Analysis of Methyl Tertiary Butyl Ether (MTBE)
in Air Sample by Gas Chromatography

Khwanlak Chongkraijak
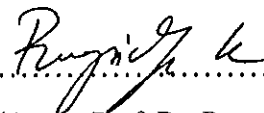
Master of Science Thesis in Analytical Chemistry
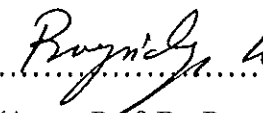
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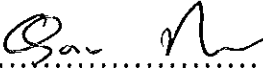
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The Graduate School, Prince of Songkla University, has approved this thesis as partial fulfillment of the requirement for the Master of Science degree in Analytical Chemistry.

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(2)

ชื่อวิทยานิพนธ์	วิเคราะห์สารประกอบเมธิลเทอเทียรี่บิวทิลอีเทอร์ในตัวอย่างอากาศ
	โดยเทคนิคก๊าซโครมาโทกราฟฟี
ผู้เขียน	นางสาวขวัญลักษณ์ จงไกรจักร
สาขาวิชา	เคมีวิเคราะห์
ปีการศึกษา	2545

บทคัดย่อ

พัฒนาวิธีวิเคราะห์เชิงคุณภาพและปริมาณของสารเมธิลเทอเทียรี่บิวทิลอีเทอร์ (เอ็มทีบีอี) ปริมาณน้อยในอากาศด้วยเทคนิคแก๊ส-โซลิดโครมาโทกราฟฟีโดยใช้ตัวตรวจวัดชนิดเฟลมไอออไนเซชัน คอลัมน์แก้วขนาดเส้นผ่านศูนย์กลางภายใน 2.5 มิลลิเมตร ยาว 2.1 เมตร ภายในบรรจุด้วยสเตชันนารีเฟสคือ Super Q ขนาด 80/100 เมช ร่วมกับเทคนิคเฮดสเปซ จากการศึกษาพบว่าสภาวะที่เหมาะสมสำหรับการวิเคราะห์เอ็มทีบีอี คือ อัตราการไหลของแก๊สพา (ไนโตรเจน) 20 มิลลิลิตรต่อนาที อุณหภูมิคอลัมน์ 220 องศาเซลเซียส อุณหภูมิหัวฉีดและตัวตรวจวัด 220 องศาเซลเซียส อุณหภูมิที่ทำให้ตัวอย่างเข้าสู่สมดุล 70 องศาเซลเซียส โดยใช้เวลา 20 นาที อัตราส่วนเฟส 0.5 และขนาดขวดบรรจุตัวอย่าง 10 มิลลิลิตร จากสภาวะที่เหมาะสมดังกล่าว สามารถตรวจวัดสารเอ็มทีบีอีได้ต่ำถึง 3.36 ไมโครกรัมต่อมิลลิลิตร โดยให้ช่วงการตอบสนองเชิงเส้นตั้งแต่ 2 ไมโครกรัมต่อมิลลิลิตร ถึง 1000 ไมโครกรัมต่อมิลลิลิตร ด้วยค่าสหสัมพันธ์ของความเป็นเส้นตรงมากกว่า 0.999 และให้ความแม่นยำสูงโดยมีค่าเบี่ยงเบนมาตรฐานสัมพัทธ์น้อยกว่า 4%

การเพิ่มความเข้มข้นของตัวอย่างประกอบด้วยการใช้หลอดบรรจุตัวดูดซับ (Chromosorb 106 ขนาด 60/80 เมช) ตามด้วยการคายการดูดซับด้วยความร้อน โดยขั้นตอนทั้งหมดทำการศึกษาด้วยอุปกรณ์ที่ประดิษฐ์ขึ้นภายในห้องปฏิบัติการซึ่งมีราคาถูกและไม่ซับซ้อน อัตราเร็วที่เหมาะสมในการดูดตัวอย่างอากาศผ่านหลอดบรรจุตัวดูดซับคือ 100.0 มิลลิลิตรต่อนาที มีค่า Breakthrough volume (BTV) 22 ลิตรต่อตัวดูดซับ 100 มิลลิกรัม สำหรับกระบวนการคายการดูดซับด้วยความร้อนใช้อุณหภูมิที่เหมาะสมคือ 200 องศาเซลเซียส ด้วยอัตราไหล 50 มิลลิลิตรต่อนาทีเป็นเวลา 20 นาที จากนั้นให้ความร้อนแก่ขวดเก็บสารที่ได้จากการคายการดูดซับที่อุณหภูมิ 70 องศาเซลเซียส เป็นเวลา 20 นาที ผลจากการวิเคราะห์ปริมาณสารเอ็มทีบีอีจากตัวอย่างอากาศบริเวณสถานีบริการน้ำมัน 3 แห่งในเขตอำเภอหาดใหญ่ จังหวัดสงขลา ด้วยเทคนิคที่พัฒนาขึ้น พบว่ามีสารเอ็มทีบีอีปนเปื้อนอยู่บริเวณสถานีบริการน้ำมันทั้งสามแห่งโดยตรวจพบอยู่ในช่วง

ความเข้มข้นตั้งแต่ 0.36 มิลลิกรัมต่อลูกบาศก์เมตรจนถึง 1.63 มิลลิกรัมต่อลูกบาศก์เมตรซึ่งมีความ
สัมพันธ์โดยตรงกับจำนวนรถที่มาใช้บริการ

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Author   Miss Khwanlak Chongkraijak

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ABSTRACT

A method for the qualitative and quantitative analysis of trace Methyl Tertiary Butyl Ether (MTBE) in air was developed. This was based on a gas chromatograph equipped with a 2.1 m × 2.5 mm ID., packed glass column, Super Q, 80/100 mesh and flame ionization detector couple with headspace technique. All of the gas chromatography and headspace parameters were optimized and the optimum conditions were obtained, *i.e.* flow rate of nitrogen carrier gas 20 ml/min, column temperature 220°C (isothermal), injector/detector temperature 220°C, equilibration temperature 70°C, equilibration time 20 minutes, phase ratio 0.5, and vial volume 10 ml. The low detection limit (3.36 μg ml^{-1}) and the wide linear dynamic range (2-1000 μg ml^{-1}) with a linear regression (R^2) of more than 0.999 and the relative standard deviation (% RSD) lower than 4% were obtained from these optimum conditions.

Preconcentration was done by active sampling using adsorbent (Chromosorb 106, 60/80 mesh) tube followed by thermal desorption technique. All procedures were carried out by the simple and low cost lab-built systems. The breakthrough volume of the adsorbent was 22 L/100 mg Chromosorb 106 and the optimum adsorpsion flow rate was 100 ml/min. In thermal desorption process, the adsorption tube was desorbed into the collection vial at 200°C for 20 minutes with a desorption flow rate of 50 ml/min. The collection vial was then heated at 70°C for 20 minutes. Air samples collected from three gas stations in Hat Yai, Songkhla were analyzed using this developed method. The

results showed that all areas were contaminated with MTBE in the range from 0.36 mg/m^3 to 1.63 mg/m^3. These values were directly correlated to the number of refueling vehicles.

