20} but for the higher molecular weight compounds from the number of carbon more than 20, glass wool displayed as the best secondary adsorption material. Carbopack C showed the higher adsorption efficiency than glass wool for C_{10} and also C_{15} to C_{19}.

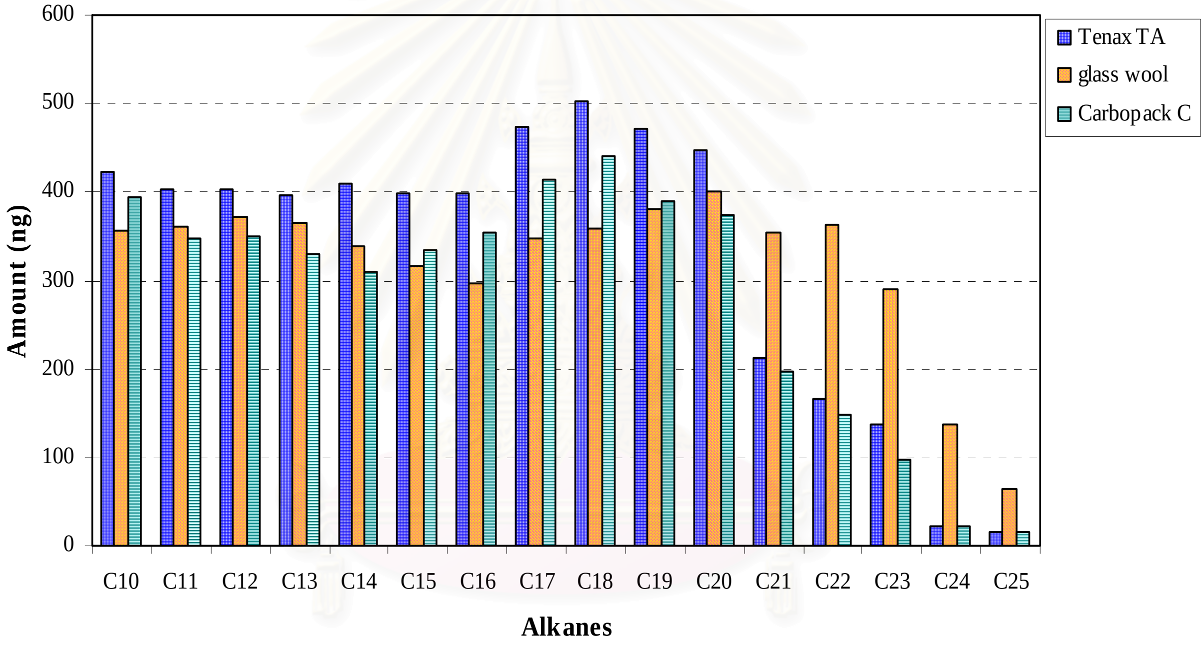


Figure 4.16 The effect of secondary adsorption material on adsorption efficiency upon the analysis of mixed alkanes (C_{10} to C_{25})

From the above data, low molecular weight compounds could be used for all secondary adsorption materials due to similar adsorptivity while high molecular weight compounds, glass wool was preferred. The possible reason was that the appearance of glass wool was like a network where the VOC molecules could be trapped and rearranged. Furthermore, the property of glass wool is different from other adsorbents, especially for adsorbed and desorbed properties.[15] It only concentrates and limits the fence of VOCs to distribute in tube.

4.3 The analysis of trace VOCs

After the high efficient adsorbent and optimized thermal desorption conditions were thoroughly examined, low amount of VOCs should be considered as the next step of investigation. To control the contamination level from HDD components, the amounts of some compounds such as tributylamine, sulfur molecule (S_8) and siloxanes[34] were critical to be kept in very low concentrations. Siloxanes are VOCs that have high impact with HDD, even a low amount of siloxane (less than 100 ng) may cause the stickiness on head disk and read/write error. For this research, to verify the preceding developed method whether it was suited for the investigation of trace components from HDD, two siloxanes were chosen. Octamethylcyclotetrasiloxane and decamethyltetrasiloxane were prepared at low concentration of 50 ng per analysis. Tenax TA was selected as an adsorbent with thermal desorption conditions as follows: thermal-extraction temperature, 250 ^{o}C; trapping temperature, -60 ^{o}C and desorption, 358 ^{o}C for 20 seconds.

The chromatograms of mixed siloxanes are displayed in Appendix A.4. Table 4.2 displays the amount of siloxane under the optimum conditions derived from the previous section.

Table 4.2 The amount of siloxane with optimum adsorbent and thermal desorption condition

Siloxane	**Amount (ng)**
Octamethylcyclotetrasiloxane	44.95
Decamethyltetrasiloxane	40.08

The above results demonstrated that trace amounts of siloxane could be detected utilizing the developed methodology. The amount of two siloxanes determined was close to those of prepared solution. Thus, the low concentration of siloxane can also be detected employing these conditions. This manifestly demonstrated that the adsorbent and thermal desorption conditions were appropriate for analysis of trace siloxane in HDD.

4.4 Real samples analysis

After the optimal conditions for thermal desorption was carefully investigated, the analysis of real samples would be concentrated. Practically, the VOCs released was collected by an equipment called outgas collector. In this research the outgas collector used was JAI model HM-04.

Adsorbent tube connecting to the chamber holder would adsorb VOCs released from samples after the outgas collector was heated up. The sampling conditions optimized were temperature and time at a fixed helium flow rate of 50 mL/min. The sampling temperatures for the evaluation were 85, 110 and 150 ^{o}C based upon the temperature used in the real product application. The sampling time was also varied from 15 minutes, 1, 3, 5 and 7 hours to gain the highest amount of VOCs for each sampling temperature. The real samples that selected for analysis were pivot cartridge and spindle motor which were the important HDD component parts.

4.4.1 Optimization of the sampling conditions for pivot cartridge

The investigation of the optimum sampling condition both sampling temperature and sampling time for pivot cartridge were first examined and the results display in Tables 4.3-4.5.

Table 4.3 The analysis result of VOCs from pivot cartridge sampling at 85 ^{o}C with various sampling time

VOCs / Amount (μg/pc)	**R.T.**	**Sampling time (hour)**			
		1	**3**	**5**	**7**
Hydroxypropyl methacrylate; HPMA	7.23	2.18	3.58	3.54	3.75
Triethyleneglycol dimethacrylate; TGDMA	20.34	0.16	0.73	2.61	4.58
Phenyldimethoxy acetophenone; DMAP	20.43	0.10	1.32	2.85	2.40
Hydrocarbons	-	7.39	23.64	43.80	62.05
Other compounds	-	4.28	4.71	8.56	14.00
Total VOCs	-	**15.43**	**32.58**	**61.35**	**86.77**

Table 4.3 presents the analysis result of VOCs from pivot cartridge sampling at 85 ^{o}C. The sampling time was varied from 1, 3, 5 and 7 hours. It was observed that the amount of VOCs released from pivot cartridge had been still increasing during the experimental time studied. The average total amount of VOCs at the highest sampling time for pivot cartridge at 85 ^{o}C was 86.77 μg/pc. For certain compounds such as HPMA and DMAP, the sampling time 5 hours could reach the maximum amount of those VOCs. Therefore, if the quantitative analysis of HPMA and DMAP was required, the sampling time of 5 hours was appropriate for the analysis protocol. Among the VOCs released from pivot cartridge, hydrocarbons was detected as the main components. It was additionally visualized that the amount of hydrocarbon VOCs increased along with the increasing of sampling time. The optimum sampling time for overall components in pivot cartridge at 85 ^{o}C was 7 hours.

Table 4.4 The analysis result of VOCs from pivot cartridge sampling at 110 ^{o}C with various sampling time

VOCs / Amount (μg/pc)	**R.T.**	**Sampling time (hour)**		
		1	**3**	**5**
Hydroxypropyl methacrylate; HPMA	7.23	2.68	4.02	3.19
Triethyleneglycol dimethacrylate; TGDMA	20.34	0.63	4.68	4.45
Phenyldimethoxy acetophenone; DMAP	20.43	0.68	1.99	1.99
Hydrocarbons	-	20.28	62.20	62.20
Other compounds	-	8.42	15.02	15.02
Total VOCs	-	**32.68**	**87.90**	**86.88**

From Table 4.4, it was found that the amount of VOCs for all compounds released from the pivot cartridge with sampling temperature at 110 ^{o}C at sampling time of 3 or 5 hours was similar. This experimental results supported the general statement that the higher sampling temperature used, the higher amount of VOCs obtained. Thus, the optimum sampling time for pivot cartridge at 110 ^{o}C was 3 hours while that at 85 ^{o}C was for 7 hours.