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Chapter 1

Introduction

1.1 Introduction

During the past decades, the contamination of volatile organic compounds (VOCs) in the environment has become one of the most important problem because many VOCs are either toxic or carcinogenic and exposure to these compounds through diet and inhalation could cause serious effects in human health. Since several industries and human activities, mainly as petrol exhaust and evaporation, produce and release VOCs and this has led to ubiquitous presence of VOCs in air, water, food, and others.

One of the most concerned VOCs over recent years was Methyl *tertiary*-Butyl Ether (MTBE). MTBE was widely used as an octane booster in gasoline and recent monitoring results showed that various environmental compartments were contaminated with MTBE (Hellen *et al.*, 2002, Borden *et al.*, 2002 and Mancini *et al.*, 2002). The toxicity and concentration of MTBE has been investigated by several authors (Vainiotalo *et al*, 1998 and Nihlen *et al*, 1998) and it was known to be an animal carcinogen and possibly a human carcinogen (Nihlen *et al*, 1998). However, there are few data available of its environmental levels and human exposure.

MTBE is the most widely used oxygen-contain, *i.e.* oxygenates, compounds because of its low cost, ease of production, favorable transfer and blending characteristics (Squillace *et al.*, 1999). The addition of MTBE to gasoline reduces motor vehicle exhaust emission of carbon monoxide (CO) and increase the octane rating (Lee and Jo, 2002). This compound was first added to gasoline in the late 1970s, to maintain octane levels with the phase-out of the alkyl lead additives. In 1990, the demand for MTBE has increased rapidly due to the regulation of US Clean Air Act, which required a minimum oxygen

content of 2.7% (w/w) for oxyfuel and 2.0% (w/w) for reformulated gasoline in CO and ozone non-attainment areas, respectively (Schmidt *et al.*, 2001). Therefore, approximate 36% of all gasoline currently sold in the US contain oxygenates, and 85% of those used MTBE at 11-15 vol % (Vance, 2002 and Werner *et al.*, 2001).

Because the main use of MTBE is an additive to gasoline, MTBE could enter the environment during all phases of petroleum fuel cycle such as releases from storage tanks, vehicular emissions and evaporation losses from gasoline station and vehicle (Squillace *et al.*, 1999). Also for a short time during refueling, MTBE can easily be released due to the extremely high levels of gasoline vapors and many people such as gas station attendants and general public could be exposed to MTBE from this source. Moreover, consumers in some areas where oxygenated gasoline is used, have complained about acute health symptoms such as headache, eye and nose irritation, cough, nausea, dizziness and disorientation (Squillace *et al.*, 1999). In these cases the gas stations have been perceived to be the major emission source. Therefore, the ambient concentration of MTBE that has been released from refueling at gas stations is the most concerned.

The analysis of VOCs concentration in ambient air normally range from hundreds of ppb (v/v) to tens of ppt (v/v) (Wang *et al.*, 1999) and this required the preconcentration step to improve the analytical detection limit, reduce matrix effects and enhance the accuracy of the results and facilitates calibration. However, before the preconcentration step, the sample collection or sampling must first be carried out. Previously, the sampling was done by collecting the air sample in a defined volume container, made from steel, glass or with flexible plastic bags (made of PVC, polyethylene, etc.) and concentrated it in the laboratory. This method was successfully used for collecting the whole air sample with a large number of compounds (mainly volatile of low polarity) (Namiesnik, 1988). But there are many disadvantages

i.e. it is costly, must extensively clean the container after each use, and has limited sample volume (Kebbekus and Mitra, 1998). The sample collected in this way could also be changed by the adsorption of the container walls, or by some chemical reactions, which makes the method impossible to be used for compounds of low volatility or high polarity.

To overcome these problems, the collection and preconcentration on solid sorbent has been extensively developed and found in many applications. Sampling of VOCs with solid sorbent was achieved by either active (pumped) or passive (diffusive) sampling (Periago *et al.*, 1997, Gautrois and Koppmann, 1999, Prado *et al.*, 1996) and this could be done directly at the sampling site. The passive sampling technique utilizes diffusion of compounds into a chamber that contain solid sorbent. The diffusion of organic vapors from the environment to the sorbent occurs according to Fick's first law of diffusion (Harper, 2000). Meanwhile, active sampling utilizes volumetric pumps to draw a known volume of air through a bed of solid sorbent (Patil and Lonkar, 1994).

For quantitative determination, the analytes that adsorbed on a solid sorbent must be completely desorbed. Solvent extraction and thermal desorption could be used for this purpose. The choice of method depended on the sorbent material, the sampler design and the analytical task. In solvent desorption, the adsorbed analytes were extracted into the suitable solvent and then analyzed by the analytical technique. This was a simple and less expensive technique than thermal desorption, and it was used for the thermally unstable analytes, or those strongly adsorbed to the surface of the adsorbent (trap material) and have high concentrations in the samples (Kebbekus and Mitra, 1998). A solvent that is suitable for desorption must not interfere with the interest analyte(s). However, the use of solvent for desorption has several disadvantages such as the use of toxic solvent, provide less sensitivity, could have the interference from the solvent, the sorbent must be regenerated before

further used and the solvent desorption is not suitable for automation (Hallama *et al.*, 1998).

For the thermal desorption technique, the equipment is commercial available. It is designed to desorbed the analyte from the sorbent trap by heating and uses gas flushing to condense the sample plug into a small volume, and to inject the plug onto the head of the column (Kebbekus and Mitra, 1998). This technique has many advantages over solvent desorption such as higher sensitivity, lower detection limit because of the entire amount of preconcentrated material could be recovered for determination, eliminated of the toxic solvent (*i.e.*, carbon disulfide), and potential to automation (Hallama *et al.*, 1998).

A rather new approach for air analysis was to use Solid Phase Microextraction (SPME) as a passive sampler (Namiesnik *et al.*, 2000 and Koziel *et al.*, 1999). SPME has many advantages over previous methods *i.e.* combined sampling and preconcentration, and the ease of transferring the analytes into a gas chromatograph (Koziel *et al.*, 2000). However, SPME is generally an expensive technique.

To quantitatively determine VOCs concentrations in air, Gas Chromatographic technique is particularly well suited for this purpose. Since this technique is the most powerful chromatographic technique combining unsurpassed separation power with extremely low detectability to provide high accuracy and sensitivity and there are many applications of Gas Chromatography technique for monitored VOCs in air (Wang *et al.*, 1999). Therefore, the combination of active sampling, thermal desorption with gas chromatographic technique to monitor VOCs concentration in air would provide a fast, high sensitivity and low detection limit technique that is suitable to analyze trace VOCs in air sample.

The aim of this work is to develop a technique that would provide better accuracy, precision, simplicity and lower cost for the analysis of MTBE in air.

This thesis emphasizes on trace analysis of MTBE in air by Gas Chromatographic technique with flame ionization detector. The sample preconcentration was done by solid sorbent and desorbed by thermal desorption technique.

1.2 Background

1.2.1 Chemical formula and chemical structure

The chemical formula of MTBE is $C_5H_{12}O$ and the chemical structure is shown in Figure 1.

$$CH_3-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$
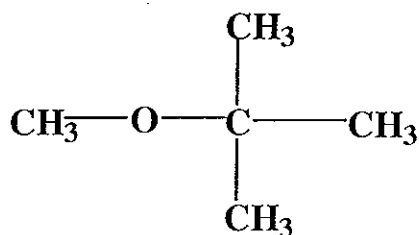
Figure 1 Chemical structure of Methyl *tertiary*-Butyl Ether (MTBE)

1.2.2 Common name and synonyms

The common name of MTBE is Methyl *tertiary*-Butyl Ether (MTBE) and the synonyms of MTBE are 2-methoxy-2-methyl-propane, 1,1-dimethylethyl methyl ether, ether *tert*-butyl methyl, methyl 1,1-dimethylethyl ether, methyl-*t*-butyl ether.

1.2.3 Physical properties

MTBE is volatile, colorless, liquid at room temperature and is flammable when exposed to heat or flame. It is not known to occur in the environment. Industrially, it derived from the catalytic reaction of isobutylene and methanol. MTBE is unstable in acid solution and is irritating fumes when heated to decomposition. The smell is like ethers and turpentine and has a low odor threshold. MTBE is miscible with gasoline and soluble in water, alcohol, and other ethers (TACI, 1997). The physical properties of MTBE are shown in Table 1.

Table 1 The physical properties of MTBE

Physical state	Value
Molecular weight	88.15 g/mol
Boiling point	55.2°C
Melting point	-109.0°C
Flash point	-28.0°C
Autoignition temperature	435°C
Density/Specific gravity	0.7404 g/cm^3 at 20°C
Vapor pressure	245 mm Hg at 25°C
Henry's law constant	5.87 x 10^{-4} atm-m^3/mol
Log octanol/water partition coefficient	1.24

Source: International Programme on Chemical Safety, 1998.

1.2.4 Applications

The main used of MTBE is an additive for gasoline (Squillace *et al.*, 1999). MTBE was first used in gasoline at low level in the late 1970s as an octane booster to replace lead, and this use continues. Since 1992, MTBE has been used at higher concentrations in some gasoline to fulfill the oxygenate

requirements mandated by the United States of America Congress in the 1990 Clean Air Act Amendment. The result from many studies indicated that, when compared to other gasoline, MTBE gasoline blends generally reduce CO and hydrocarbon exhaust emissions (Hallama *et al.*, 1998).

For *in vivo*, MTBE is used to dissolute of cholesterol gallstones in human (Squillace *et al.*, 1999).

1.3 Literature Review

The analytical method to investigate VOCs concentration in ambient air by gas chromatographic technique (GC) has been widely reported. The difference between each method was the factors that influence the analysis such as the types of column and detector. Appropriate gas chromatographic conditions give a highly sensitive to VOCs and good precision including a wide linear range. Normally the VOCs in the air sample have low level, therefore in all cases, preconcentration steps are mostly required.

Bellar *et al.* (1963) reported the determination of atmospheric pollutants in part per billion (ppb) range with gas chromatographic technique equipped with flame ionization detector. To extend the sensitivity range of flame ionization detector, the concentrating method was designed by attaching a trap (packed with 10% Carbowax on firebrick 50/60 mesh) to the gas sampling and the sample was drawn through the trap by a pump. The trap was then cooled with liquid nitrogen to condense the sample. The trapped sample was desorbed by removing the liquid nitrogen and replaced by hot water. The sample was injected into a GC by flushing with carrier gas. This system provided an efficient method of trace analysis of the atmospheric hydrocarbons in the 0.1 ppb level. This type of preconcentration method that included cryofocusing step has been used widely and was further developed by many authors because of no adsorbent is needed and allows desorption at moderate temperatures (40-

70°C), thus minimized interferences from the thermal degradation step (Park *et al*, 1998). Another example is the determination of 52 VOCs, including alkanes, alkenes, aromatics and terpenes, in ambient air by combined canister-based sampling technique with solid adsorbents (Tolnai *et al*. 2000). This was achieved by using a stainless steel canister to collect 800 ml of air samples and trapped the VOCs (analytes) on solid sorbents. A multibed adsorbent tube was used to trap the wide range of VOCs. The adsorbents included Carbosieve S-III 60/80 mesh Carbon Molecular Sieve (for small airborne molecules, such as C_2-C_4 hydrocarbons), Carbotrap 20/40 mesh Graphitized Carbon Black (for C_5-C_9 compounds), and Carbotrap C 20/40 mesh Graphitized Carbon Black (for relative high molecular weight airborned contaminants). After being trapped by the adsorbents, the analytes were thermally desorbed and the organic components were cryofocused before the gas chromatographic separation. The analysis was carried out by a GC coupled to an Automatic Thermal Desorption unit (ATD). The GC column was Permabond OV-624-DF, equipped with mass spectrometer. The system was suitable for determination of low pptv-concentrations of VOCs. The system also showed contaminants removal efficiency and minimization of the sample carryover from the previous runs. However, there were some disadvantages. The use of liquid nitrogen in the system led to various problems *i.e.* tube plugging, transfer of water to GC column by high water content in air. For a remote locations there would be some difficulties in the supply of liquid cryogen and this would lead to high cost (Park *et al*, 1998).

These limitations can be overcome by using only solid sorbent to collect and preconcentrate VOCs in ambient air combining with solvent desorption. The sampling with solid sorbent were achieved by either active (pumped) or passive (diffusive) sampling. Periago *et al.* (1997) reported the use of diffusive sampling to evaluate the environmental levels of aromatic hydrocarbons in gasoline service station and the occupational risk of gasoline service station

attendants. The sampling was done in two different periods, *i.e.* at different temperature (March and July). The investigation was done by attaching the 3M-3500 personal diffusive samplers to the clothing within the breathing zone to collected the sample. These samplers were designed to measure average concentrations over a time interval. The contaminants entered the monitor by diffusion and was adsorbed on the adsorbent (activated charcoal) inside the badge. The diffusive sampler was desorbed with 1.5 ml of carbon disulphide (free of benzene) for 30 min and 3-5 µl of the desorbed solvent was analyzed by GC-FID with methyl silicone capillary column. The results showed that the ambient concentration of VOCs was depended on the volume of gasoline sold and the ambient temperature.