Table 4.5 The analysis result of VOCs from pivot cartridge sampling at 150 ^{o}C with various sampling time

VOCs / Amount (μg/pc)	**R.T.**	**Sampling time (minute)**			
		15	**30**	**45**	**60**
Hydroxypropyl methacrylate; HPMA	7.24	2.01	2.99	3.38	2.76
Triethyleneglycol dimethacrylate; TGDMA	20.34	1.59	4.05	4.26	3.46
Phenyldimethoxy acetophenone; DMAP	20.43	1.90	2.14	2.24	1.81
Hydrocarbons	-	31.13	58.74	61.92	56.06
Other compounds	-	7.33	10.40	15.21	11.40
Total VOCs	-	**43.98**	**78.31**	**87.00**	**75.53**

Table 4.5 still reveals the same trend. The analysis result of VOCs for pivot cartridge with the sampling temperature at 150 ^{o}C displayed that at 45 minutes the amount of VOCs observed were similar to those for other sampling temperatures (85 and 110 °C). Within 1 hour, the maximum amount of all VOC components was reached. For instance, the highest amounts of HPMA, TGDMA and DMAP were detected for 15 minutes. At 60 minutes, the amount of all components was dropped. This may derive from some leak taking place while sampling process. Therefore, the optimum sampling time for pivot cartridge at 150 ^{o}C was 30 or 45 minutes.

It was clearly seen that the higher temperature performed, the higher amount of VOCs detected. In addition, when higher temperature was applied, less sampling time was required. Thus, to save time for sampling, higher temperature should be selected. Nevertheless, it should be noted at this point that in case of employing high temperature (for instance, more than 150°C), although less sampling time was needed, some compounds may not completely be trapped by a sample tube.

4.4.2 Optimization of the sampling conditions for spindle motor

The optimum sampling condition for spindle motor which released the higher amount of VOCs were further investigated and the results display in Tables 4.6-4.8.

Table 4.6 The analysis result of VOCs from spindle motor sampling at 85 ^{o}C with various sampling time

VOCs / Amount (μg/pc)	**R.T.**	**Sampling time (hour)**			
		1	**3**	**5**	**7**
2-Furanmethanol, tetrahydro	3.57	5.85	19.06	18.11	19.27
Isopropylbenzene	4.21	4.08	16.05	41.44	51.55
2-Hydroxyethyl acrylate; 2-HEA	5.19	10.47	40.98	69.93	72.73
Tetrahydrofuran derivatives	9.78	13.92	46.67	94.55	127.33
Phthalate compounds	-	0.10	0.10	0.65	0.68
Hydrocarbons	-	55.61	107.40	122.65	127.33
Other compounds	-	72.84	189.23	214.08	209.81
Total VOCs	-	**162.86**	**419.47**	**561.41**	**609.18**

Table 4.6 displays the analysis of VOCs from another real sample, spindle motor sampling at 85 ^{o}C. The sampling time was varied from 1, 3, 5 and 7 hours. The average total amount of VOCs at the highest sampling time for spindle motor at 85 ^{o}C was 609.18 μg/pc. For hydrocarbons, the maximum amount of VOCs (~ 125 μg/pc) could be reached approximately 5 hours of sampling time. Thus, the optimum sampling time for spindle motor at 85 ^{o}C was 7 hours. Table 4.7 presents the analysis results of VOCs from spindle motor with sampling temperature at 110 ^{o}C. It was observed that the sampling time at 5 and 7 hours showed similar extents for all compounds. Thus, the optimum sampling time for spindle motor at 110 ^{o}C was 7 hours or for the analysis of common sample, the sampling time 5 hours could be used to save time.

Table 4.7 The analysis result of VOCs from spindle motor sampling at 110 ^{o}C with various sampling time

VOCs / Amount (µg/pc)	R.T.	Sampling time (hour)			
		1	**3**	**5**	**7**
2-Furanmethanol, tetrahydro	3.57	10.90	13.09	18.12	19.15
Isopropylbenzene	4.21	13.06	34.83	47.93	52.79
2-Hydroxyethyl acrylate; 2-HEA	5.19	59.90	51.12	82.00	82.81
Tetrahydrofuran derivatives	9.78	20.01	92.52	123.40	128.52
Phthalate compounds	-	0.24	0.18	0.56	0.61
Hydrocarbons	-	90.74	103.24	125.91	128.11
Other compounds	-	156.84	184.81	204.75	217.25
Total VOCs	-	**351.67**	**479.78**	**602.66**	**628.22**

Table 4.8 The analysis result of VOCs from spindle motor sampling at 150 ^{o}C with various sampling time

VOCs / Amount (µg/pc)	R.T.	Sampling time (minute)			
		15	**30**	**60**	**90**
2-Furanmethanol, tetrahydro	3.57	10.29	17.78	18.44	20.82
Isopropylbenzene	4.21	24.09	50.88	51.59	54.97
2-Hydroxyethyl acrylate; 2-HEA	5.19	21.17	78.95	80.43	83.91
Tetrahydrofuran derivatives	9.78	53.29	117.49	125.79	130.76
Phthalate compounds	-	0.29	0.63	0.64	0.93
Hydrocarbons	-	96.29	119.08	128.80	131.15
Other compounds	-	202.40	202.39	215.94	224.94
Total VOCs	-	**407.81**	**587.18**	**621.62**	**630.46**

Table 4.8 tabulates the analysis result of VOCs from spindle motor with the sampling temperature at 150 ^{o}C. At 60 and 90 minutes, the amount of VOCs were detected similar to that attained for sampling temperature at 110 ^{o}C for 7 hours (628.22 μg/pc). Thus, the optimum sampling time for spindle motor at 150 ^{o}C was 60 or 90 minutes.

From the aforementioned results, the larger size of samples (spindle motor) released higher amount of VOCs. The suitable time for the analysis of the larger sizes of samples was thus found to be longer than the smaller sample (pivot cartridge).

It could be summarized at this point that for the VOCs analysis, various conditions were needed to be carefully considered. The sampling conditions and the analysis steps such as sampling temperature together with sampling time, flow rate of gas during sampling, adsorbent type, *etc*. were among those crucial parameters.

CHAPTER V
CONCLUSION AND SUGGESTION

In this research, the determination of VOCs released from HDD was investigated. The analysis was conducted using adsorption/thermal desorption-GC-MS. Six adsorbents were evaluated for their adsorption efficiency. For porous polymer adsorbents (Tenax TA and Tenax GR) revealed higher adsorption efficiency for a wide range of molecular weight while for high molecular weight samples, graphitized carbon black adsorbents (Carbopack C and Carbotrap C) were more suitable. For graphitized carbon black, the lower density adsorbents (Carbopack B and Carbotrap B) exhibited the lower adsorption efficiency. To improve the adsorption efficiency for the analysis of hydrocarbons, dual-sorbents ratio 1:1 were examined. The results showed that for all ranges of hydrocarbons C_{10} to C_{25}, dual-sorbent Carbopack C/B, Carbotrap C/B provided better adsorption efficiency than single-sorbent, especially for higher molecular weight alkanes (C_{21} to C_{25}). According to these results, porous polymers were the best adsorbents for a wide range of hydrocarbons. For low molecular weight compounds such as C_{10} to C_{15}, the utilization of dual-sorbent Carbopack C/B or Carbotrap C/B was superior to that of single-sorbent. For monomers, Tenax TA and Carbopack C were the best.

The optimizaton of the analytical conditions for better adsorption efficiency of VOCs analysis was explored. Thermal desorption condition including purge and trap time, trapping temperature, desorption temperature, desorption time and secondary adsorption materials were thoroughly examined. For certain compounds such as 2-HEA, HEMA, HPMA, AP, EHA, IBOMA and CHAP, the suitable purge and trap time was found to be 15 minutes. For TGDMA, DMAP and DOP, the results revealed the different tendency from other monomers, especially DOP. These observed different results may derive from their high molecular weight. For hydrocarbons with low molecular weight compounds, the optimum purge and trap time could be 20 minutes while for medium molecular weight, this time could be 10 minutes. The optimum trapping temperature was -60 ^{o}C, desorption temperature at 358 ^{o}C and the optimum desorption time at 20 seconds. For all secondary adsorption materials: Tenax

TA, glass wool, Carbopack C displayed similar adsorptivity especially for low molecular weight compounds while high molecular weight compounds, glass wool was preferred.

In addition, real samples were analyzed after the optimum parameters for VOCs analysis was disclosed. The optimum sampling times for pivot cartridge at 85, 110 and 150 ^{o}C were 7 hours, 3 hours and 30 or 45 minutes, respectively. The optimum sampling time for spindle motor at 85, 110 and 150 ^{o}C were 7 hours, 5 or 7 hours and 60 or 90 minutes, respectively.