In another report, Vainiotalo *et al.* (1998) monitored MTBE in the service station using active sampling where a pump was used to collect air samples through a charcoal tube that mounted pointing downwards 1.50 m above ground. The trapped compounds were desorbed with carbon disulphide and the eluate was analyzed by gas chromatography using mass-selective detection. The detection of the method was 0.55 μgm^{-3}. The results indicated that the levels of MTBE depend on MTBE content of the fuel, ambient conditions and the station-specific factors, such as volumes of gasoline sold and exhaust emissions from passing traffic.

The main disadvantage for solvent desorption used in the work just described is the toxicity of the solvent. This limitation could be overcome by using thermal desorption technique. Park *et al* (1998) reported the method for the analysis of 12 VOCs in ambient air. Six liters of air sample was collected, near a petroleum industrial park, in a stainless steel canister and then preconcentrate by using adsorbent trap and it was dry purging for 0.5 min before thermally desorbed at 200°C for 5 min. The desorbed compounds were subsequently analyzed by gas chromatography equipped with mass spectrometer. The separation was performed with DB-5 fused silica capillary

column. The detection limit ranged from 0.05 to 0.74 ppbv and the relative standard deviation (RSD) for seven measurements were 5.8-12.9% with correlation coefficients of 0.90-0.99. The results showed that VOCs could quantitatively be trapped and desorbed from an adsorbent trap without the use of liquid cryogens and the results were acceptable on the basis of the US Environmental Protection Agency. In this particular report there were some disadvantages due to the canister sampling, *i.e.* the bottles are heavy, and the special inner bottle surface and clean shut-off valves are rather expensive. The sample could also contained a significant amount of water, which should be removed before analysis, resulting in evaporation losses of less volatile ($> C_8$ hydrocarbons) compounds (Tonai *et al.*, 2000).

Yamamoto *et al.* (1998) also used thermal desorption technique for the continuous determination VOCs by an automated gas chromatographic system. The method consisted of a gas chromatographic system, DB-646 capillary column, photoionization detection (PID) and electrolytic conductivity detection (ELCD) connected to a series of combined preconcentrating device using an adsorbent tube and thermal desorption apparatus. The preconcentration method was based on the multibed tube (Carbotrap B, Carboxen 1000, Carboxen 1001) for the analysis of 54 selected VOCs. Air sample was drawn through a PTFE prefilter into the sampling line (in order to remove particulates from the sampled air). Then the samples were preconcentrated by passing through the adsorbent tubes and dry purge these adsorbent tubes with nitrogen to remove any water vapor from sampled air after completed adsorption. The adsorbent tubes were simultaneously thermally desorbed by rapidly heated to 280°C for 8 min. The trapped sample was desorbed and introduced into the GC column by back-flushing with carrier gas. The system was simple, sensitive and effective for the sequential and repetitive measurements for the continuous determination of trace levels of VOCs (ppt level) with a short resolution time (60 min). Although solid sorbents are now widely used, many precautions are

required to prevent contamination built up in the adsorbent during preparation, storage and analysis. Helmig (1996) reported the technical details on preparation, conditioning, storage and analysis of solid adsorbent in order to avoid contaminant and artifact information. The results from his work indicated that these problems came from a gradual build-up of these contaminations during storage from passive sampling or introduction of contaminants with the material used during cartridge assembly or during one of their analytical procedures. In order to reduce these contaminants, the condition temperature must be done at higher than the thermal desorption temperature and sealed the adsorbent tube with Swalogelok ferrule and cap during storage. These could prevent the air from diffusing into the tubes during conditioning, furthermore, the tubes must be stored under purified atmosphere and at freezing temperature.

The other problem could come from the sorption of water vapor and carbon dioxide. Because of water accumulating as ice can clog the freezeout trap which may even lead to the loss of sample. A background, caused by water, poses another problem in GC detection, *i.e.* interference with detector performance, retention time shift, and faster deterioration of the chromatographic column (Gawlowski *et al.*, 1999). Gawlowski *et al.*(1999) reported the adsorption of water vapor in many solid sorbents that was used to sample VOCs. Their studied indicated that the Graphitized carbons and non-polar polymeric sorbents (such as Tenax and Chromosorb 106) showed poor water trapping, generally less than 5 mg of water per gram of sorbent. Polar polymeric sorbents (e.g. Chromosorb 108 and Porapak N) adsorbed more water but weakly bound and easily removed by purging with dry gas. Carbon molecular sieves (e.g. Carbosieve S-III and Carboxen 1000) adsorb more substantial amounts of water, that corresponding to the volume of micropores.

There are several techniques which can be used to remove water from air and water sampling adsorbents (Karbiwnyk *et al.*, 2002). The first technique was done by heating the cartridge to $10^{o}C$ above ambient temperature. This

could prevent the adsorption of water vapor. VOCs and CFCs ranging from C_3-C_{12} (except propane) could then be collected and analyzed with a recovery of > 90%. The second method was done by purging with dry air. This successfully reduced the relative humidity and prevented water adsorption on the solid adsorbent even at the ambient temperature. These 2 techniques had some advantages over others because of the higher recoveries for lighter VOCs and they circumvented the additional analytical dry purge step.

In recent years, a new, rapid air sampling/sample preparation method using solid phase microextraction (SPME) has been reported. By this technique, sampling and sample preconcentration were combined in a single step and allows for direct transfer into a standard gas chromatograph (GC). The SPME, consisted of a coated fiber, was exposed to the sample matrix (e.g. air). The analytes would partition between coating and the sample until equilibrium is reached. The amount of analytes partitioned to the coating were proportional to their initial concentrations in the matrix (Koziel, *et al.*, 2000). Koziel, *et al.* (2000) reported the application of SPME for determination of VOCs and semi-VOCs. The PDMS/DVB (polydimethylsiloxane/divinylbenzene) -65 μm fiber was used for field air VOCs analysis with a sampling time of 1 min. This technique was compared with NIOSH (the National Institute for Occupational Safety and Health)-1501 method that sampling with the large charcoal tubes (sampling time 2 hour). The SPME samples were analyzed immediately after sample collection in the portable SRI-8610C GC equipped with PID/FID/DELCD detectors. The charcoal tube samples were analyzed during the 2 days following sample collection using carbon disulfide extraction, direct injection and analysis with a Varian 3400CX GC/FID. The results for toluene concentrations ranged from approximately 19-38 ppb and showed good correlation between these two methods. However, for airborne formaldehyde, air sampling with SPME devices proved more sensitive than conventional sampling (NIOSH-1541 method)

Although, there are many advantages in the SPME technique, there are also many limitations *i.e.* (1) a fiber is quite fragile; (2) if partition coefficient is high and/or a sample is small it can be analyzed only once; (3) in combination with GC, high mass compounds cannot be analyzed; (4) in many situations difficulty to select fiber coating of polarity close to polarity of analytes (Namiesnik *et al.*, 2000).

1.4 Objectives

1.4.1   To study the appropriate sample preconcentration technique and the qualitative and quantitative analysis of Methyl *tertiry*-Butyl Ether (MTBE) in air using Gas Chromatography-Flame ionization detector technique.

1.4.2   Quantitative analysis MTBE concentration at gasoline stations.

Chapter 2

Experimental

2.1 Chemicals and materials

2.1.1 Standard chemical

- Methyl tertiary butyl ether, MTBE (purity, 99.5%, AR Grade: Fluka Chemie AG, Switzerland)

2.1.2 General chemicals and solvents

- Super Q, 80/100 mesh (Alltech Associates, Inc., USA)
- Chromosorb 106, 60/80 mesh (Supelco, USA)
- Sodium sulphate anhydrous (AR Grade: Merck, Germany)
- Methanol (AR Grade: Merck, Germany)
- Ultra pure water (H_2O, Synthesis in laboratory by Maxima, ELGA, England)
- Glass wool

2.2 Instruments and Apparatus

2.2.1 Gas Chromatography-Flame Ionization Detector (GC-FID)

- Gas Chromatograph model GC-8A equipped with flame ionization detector (Shimadzu, Japan)
- Data processor model C-R6A Chromatopac (Shimadzu, Japan)
- Packed glass column: Super Q 80/100 mesh, 2.1 m × 2.5 mm ID.

- Oxygen Free-Nitrogen Carrier Gas: (purity 99.99%: TIG, Thailand)

2.2.2 Apparatus for inject standard solution

- Gas-tight syringe 1.0 ml, Series A-2
  (VICI Precision Sampling, Inc., Louisiana, USA)
- Syringe 10 µl (Hamilton, Switzerland)
- Syringe cleaner (Hamilton, Switzerland)
- Headspace vial with standard flat top, flat bottom 10, 60 ml
  (Alltech Associates, Inc., USA)
- Chlorobutyl Rubber Stopper
- Aluminum cap
- Crimper/ Decrimper (Supelco, USA)
- Flow meter

2.2.3 Apparatus for Headspace technique

- In- house water bath with thermostat (Gallenkanb, UK)
- Thermometer
- Headspace vial with standard flat top, flat bottom 10, 60 ml
  (Alltech Associates, Inc., USA)
- Chlorobutyl Rubber Stopper
- Aluminum cap
- Crimper/ Decrimper (Supelco, USA)

2.2.4 Apparatus for preconcentration step

- Adsorbent tube (70 mm × 6 mm O.D.)
- Lab-built thermal desorption unit
- Freeze-Dryer (DURA-STOP^{TM}µP, USA)

- Analytical Balance (Denver Industrial Company, USA)
- Microliter auto pipette 200, 1000, 5000 ml (Gilson, France)
- Vacuum pump (GAST manufacturing, Inc., USA)
- Multimeter (Fluke, USA)
- Thermocouple Module 80TK with sensor (Fluke, USA)
- Heating mantle
- Headspace vial 10 ml with stopper and aluminum cap
- 2-necked glass round bottom flask 250 ml (Pyrex, USA)
- 3-necked glass round bottom flask 500 ml (Pyrex, USA)

2.2.5 Apparatus for sampling step

- Personal Sampling Pump Model I.H. PUMP
  (A.P.BUCK INC., Florida, USA)
- BUCK "AUTO-QUIK" CHARGER
  (A.P.BUCK INC., Florida, USA)
- HAIR-HYGROMETER (Fisher, GDR)
- Thermo-Anemometer (Extech Instrument, USA)
- Adsorbent tube (70 mm × 6 mm O.D.)
- Adsorbent holding unit

2.3 Methods

2.3.1 Preparation of MTBE standard solution

Standard solution of MTBE was prepared in methanol at the concentration of 1000 $\mu g\ ml^{-1}$ and stored at 4°C in a glass bottle sealed with PTFE-lined lid.

2.3.2 Preparation of standard MTBE working solution

Standard working solution of MTBE was prepared in methanol by added a calculated amount of standard solution delivered by a micro syringe into a 60 ml headspace vial that contain methanol. The final concentration and volume in the vial were 10 μg ml^{-1} and 3 ml respectively. Then sealed the vial immediately with a stopper and an aluminum crimp top cap.

2.3.3 Optimization of the GC-FID conditions for MTBE analysis

The following parameters for GC-FID were studied: flow rate of carrier, oxidant and fuel gas, oven temperature, and injector/detector temperature. In all the optimizations in this section 10 μg ml^{-1}, 3 ml of MTBE working solution in a seal vial was placed in the in-house water bath at 60°C. After 20 minutes a Hamilton gas-tight syringe was used to withdraw the vapor phase and this was injected into the gas chromatograph for analysis.

2.3.3.1 Optimization of carrier gas (N$_2$) flow rate

To optimize the carrier gas flow rate, 1.0 ml of the vapor phase was injected to the gas chromatograph, Shimadzu GC-8A with Shimadzu C-R6A Chromatopac data processor. The packed glass column was a 2.1 m × 2.5 mm ID where Super Q, 80/100 mesh was used as the stationary phase. The analysis was done by setting the column and injector/detector temperatures at 180°C (isothermal) and 200°C respectively. Hydrogen and air were used as the fuel and oxidant gases at the flow rates of 50 ml/min and 500 ml/min respectively. This were the recommended flow rates for Shimadzu gas chromatograph model GC-8A (Shimadzu, 1989).

The optimum carrier gas flow rate was determined by varying the flow rate of the nitrogen carrier gas at 10, 20, 30, 40, 50 and 60 ml/min. Five replications of the analysis were performed for each flow rate. The retention time and the height half width determined from the chromatogram

were used to calculate the plate number and height equivalent to a theoretical plate (HETP) respectively. From a van Deemter plot, the optimum flow rate was obtained at the lowest HETP.

2.3.3.2 Optimization of fuel (H$_2$) flow rate

The GC-FID analysis was carried out on a Shimadzu GC-8A gas chromatograph equipped with a flame ionization detector (FID). GC separation was achieved with a packed glass column, 2.1 m × 2.5 mm I.D. packed with Super Q (80/100 mesh). The column temperature and the injector/detector temperature were 180 (isothermal) and 200°C respectively. The nitrogen carrier gas flow rate was 20 ml/min (the obtained result from experiment 2.3.3.1) and the air oxidant gas flow rate was 500 ml/min.

To optimize the flow rate of hydrogen that was used as the fuel gas, its flow rate was varied from 20 ml/min to 60 ml/min with an increment of 10 ml/min. The responses at different hydrogen flow rates were compared and the optimum hydrogen flow rate was selected from the highest response.

2.3.3.3 Optimization of oxidant (air) flow rate

In this experiment, 1.0 milliliter of the gas phase was transferred to the gas chromatograph that was set at the optimum carrier and fuel gas flow rates obtained from 2.3.3.1-2.3.3.2 respectively. The temperatures of the column and the injector/detector were set at 180 (isothermal) and 200°C respectively.