From this research, adsorbent which possesses high efficiency for the determination of VOCs from HDD was explored with the better understanding for the correct selection of an adsorbent. Moreover, the optimized thermal desorption could be indicated the effect of each parameter to the adsorption efficiency and could be supported as a guideline in future VOCs analysis.

For the future work, other adsorbents such as Carbosieve S-II and Carboxen-1000 (carbon molecular sieves for light hydrocarbons) or dual-sorbent such as Carbosieve S-II/Tenax TA or Carboxen-1000/Carbopack C with various ratios could be investigated for improving the adsorption efficiency and extending the VOCs application, especially for very low molecular weight compounds. Furthermore, small parts of HDD components such as bearing or stator assembly could be analyzed.

REFERENCES

1. IDEMA Standards Technical Committee Ballot Microcontamination Committee, “Effect of contamination in disk drive”, Document no.M3-98, **1999**, 1-4.
2. Balazs Analytical Laboratory, [On-line.] Available from: http://www.balazs.com/orgoutgasancomponts.html [2002, November.]
3. Poole, C.F. and Poole, S.K. “Chromatography today”, Elsevier, Amsterdam, The Netherlands, 1995.
4. Christian, G.D. and O’Reilly, J.E. 2nd edition. “Instrument analysis”, Allyn and Bacon, Inc, Singapore, 1998.
5. Davis, R. and Frearson, M. “Mass spectrometry analytical chemistry by open learning”, John Wiley & Sons, Singapore, November 1989.
6. “Hardware manual for HP5973 Mass Selective Detector”, Hewlette Packard, August 1998.
7. “Instrument manual headspace sampler (purge and trap) model JHS-100/JHS-100A”, Japan Analytical Industry Co.,Ltd, November 1995.
8. Manura, J.J., “Selection of thermal desorption and cryo-trap parameters in the analysis of teas.” [On-line.] Available from: http://www.sisweb.com [2002, September.]
9. Manura, J.J., “Comparison of sensitivity of headspace GC, purge and trap thermal desorption and direct thermal extraction techniques for volatile organics.” [On-line.] Available from: http://www.sisweb.com [2002, September.]
10. “Instrument manual curie point headspace sampler for purge and trap in GC”, Japan Analytical Industry Co.,Ltd, May 1994.
11. “Instrument manual curie point pyrolyzer JHP-3S”, Japan Analytical Industry Co., Ltd, May 1994.
12. Patrick, J.W. “Porosity in carbon: Characterization and application”, Edward Arnold, Great Britain, 1995.
13. Peters, R. and Bakkeren, H., “Sorbent in sampling ability and breakthrough measurement, **1994,** *119*, 71-74.
14. Griffith, M. and Hirst, W. “Ultra-fine structure of coals and cokes”

British Coal Utilis. Res. Assoc., London., **1944**, 80.

15. Butrym, E.D., “Analysis of silicone contaminants on electronic components by thermal desorption GC-MS.” [On-line.] Available from: http://www.sisweb.com [2000, April.]
16. Ghoshal, A.K. and Manjare, S.D. “Selection of appropriate adsorption technique for recovery of VOCs: analysis” *Journal of Loss Prevention in the process Industries,* **2002,** *15,* 413-421.
17. Mastrogiacomo, A.R., Pierini, E., Sampaolo, L. and Bruner, F. “Evaluation of new graphitized carbon black employed in sampling volatile organic compounds.” *J. Chromatogr. A*., **1998**, *810*, 131-139.
18. Sunesson, A.L., Nilsson, C.A. and Andersson, B. “Evaluation of adsorbents for sampling and quantitative analysis of microbial volatiles using thermal desorption-gas chromatography.” *J. Chromatogr. A*., **1995**, *699*, 203-214.
19. Wartelle, L.H., Marshall, W.E., Toles, C.A. and Johns, M.M. “Comparison of nutshell granular activated carbons to commercial adsorbents for the purge-and-trap gas chromatographic analysis of volatile organic compounds.” *J. Chromatogr. A*., **2000**, *879*, 169-175.
20. Clement, M., Arzel, S., Bot, B.L., Seux, R. and Millet, M. “Adsorption/thermal desorption-GCMS for the analysis of pesticides in the atmosphere.” *Chemosphere*., **2002**, *40*, 49-56.
21. Hollender, J., Sandner, F., Moller, M. and Dott, W. “Sensitive indoor air monitoring of monoterpenes using different adsorbents and thermal desorption gas chromatography with mass-selective detection.” *J. Chromatogr. A*., **2002**, *962*, 175-181.
22. Esteban, J.L., Castro, I.M. and Sanz, J. “Evaluation and optimization of the automatic thermal desorption method in the gas chromatographic determination of plant volatile compounds.” *J. Chromatogr. A*., **1993**, *657,* 155-164.
23. Holdren, M., Danhof, S., Grassi, M., Stets, J., Keigley, B. and Woodruff, V. “Development and evaluation of a thermoelectric cold trap for the gas chromatographic analysis of atmospheric compounds.” *Anal. Chem*., **1998**, *70,* 4836-4840.

24. Yamamoto, N., Matsubasa, T., Kumagai, N., Mori, S. and Suzuki, K. “A diffusive badge sampler for volatile organic compounds in ambient air and determination using a thermal desorption-GC/MS system.” *Anal. Chem.*, **2002**, *74,* 484-487.

25. Hallama, R.A., Rosenberg, E. and Grasserbauer, M. “Development and application of a thermal desorption method for the analysis of polar volatile organic compounds in workplace air” *J. Chromatogr. A.*, **1998**, *809,* 47-63.

26. Ehara, Y. and Sakamoto, K. “Purge-and-trap gas chromatography/mass spectrometry for the analysis of carboxylic acids by esterification” *Anal. Sci.*, **2000**, *16,* 283-286.

27. “Catalog for adsorbent and solid support”, Supelco Company, September, 2000.

28. Manura, J.J., “Hydrocarbon breakthrough volumes on Tenax TA.” [On-line.] Available from: http://www.sisweb.com [2002, September.]

29. “Characterization of sorbent resins for use in airborne environmental sampling”, US EPA Document no. 600/7-78-054, 1978.

30. Chan, L.Y., Lau, W.L., Wang, X.M. and Tang, J.H. “Preliminary measurement of aromatic VOCs in public transportation modes in Guangzhou, China” *Environmental International*, **2003**, *29*, 429-435.

31. Bertoni, G. and Tappa, R. “Improvement in breakthrough volume evaluation methods for light adsorbent traps employed for volatile organic compounds determination at atmospheric concentration levels” *J. Chromatogr. A.*, **1997**, *767*, 153-161.

32. Baraniecki, C.J.J., Riley, H.L. and Stretter, E. “Industrial carbon and graphite” *Soc. Chem. Ind., London.*, **1958**, 283.

33. “GC MSD Chemstation”, Agilent Technologies, December 2001.

34. IDEMA Standards Technical Committee Ballot Microcontamination Committee, “Materials used in hard disk drives”, Document no.M2-98, **1999**, 1-6.

APPENDICES

Appendix A.1 Physical property of Tenax TA

Properties

Name: 2,6-diphenylene-oxide polymer resin

Temperature limit: 350 °C

Affinity for water: low

Specific surface area: 35 sq. m/g

Pore volume: 2.4 mL/g

Average pore size: 200 nm

Density: 0.25 g/mL

Mesh size: 60/80 mesh

Major areas of application

Purge and trap of volatiles from water

Trapping volatiles from environmental air

Trapping of volatiles from human breath

Trapping flavors and fragrances from plants and commercial products

Trapping of volatiles from soil (PNA's and PCB's)

Personal exposure monitoring

Advantage for Tenax TA

Trap volatiles from air, liquids and solids

High temperature limit of 350 ^{o}C

Low affinity for water

Stable baseline after conditioning

Replaces Tenax GC

Appendix A.2 Physical property of Tenax GR

Properties

Name: 2,6-diphenylene-oxide polymer resin plus 30% graphite

Temperature limit: 350 ^{o}C

Affinity for water: low

Specific surface area: 24.1 sq. m/g

Pore volume: 2.4 mL/g

Average pore size: 200 nm

Density: 0.55 g/mL

Mesh size: 60/80 mesh

Major areas of application

Purge and trap of volatiles from water

Trapping volatiles from environmental air

Trapping volatiles from human breath

Trapping flavors and frangrances from plants and commercial products

Trapping of volatiles from soil (PNA's and PCB's)