The optimum oxidant flow rate was investigated by varying the flow rate of the oxidant at 100, 200, 300 and 400 ml/min. The peak areas obtained from all flow rates were compared and the optimum oxidant flow rate was determined from the highest response.

2.3.3.4 Optimization of column temperature

The column temperature was performed using the isothermal mode, the only available mode of the Shimadzu GC-8A. To optimize the column temperature, 1.0 ml of the MTBE gas phase was transferred from the headspace to the gas chromatograph system.

The gas chromatographic conditions were maintained as: Injector /Detector temperature at 200°C, flow rates of hydrogen and air were 20 and 200 ml/min respectively, and flow rate of carrier gas (N_2) was 20 ml/min (the results from experiments 2.3.3.1-2.3.3.3).

The optimization of the column temperature was investigated by varying the column temperature at 150, 160, 180, 190, 200 and 220°C. Five replications were analyzed for each temperature. The optimum column temperature was the temperature that increased detectability, sample throughput and reduced the operation time.

2.3.3.5 Optimization of injector/detector temperature

The injector and detector temperature of GC-8A Shimadzu was designed to be set at the same temperature. Therefore, they would be optimize at the same time. In this study, 1.0 ml of the headspace was taken and injected into the gas chromatograph. The flow rate of carrier, fuel gas, oxidant, and the column temperature were set using the results of the experiments 2.3.3.1 to 2.3.3.4.

The optimization of injector/detector temperature was determined by varying the injector/detector temperature at 150, 180, 190, 200 and 220°C. The analysis was performed at each temperature for five times. The temperature that obtained the highest detectable was the optimization injector/detector temperature.

2.3.4 Optimization of the headspace conditions for prepare MTBE standard gas

The sensitivity of the headspace technique or the equilibrium concentration of MTBE in the headspace depends on several parameters. These parameters are equilibration time, heating temperature, phase ratio and vial volume. The GC-FID conditions used to optimize the headspace conditions are shown in Table 2.

Table 2 The GC-FID conditions for the optimization of headspace conditions.

Gas Chromatography	Shimadzu GC-8A equipped with C-R6A Chromatopac recorder
Column	Glass column (2.1 m × 2.5 mm ID.) packed with Super Q (80/100 mesh)
Flow rate : Carrier gas	N_2 : 20 ml/min
: Fuel gas	H_2 : 20 ml/min
: Oxidant gas	Air : 200 ml/min
Temperature: Column	220°C (isothermal)
: Injector/Detector	220°C
Injection volume	1.0 ml

2.3.4.1 Optimization of equilibration time

The 10 μg ml^{-1}, 3 ml MTBE working standard solution in the headspace vials were equilibrated at 60°C in the in-house water bath for different periods of time i.e. 10, 15, 20, 25, 30 and 40 min. After each equilibrated time was reached, 1.0 ml of the gas phase was taken from the headspace by a gas-tight syringe and injected to the gas chromatograph. The resulting peak areas were plotted against the equilibration time. The time

needed to reach an equilibrium was obtained as the time that the analytical signal was constant.

2.3.4.2 Optimization of equilibration temperature

The MTBE working standard solution of 10 µg ml^{-1}, 3 ml in the headspace vials were placed in the in-house water bath for 20 min (the equilibration time obtained from experiment 2.3.4.1) at 40, 50, 60, 70 and 80°C respectively. A gas-tight syringe was used for transferring 1.0 ml of gas phase from the headspace to the gas chromatograph. The resulting peak area values were plotted *versus* the heating temperature. The appropriate heating temperature was the temperature that provided the highest sensitivity and good precision. The precision was considered from the relative standard deviation.

2.3.4.3 Optimization of phase ratio and vial volume

This experiment studied the effect of phase ratio and vial volume that would give a high sensitivity in the headspace technique. The MTBE standard stock solution (2.3.1), 1000 µg ml^{-1}, was diluted with methanol to give the final concentration of 10 µg ml^{-1}. The solution was placed in 2 sizes of vials i.e. 10 and 60 ml with various phase ratio (gas:solution), i.e. 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0. Each vial was immediately sealed with a septum and capped by a crimper. The vials were equilibrated in the in-house water bath at 70°C for 20 min (the values obtained from experiment 2.3.4.1 and 2.3.4.2 respectively) and the gas-tight syringe was used to take the gas phase from the headspace and analyzed by GC/FID at the optimum conditions shown in Table 2. The response, peak area, of each vial volume was plotted *versus* the phase ratio. The suitable phase ratio and vial volume was the value that accomplished the highest response and precision.

2.3.5 Linear dynamic range (linearity)

A series of MTBE standard solution, 2-1000 μg ml^{-1} were prepared by diluting the 1000 μg ml^{-1} stock solution (2.3.1) with methanol. Each standard solution, 6.70 ml, was pipetted into a 10 ml vial, it was tightly sealed with the septum and placed in the in-house water bath at the optimum equilibrated conditions that were obtained from 2.3.4.1-2.3.4.3. One milliliter of the gas phase was drawn by a gas-tight syringe and introduced to the gas chromatograph at the optimum conditions for GC-FID and headspace technique as shown in Table 3.

Linear dynamic range was investigated by plotting the obtained peak area versus the concentration. The linearity of the response was determined by considering the correlation coefficient of the curve.

Table 3 The optimum GC-FID and headspace conditions for MTBE analysis.

Gas Chromatography	Shimadzu GC-8A equipped with C-R6A Chromatopac recorder
Column	Glass column (2.1 m × 2.5 mm ID.) packed with Super Q (80/100 mesh)
Flow rate : Carrier gas	N_2 : 20 ml/min
: Fuel gas	H_2 : 20 ml/min
: Oxidant gas	Air : 200 ml/min
Temperature: Column	220°C (isothermal)
: Injector/Detector	220°C
Equilibration time	20 min
Heating temperature	70°C
Phase ratio	0.5
Vial volume	10.0 ml
Injection volume	1.0 ml

2.3.6 Limit of detection

The standard deviations of the standard solutions at 2, 4, 6, 8 and 10 $\mu g \ ml^{-1}$ from experiment 2.3.5 were used to determine the limit of detection. This was done by plotting the standard deviation *versus* the concentration of the standard solution. The x-axis was the concentration of the standard solution and the y-axis was the standard deviation. The calibration curve was then extrapolated to obtain S_0, the value of the standard deviation (y) at concentration (x) $\rightarrow$ 0 (Taylor, 1987). The limit of detection was then defined as $3S_0$.