Personal exposure monitoring

Advantage for Tenax GR

Trap volatiles from air, liquids and solids

High breakthrough volumes for low molecular weight volatiles

High temperature limit of 350 ^{o}C

Low affinity for water

Contains 30% graphite in Tenax

Superior trapping of volatiles

Appendix A.3 Physical property of Carbotrap

Properties

Name: graphitized carbon black

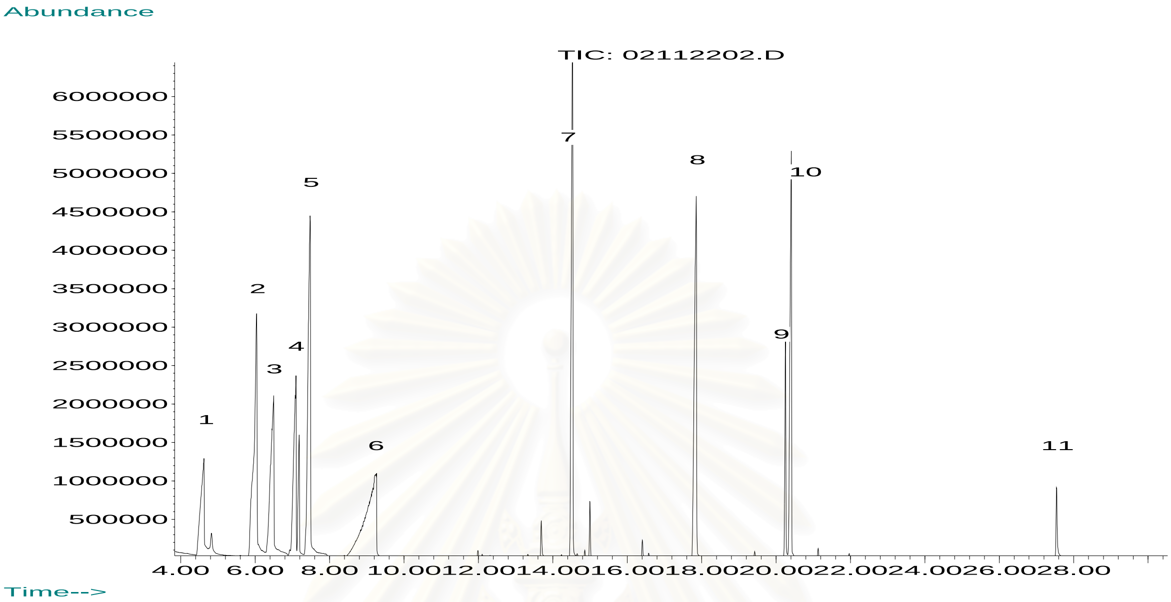
Temperature limit: 400 °C

Affinity for water: relatively low

Specific surface area: 100 square meter per gram

Mesh size: Depends on application

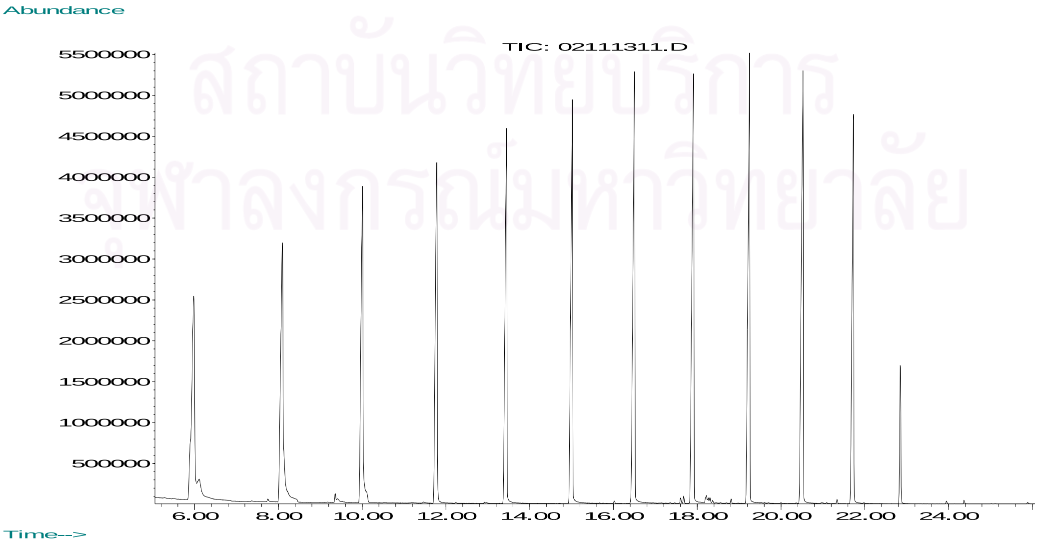
APPENDIX B.1 GC-MS chromatogram of mixed monomer



Remark:

Peak 1 = 2-HEA
Peak 2 = Decane
Peak 3 = HEMA
Peak 4 = HPMA
Peak 5 = AP
Peak 6 = EHA
Peak 7 = IBOMA
Peak 8 = CHAP
Peak 9 = TGDMA
Peak 10 = DMAP
Peak 11 = DOP

APPENDIX B.2 GC-MS chromatogram of mixed alkanes (C_{10} to C_{25})



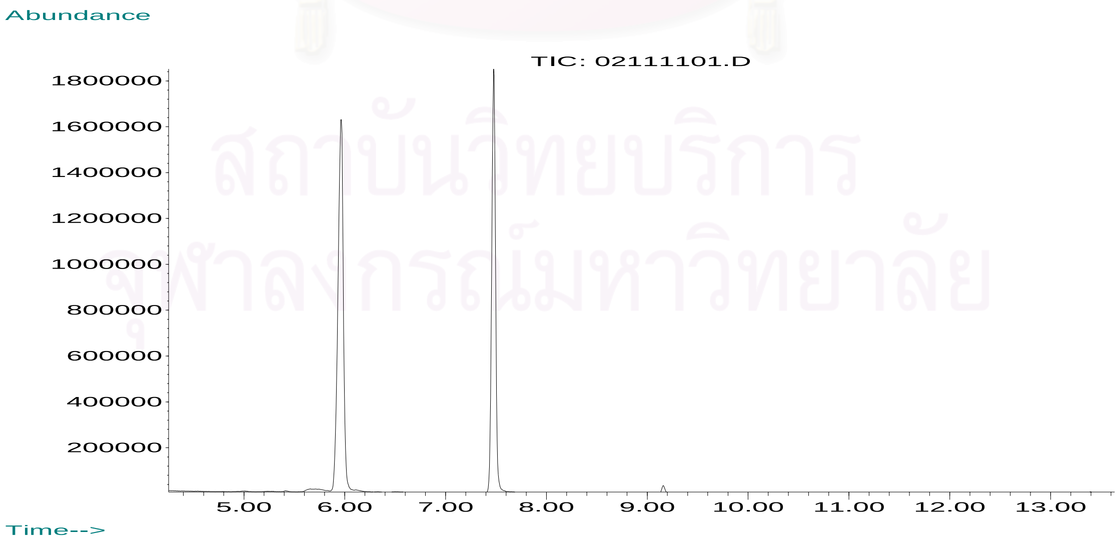
APPENDIX B.3 The calculation of VOCs amount

$$\text{Amount (ng)} = \frac{\text{peak area of compound x concentration of internal standard x C.F.}}{\text{peak area of internal standard}}$$

$$\text{Correction factor (C.F.)} = \frac{\text{real amount}}{\text{prepared amount}}$$

$$\text{VOCs amount (real samples)} = \frac{\text{peak area of compound x concentration of decane}}{\text{peak area of decane}}$$

APPENDIX B.4 GC-MS chromatogram of mixed siloxanes



APPENDIX C.1 Adsorption efficiency of six selected adsorbents upon the analysis of mixed monomers

Monomers	The amount of VOCs (ng)					
	Tenax TA	Tenax GR	Carbopack B	Carbopack C	Carbotrap B	Carbotrap C
2-HEA	798	675	523	781	586	771
HEMA	904	852	652	871	681	865
HPMA	901	923	726	907	719	908
AP	1,012	979	770	913	738	952
EHA	952	923	728	998	698	947
IBOMA	856	804	658	897	602	953
CHAP	926	847	580	921	526	837
TGDMA	698	671	458	721	398	684
DMAP	944	822	515	952	396	888
DOP	85	52	12	74	7	69

APPENDIX C.2 Adsorption efficiency of six selected adsorbents upon the analysis of mixed alkanes (C_{10} to C_{25})

Alkanes	The amount of VOCs (ng)					
	Tenax TA	Tenax GR	Carbopack B	Carbopack C	Carbotrap B	Carbotrap C
C_{10}	400	366	252	351	320	391
C_{11}	380	342	191	334	238	361
C_{12}	381	328	149	340	193	369
C_{13}	374	338	123	357	166	371
C_{14}	387	349	99	334	174	354
C_{15}	377	346	189	310	136	302
C_{16}	377	356	217	320	275	290
C_{17}	448	387	244	346	244	328
C_{18}	474	445	200	311	220	330
C_{19}	446	439	179	301	201	282
C_{20}	422	389	161	262	184	266
C_{21}	241	208	123	169	151	148
C_{22}	165	135	31	117	57	170
C_{23}	137	109	21	71	26	102
C_{24}	22	18	2	12	3	16
C_{25}	16	2	1	5	1	6

APPENDIX C.3 Adsorption efficiency of dual-sorbent upon the analysis of mixed alkanes (C_{10} to C_{25})

Alkanes	The amount of VOCs (ng)				
	Tenax TA	Carbopack C/B	Carbotrap C/B	Carbopack B/C	Carbotrap B/C
C_{10}	400	375	449	357	384
C_{11}	380	400	425	278	282
C_{12}	381	468	445	209	94
C_{13}	374	480	467	153	105
C_{14}	387	416	428	119	79
C_{15}	377	358	373	98	67
C_{16}	374	377	354	81	62
C_{17}	448	386	391	54	42
C_{18}	474	416	436	27	22
C_{19}	446	380	387	11	19
C_{20}	422	359	353	14	16
C_{21}	241	243	224	15	14
C_{22}	165	205	194	12	13
C_{23}	137	175	142	11	10
C_{24}	22	24	24	9	10
C_{25}	16	20	16	8	6

APPENDIX C.4 The effect of the amount of adsorbents on adsorption efficiency upon the analysis of mixed monomers

Monomers	The amount of VOCs (ng)			
	Tenax TA (small)	Tenax TA (large)	Tenax GR (small)	Tenax GR (large)
2-HEA	802	753	580	0
HEMA	884	893	750	0
HPMA	911	850	745	0
AP	760	732	741	528
EHA	994	923	509	342
IBOMA	843	857	581	5
CHAP	860	470	370	1
TGDMA	935	427	281	3
DMAP	703	57	307	2
DOP	194	187	94	1

APPENDIX C.5 The effect of the amount of adsorbents on adsorption efficiency upon the analysis of mixed alkanes (C_{10} to C_{25})

Alkanes	The amount of VOCs (ng)			
	Tenax TA (small)	Tenax TA (large)	Tenax GR (small)	Tenax GR (large)
C_{10}	437	496	419	257
C_{11}	410	504	384	198
C_{12}	421	486	409	182
C_{13}	405	448	400	162
C_{14}	405	414	411	155
C_{15}	420	431	425	78
C_{16}	390	356	346	170
C_{17}	359	306	318	97
C_{18}	375	262	341	18
C_{19}	476	351	471	10
C_{20}	475	360	454	3
C_{21}	495	176	145	2
C_{22}	346	14	3	0
C_{23}	109	0	0	5
C_{24}	8	0	8	0
C_{25}	13	0	13	0

APPENDIX C.6 The effect of purge and trap time on adsorption efficiency upon the analysis of mixed monomers

Monomers	The amount of VOCs (ng)				
	5 minutes	10 minutes	15 minutes	20 minutes	25 minutes
2-HEA	542	535	652	771	663
HEMA	779	812	864	874	827
HPMA	803	842	905	930	861
AP	739	968	991	1,012	976
EHA	599	560	947	976	907
IBOMA	762	817	888	894	866
CHAP	544	544	1,009	1,016	1,033
TGDMA	0	494	490	655	538
DMAP	74	169	1,022	1,016	1,021
DOP	3	49	201	91	21

APPENDIX C.7 The effect of purge and trap time on adsorption efficiency upon the analysis of mixed alkanes (C_{10} to C_{25})

Alkanes	The amount of VOCs (ng)					
	5 minutes	10 minutes	15 minutes	20 minutes	25 minutes	30 minutes
C_{10}	157	147	315	385	388	379
C_{11}	159	185	236	389	394	368
C_{12}	170	178	176	371	339	334
C_{13}	116	123	248	343	356	361
C_{14}	171	161	302	345	388	380
C_{15}	261	289	352	375	484	469
C_{16}	301	389	371	371	383	329
C_{17}	392	504	411	486	244	188
C_{18}	318	395	248	347	112	90
C_{19}	239	304	145	182	58	58
C_{20}	90	259	101	103	40	42
C_{21}	8	257	89	82	36	41
C_{22}	2	154	56	67	29	39
C_{23}	1	31	29	51	24	38
C_{24}	0	1	18	25	23	35
C_{25}	0	0	1	13	14	7

APPENDIX C.8 The effect of trapping temperature on adsorption efficiency upon the analysis of mixed monomers

Monomers	The amount of VOCs (ng)				
	20 ^oC	0 ^oC	-20 ^oC	-40 ^oC	-60 ^oC
2-HEA	198	375	523	781	798
HEMA	104	532	652	871	904
HPMA	151	623	726	907	901
AP	202	592	770	913	1,013
EHA	152	603	728	998	952
IBOMA	126	504	658	897	856
CHAP	75	447	581	841	926
TGDMA	98	371	458	721	698
DMAP	44	447	515	877	944
DOP	1	7	12	74	85

APPENDIX C.9 The effect of trapping temperature on adsorption efficiency upon the analysis of mixed alkanes (C_{10} to C_{25})

Alkanes	The amount of VOCs (ng)				
	20 °C	0 °C	-20 °C	-40 °C	-60 °C
C_{10}	66	145	312	381	384
C_{11}	69	183	233	384	390
C_{12}	79	176	174	336	367
C_{13}	61	122	246	339	357
C_{14}	80	159	299	341	384
C_{15}	80	286	348	371	479
C_{16}	57	364	367	367	378
C_{17}	31	241	407	481	499
C_{18}	47	110	246	344	391
C_{19}	58	57	143	224	301
C_{20}	18	39	100	173	256
C_{21}	7	32	79	162	229
C_{22}	2	29	56	107	154
C_{23}	1	12	29	41	51
C_{24}	0	5	18	22	23
C_{25}	0	0	1	13	14

APPENDIX C.10 The effect of desorption temperature on adsorption efficiency upon the analysis of mixed monomers

Monomers	The amount of VOCs (ng)		
	255 °C	315 °C	358 °C
2-HEA	776	781	798
HEMA	899	901	904
HPMA	892	907	901
AP	998	1,003	1,013
EHA	948	968	952
IBOMA	839	847	856
CHAP	919	921	926
TGDMA	693	701	698
DMAP	936	952	944
DOP	71	79	85

APPENDIX C.11 The effect of desorption temperature on adsorption efficiency upon the analysis of mixed alkanes (C_{10} to C_{25})

Alkanes	The amount of VOCs (ng)		
	255 °C	315 °C	358 °C
C_{10}	415	428	431
C_{11}	423	432	438
C_{12}	388	398	400
C_{13}	378	395	401
C_{14}	419	423	431
C_{15}	471	479	495
C_{16}	409	412	425
C_{17}	286	290	271
C_{18}	375	386	375
C_{19}	197	202	204
C_{20}	109	114	144
C_{21}	39	45	36
C_{22}	25	30	29
C_{23}	29	34	24
C_{24}	19	25	23
C_{25}	12	13	14

APPENDIX C.12 The effect of desorption time on adsorption efficiency upon the analysis of mixed monomers

Monomers	The amount of VOCs (ng)			
	5 seconds	10 seconds	20 seconds	25 seconds
2-HEA	476	681	798	786
HEMA	699	801	904	897
HPMA	592	707	901	895
AP	458	823	1,013	1,012
EHA	548	768	952	965
IBOMA	439	647	856	865
CHAP	439	761	926	931
TGDMA	393	601	698	689
DMAP	411	727	944	949
DOP	41	59	85	90

APPENDIX C.13 The effect of desorption time on adsorption efficiency upon the analysis of mixed alkanes (C_{10} to C_{25})

Alkanes	The amount of VOCs (ng)			
	5 seconds	10 seconds	20 seconds	25 seconds
C_{10}	215	328	431	441
C_{11}	223	332	438	432
C_{12}	188	308	400	410
C_{13}	178	305	401	411
C_{14}	219	323	431	425
C_{15}	312	421	495	505
C_{16}	209	312	425	420
C_{17}	186	200	271	276
C_{18}	205	286	375	385
C_{19}	97	102	204	214
C_{20}	69	74	144	134
C_{21}	29	35	36	34
C_{22}	15	20	29	31
C_{23}	19	24	24	26
C_{24}	9	15	23	21
C_{25}	3	9	14	12