2.3.7 Preconcentration of MTBE in air sample by active sampling using adsorbent tube.

The adsorbent used in this study was the Chromosorb 106, 60/80 mesh. The properties of Chromosorb 106 is shown in Table 4

Table 4 Properties of Chromosorb 106, 60/80 mesh (Namiesnik, 1988)

Chemical structure	Styrenedivinylbenzene polymer
Sorbent maximum temperature	$250^{\circ}C$
Polarity	Non-polar
Sorbent strength	Medium
Specific surface area	$750 \ m^2/g$
Density	0.28 g/cc

2.3.7.1 Conditioning of the adsorbent

The adsorbent was activated or conditioned by heating to an appropriate temperature ($230^{\circ}C$) in the stream of inert gas, N_2, then cooled and stored in a desicator. Chromosorb 106 was conditioned by using the apparatus that was made in the laboratory and this is illustrated in Figure 2. The

conditioning was done by placing the Chromosorb 106 into the 3-necked round bottom flask. The thermometer and the inert gas (N_2) flow line were connected to the flask by using modified connectors sealed with parafilm. After the N_2 valve was turned on and the N_2 stream passed through the Chromosorb 106 in the flask, the heating mantle was turned on to heat the Chromosorb 106 at 230°C with nitrogen gas flowing through at 100 ml/min. The heating mantle was turned off after 1 hour of heating and the Chromosorb 106 was allowed to cool down in the nitrogen stream. The conditioned adsorbent was then kept in a clean plastic bottle and stored in a desicator.
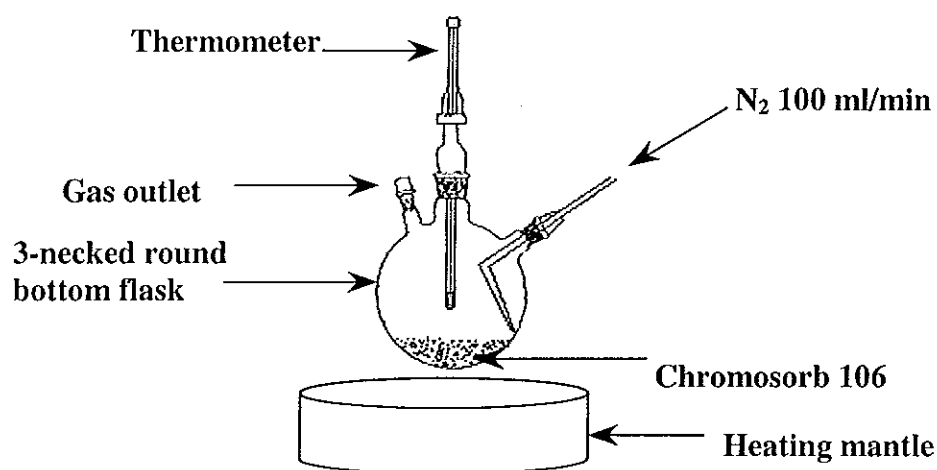
Figure 2 Laboratory-built apparatus used for the conditioning of Chromosorb 106

2.3.7.2 Preparation of the adsorbent tube

A 70 mm x 4.0 mm (I.D.) glass tube, fused at one end, was used for the preparation of an adsorbent tube. Glass tubes were cleaned by washing with detergent solution and sonicated in an ultrasonic bath for 1 hour, rinsed with distilled water, dried in an oven and then kept in the desicator.

An adsorbent tube was made by filling Chromosorb 106 (60/80 mesh) into a cleaned glass tube in two sections (Figure 3). The front section contained 0.1000 g (±0.0005 g) and the back section contained 0.0500 g (±0.0005 g) of Chromosorb 106 (60/80 mesh), the sections were separated by glass wool plugs and sealed with a plastic end cap. An adsorbent tube that used in this study is illustrated in Figure 3.
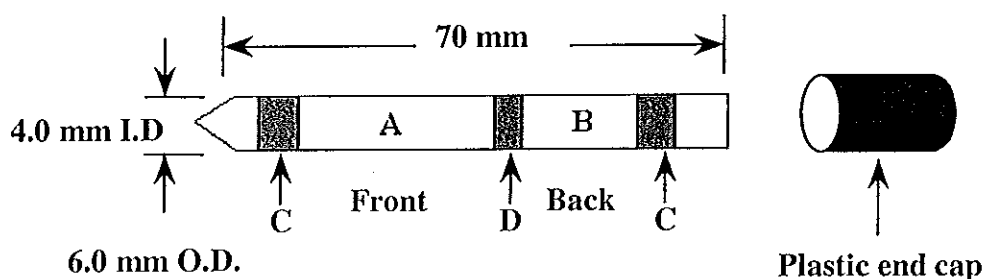
A = Chromosorb 106: 0.1000 g

B = Chromosorb 106: 0.0500 g

C = Glass wool 50 mg

D = Glass wool 25 mg

Figure 3 A lab-made adsorbent tube

2.3.7.2 Breakthrough volume of the adsorbent

Breakthrough volume of the adsorbent was defined by the volume of air sample when the amount of analyte collected in a back section of adsorbent tube reach a certain percentage (typically 5%) of the amount collected by front section of adsorbent tube.

For this study, 1000 µg ml^{-1} MTBE standard stock solution was diluted with ultra pure water to the final concentration and volume of 0.2 µg ml^{-1} and 100 ml, respectively (2 times the lowest concentration that can be

detected by this method). Before sampling, the fused end of the adsorbent tube was broken of and the tube was connected such that the back section of the adsorbent tube was nearest to the pump. MTBE standard solution (0.2 μg ml^{-1}, 100 ml) in ultra pure water was purged by nitrogen at a purging flow rate of 200 ml/min. The gas phase in the headspace was collected on the adsorbent tube by using a calibrated pump. The adsorption flow rate was 100 ml/min.

After MTBE was adsorbed in the tube, the desorption was done by removing Chromosorb 106 from adsorbent tube and carefully transferring each section of the Chromosorb 106 into a 10 ml headspace vial. The vial was sealed with a septum and an aluminum cap, then equilibrated in the in-house water bath at 70°C for 20 min. One milliliter of gas phase was transferred from headspace by a gas-tight syringe and injected to the gas chromatograph. The conditions of the gas chromatograph were shown in Table 2.

The breakthrough volume of the Chromosorb 106 for MTBE in air sample was investigated by varying the air sample volume at 12, 16, 20, 22 and 24 liters. The breakthrough volume was taken as the sample volume that the percentage of the amount of analyte adsorbed in the back section of the adsorbent tube reached 5% of the amount that adsorbed in the front section. The apparatus for study breakthrough volume is shown in Figure 4.