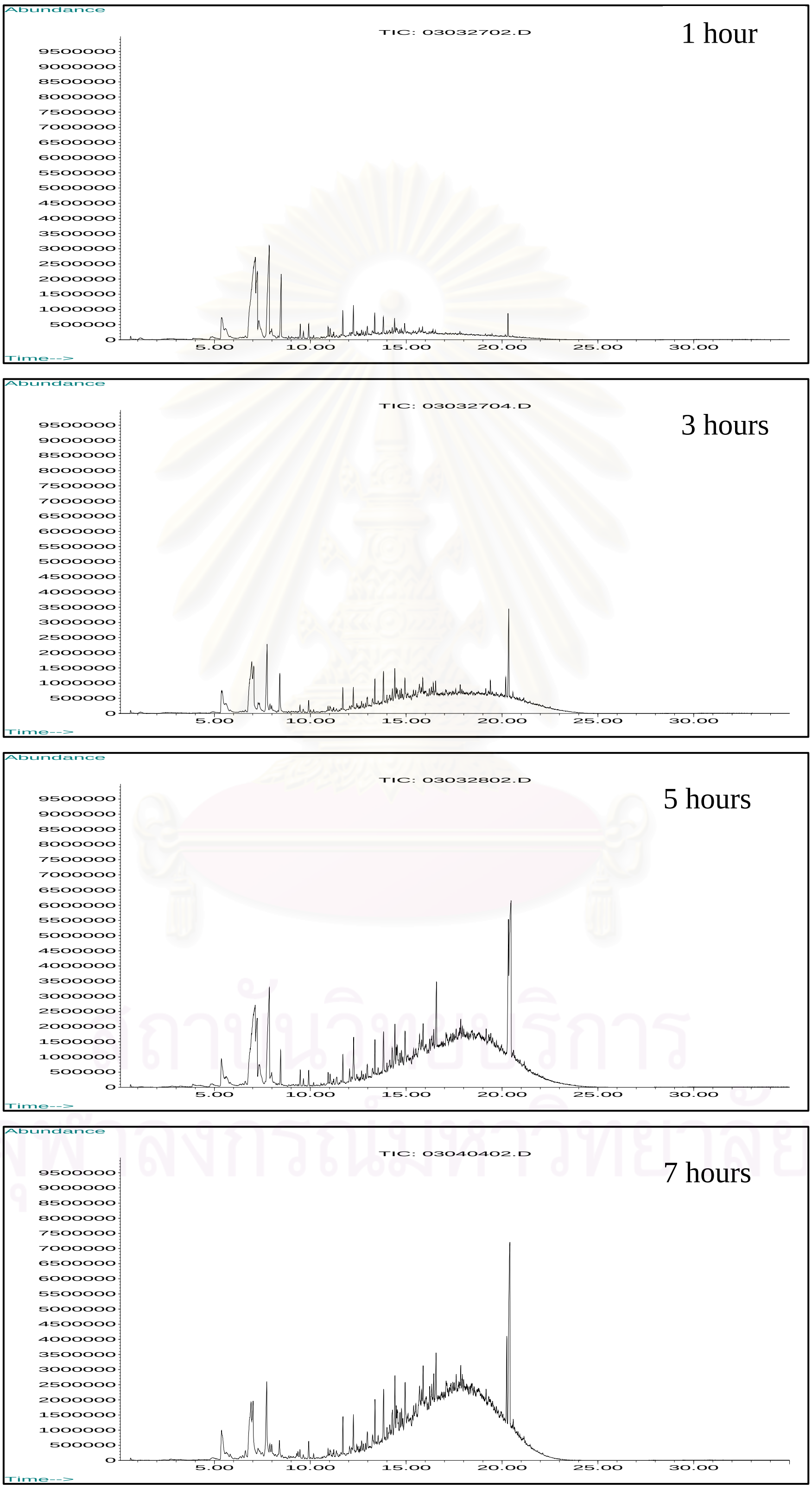
APPENDIX C.14 The effect of secondary adsorption material on adsorption efficiency upon the analysis of mixed monomers

Monomers	The amount of VOCs (ng)		
	Tenax TA	glass wool	Carbopack C
2-HEA	798	678	774
HEMA	904	891	923
HPMA	901	924	893
AP	1,013	1,037	941
EHA	952	921	876
IBOMA	856	837	764
CHAP	926	1,028	834
TGDMA	698	865	672
DMAP	944	1,039	821
DOP	85	249	64

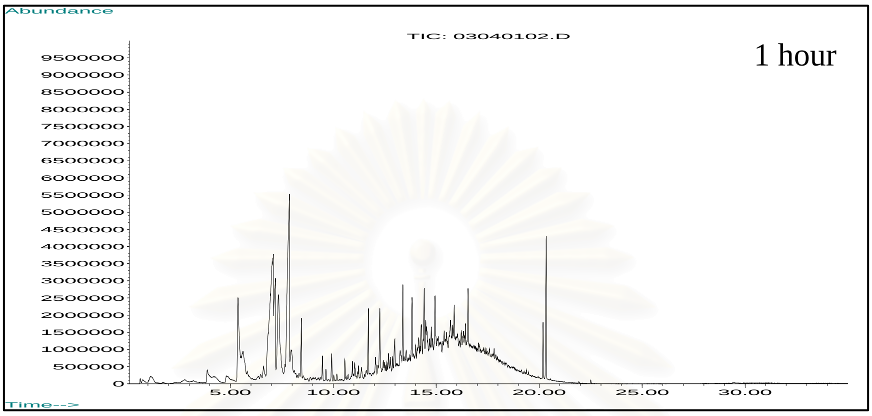
APPENDIX C.15 The effect of secondary adsorption material on adsorption efficiency upon the analysis of mixed alkanes (C_{10} to C_{25})

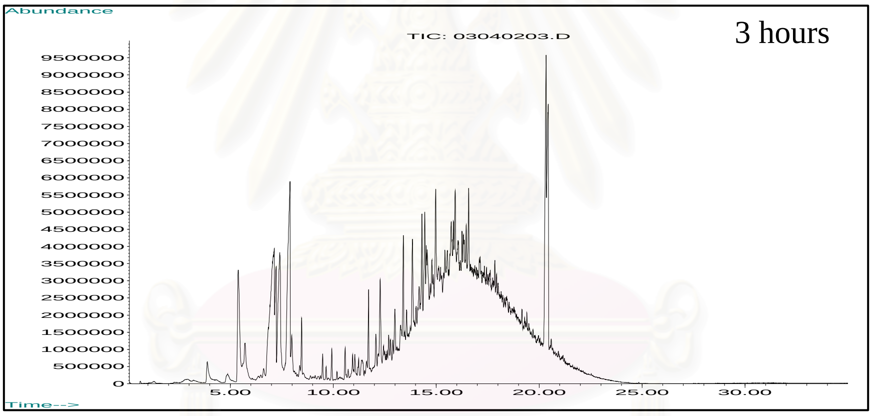
Alkanes	The amount of VOCs (ng)		
	Tenax TA	glass wool	Carbopack C
C_{10}	424	356	393
C_{11}	402	362	347
C_{12}	403	373	349
C_{13}	396	365	330
C_{14}	410	338	310
C_{15}	400	318	334
C_{16}	399	297	355
C_{17}	474	347	414
C_{18}	502	359	441
C_{19}	473	382	389
C_{20}	447	401	374
C_{21}	212	354	197
C_{22}	165	364	148
C_{23}	137	289	97
C_{24}	22	138	22
C_{25}	16	65	16

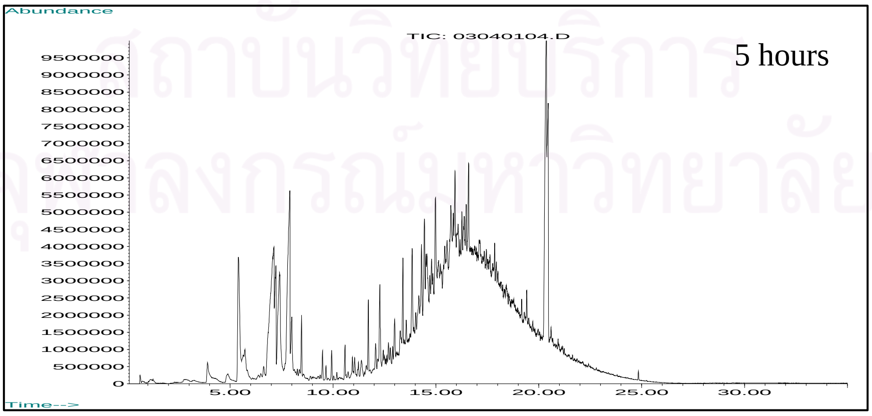
APPENDIX D.1 GC-MS chromatograms of pivot cartridge at 85 ^{o}C for 1, 3, 5 and 7 hours



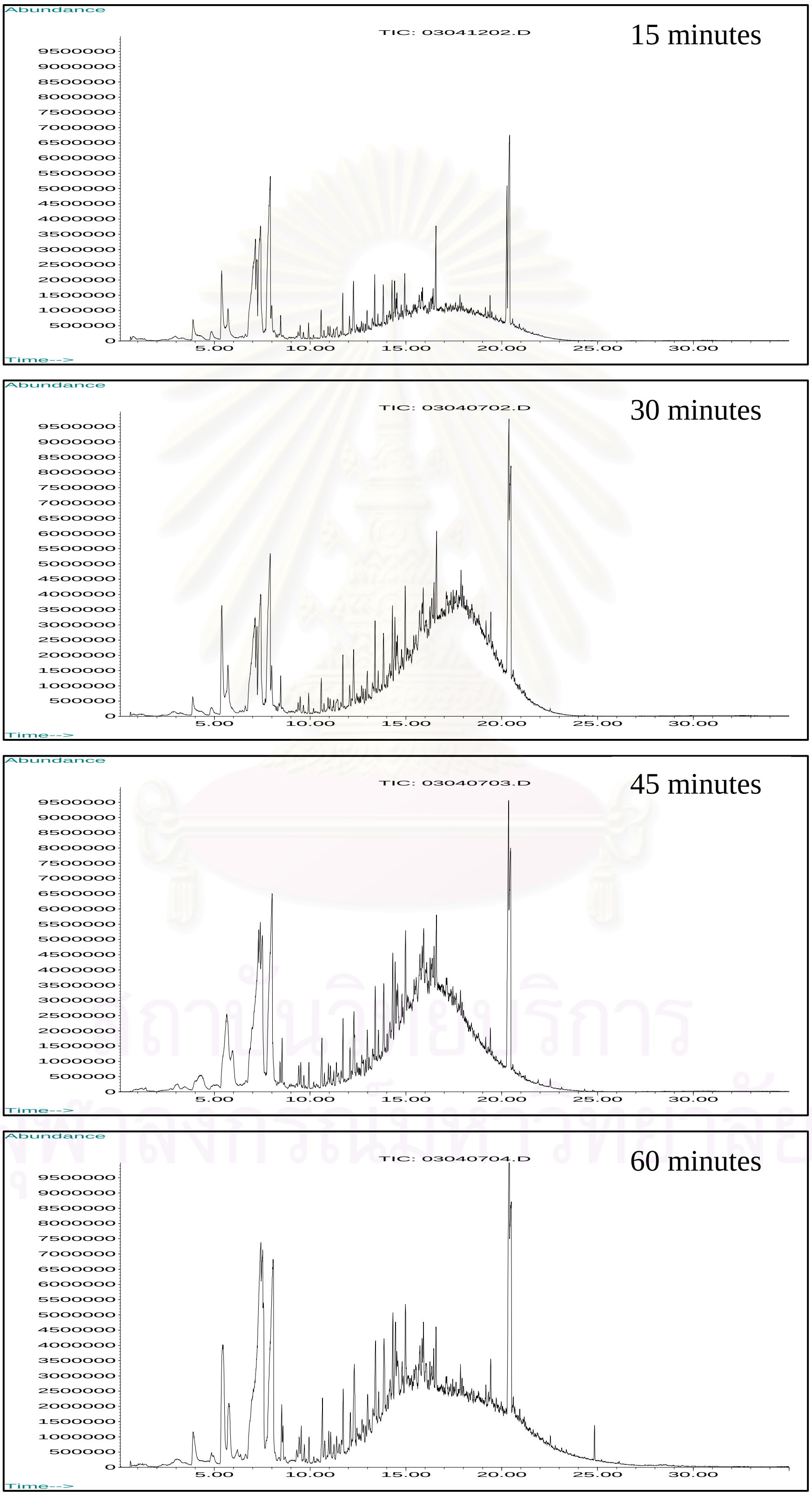
APPENDIX D.2 GC-MS chromatograms of pivot cartridge at 110 ^{o}C for 1, 3 and 5 hours


1 hour

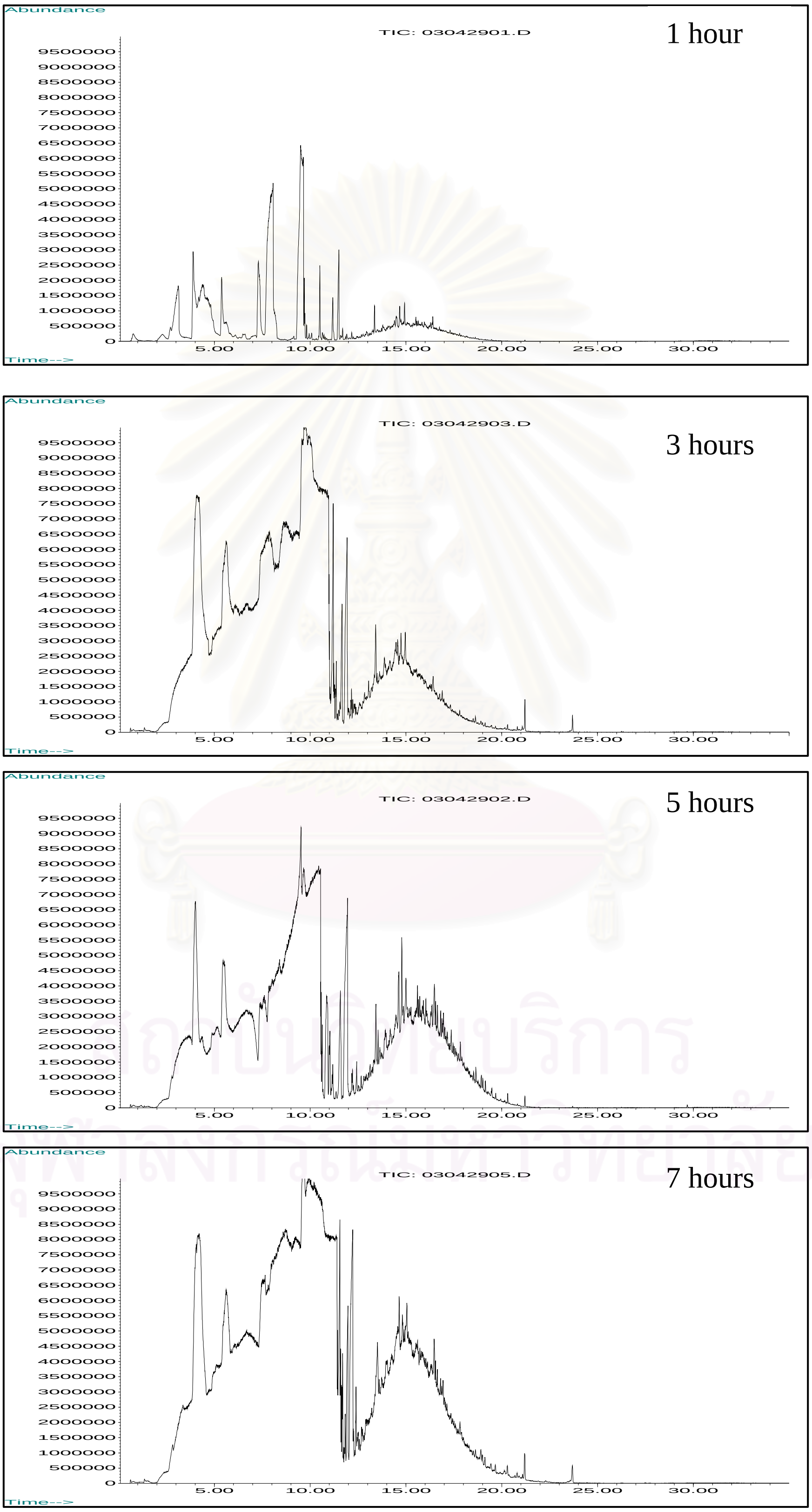

3 hours


5 hours

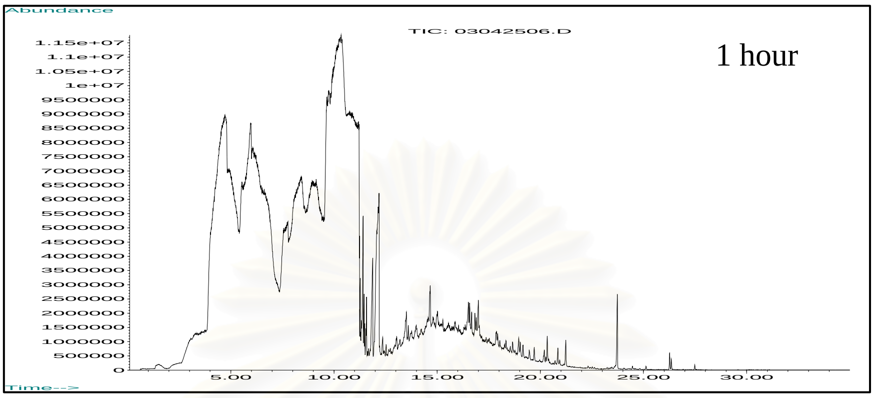
APPENDIX D.3 GC-MS chromatograms of pivot cartridge at 150 ^{o}C for 15, 30, 45 and 60 minutes

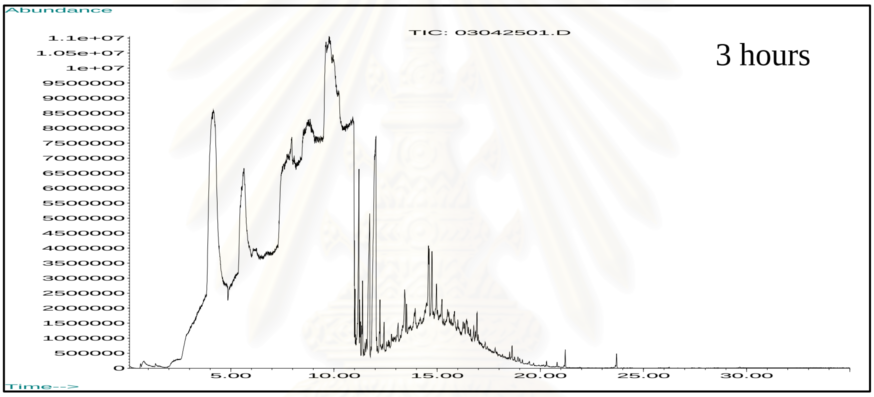


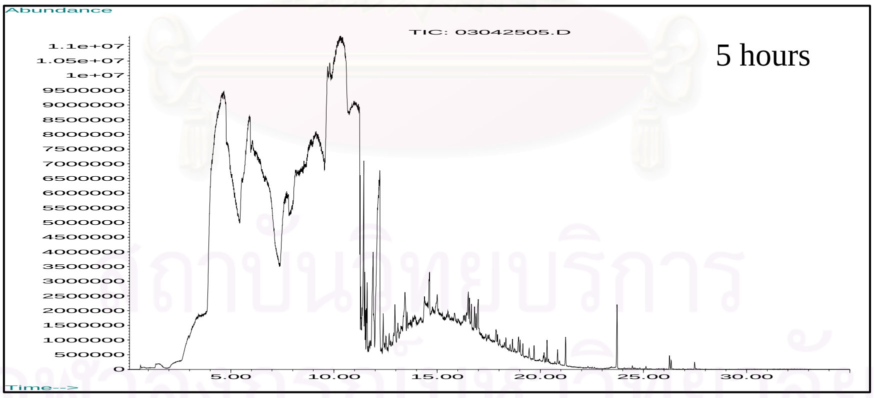
APPENDIX D.4 GC-MS chromatograms of spindle motor at 85 ^{o}C for 1, 3, 5 and 7 hours

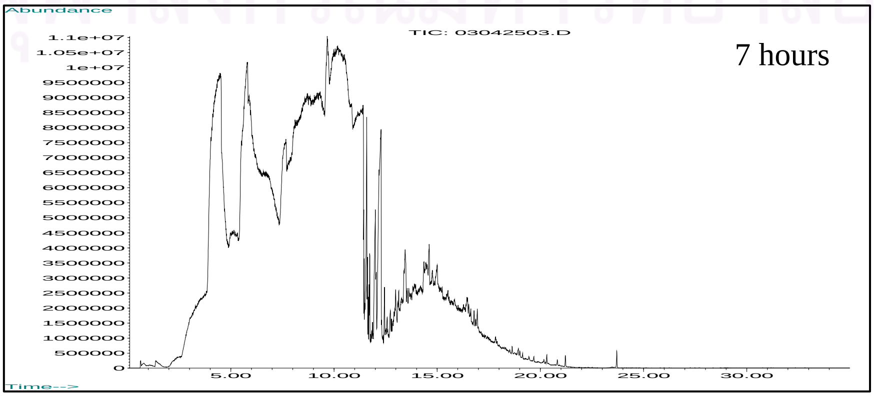


APPENDIX D.5 GC-MS chromatograms of spindle motor at 110 ^{o}C for 1, 3, 5 and 7 hours

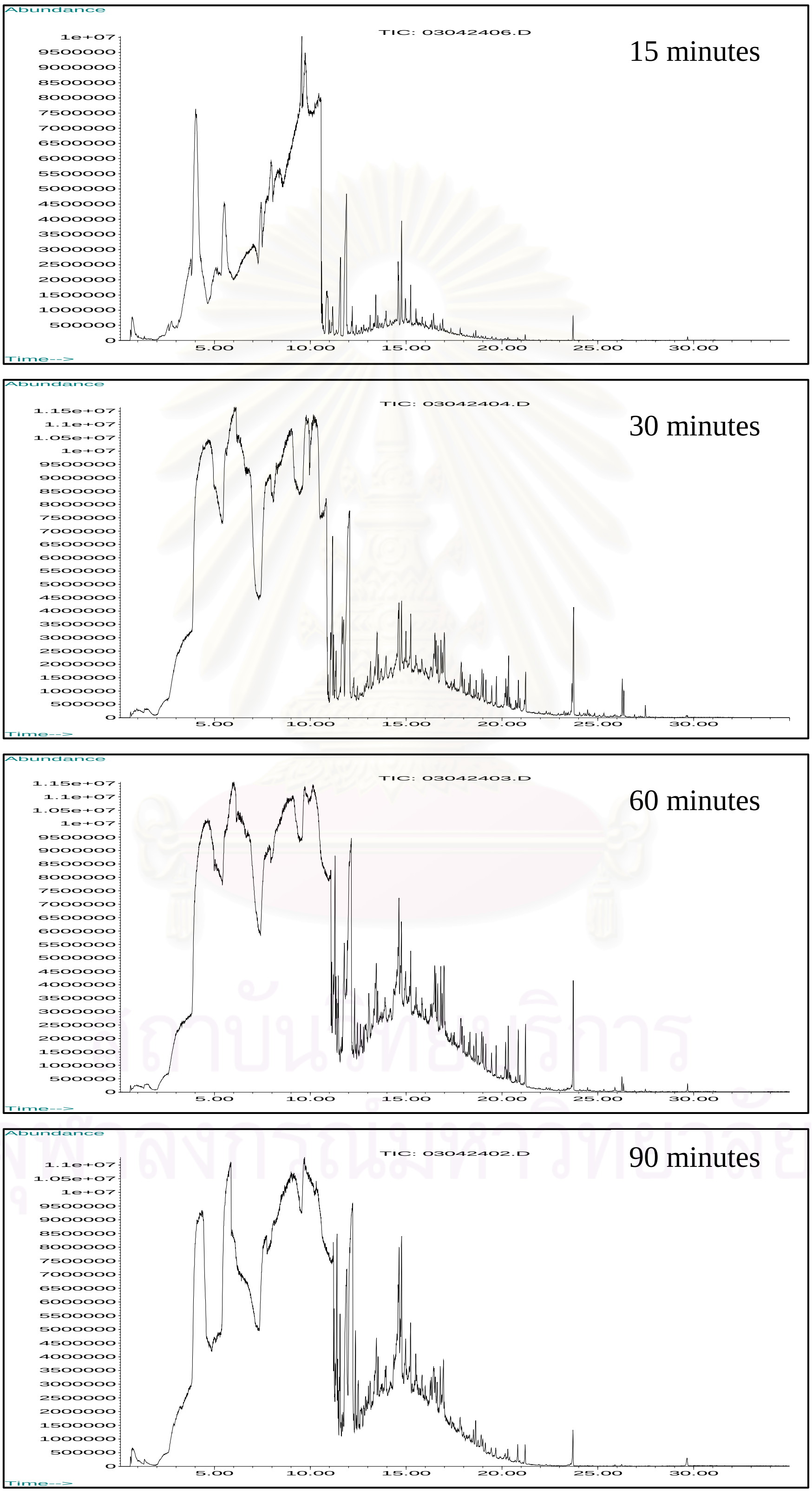








APPENDIX D.6 GC-MS chromatograms of spindle motor at 150 ^{o}C for 15, 30, 60 and 90 minutes



VITA

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