Vacuum pump, ←————
100ml/min

Adsorbent tube

N₂

Glass round
bottom flask, ————————— **MTBE 0.2 µg ml⁻¹,**
250 ml **100 ml**
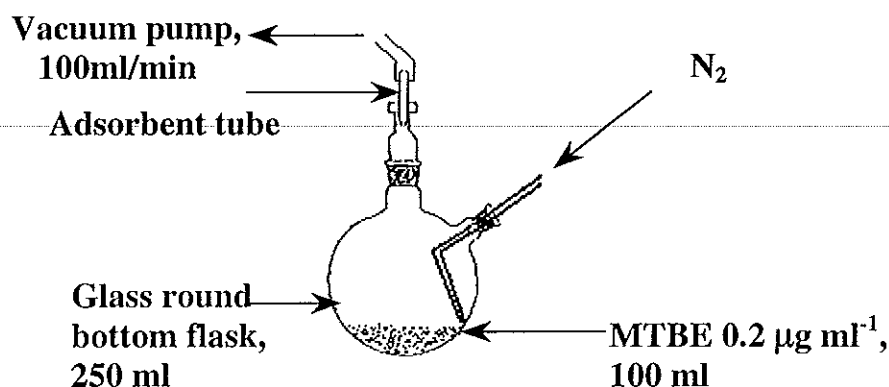
Figure 4 Apparatus for determining breakthrough volume

2.3.7.3 Optimization of the flow rate through adsorbent

In this study 1000 µg ml⁻¹ MTBE standard stock solution was diluted with ultra pure water to the final concentration of 0.2 µg ml⁻¹, 100 ml. The adsorption procedure followed the same procedure used to determine the breakthrough volume (2.3.7.2).

The optimization of the flow rate through adsorbent was determined by varying the adsorption flow rate at 70, 100, 150 and 200 ml/min to get the final air volume of 22 liters. Five replicates were performed for each flow rate and the optimum flow rate through adsorbent was chosen as the one that gave the highest response.

2.3.7.4 Adsorption time optimization

The optimum adsorption time was determined by directly injected 1.0 µl of standard solution containing 20 µg of MTBE (MTBE content per sample in breakthrough volume study) to the front section of each adsorbent tubes and stored them for 2, 4, 5, 6, 8, 10 and 16 hours at room temperature (25°C).

After the storage time was reached, the adsorbent was removed from the glass tube where the two sections were placed separately in two 10 ml headspace vials. Each vial was sealed immediately with septum and aluminum cap and was placed in the in-house water bath for equilibration at 70°C for 20 min. The peak areas obtained from the analysis of the gas phase of both sections were then compared. The optimum adsorption time was the time that complete adsorption occurred in the front section, i.e. the lowest lost amount of MTBE was transferred from the front to the back section.

2.3.7.5 The storage time of the adsorbent tube

The storage time of the adsorption for MTBE was investigated by preparing thirty-three adsorbent tubes. The fused end of each tube was broken off and the front section was spiked with 1.0 µl of 20 µg MTBE standard solution (MTBE content per sample in breakthrough volume study). Three adsorbent tubes were analyzed on the day of preparation. Fifteen tubes were stored in the refrigerator at 4°C and the other fifteen were stored in a closed drawer at ambient temperature (25°C). At 3-day intervals, three adsorbent tubes from each of the two storage places were analyzed and their responses were compared.

2.3.8 Lab-built thermal desorption unit

The lab-built thermal desorption unit was designed to desorb MTBE from the adsorbent tube. The lab-built desorption unit is shown in Figure 5. A small heater (1) was constructed to desorb the collected MTBE. It consisted of an aluminium tube, the inner diameter of which closely fitted the outer diameter of the adsorbent tube. With the aid of the heating cord that connected to the heating sensor and the temperature-time control unit (2), the adsorbent tube could be heated from the room temperature to the set temperature with a heating rate of 15-18°C/min. The upper end of the adsorbent tube was

connected to a flow meter (3) and a nitrogen source and the bottom end of the adsorbent tube was connected to a needle (4) that directed the desorbed components into a 10 ml vacuum collection vial (5). The time and final temperature of the desorption unit was set before the operation.
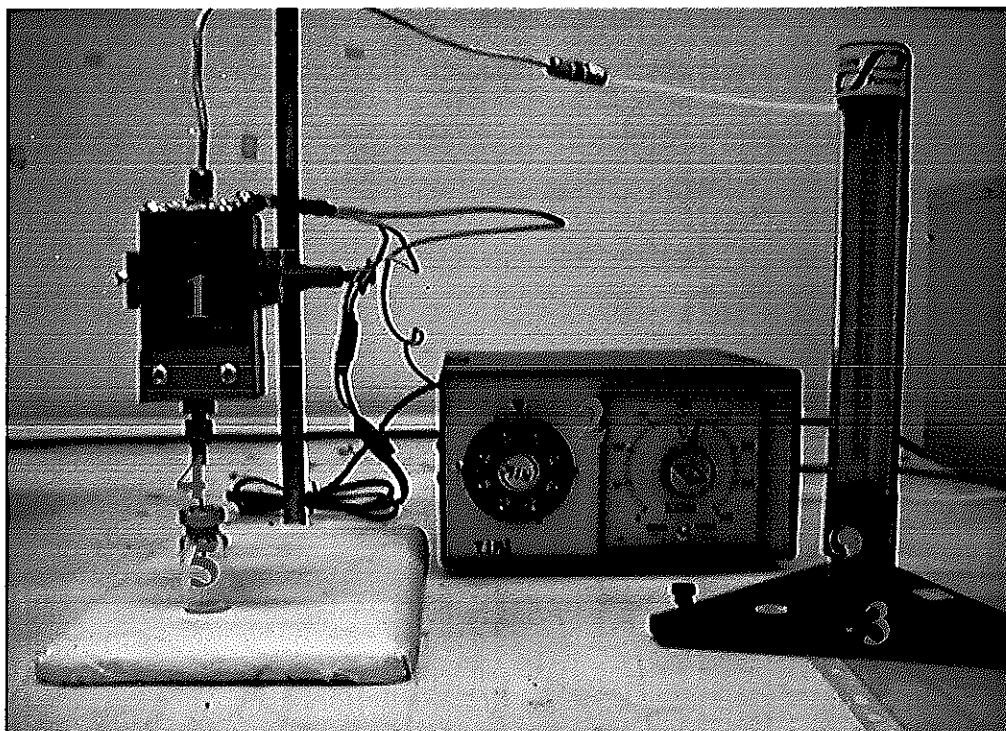
Figure 5 The lab-built desorption unit

For the desorption procedure, the adsorbent tube was inserted in the aluminium tube inside the desorption unit and checked for leakage. It was then heated to an appropriate temperature and time while the optimum flow rate of inert gas (nitrogen) was purged through the trap with the flow in a reverse direction from that use for sample collection. By this procedure, the adsorbed analytes were desorbed and collected in the vacuum collection vial. After desorption, the collection vial was placed in the in-house water bath to equilibrate at 70°C for 20 minutes. Then a gas-tight syringe was used to

equilibrate at 70°C for 20 minutes. Then a gas-tight syringe was used to transfer 1.0 ml of gas from the vial to the gas chromatograph that was set at optimum conditions (Table 2).

2.3.8.1 Calibration temperature of the lab-built thermal desorption unit

The temperature of the lab-built thermal desorption unit was calibrated by using a thermocouple. A blank adsorbent tube was placed inside the aluminium tube in the small heater, the thermocouple was then inserted into the cavity of the blank adsorbent tube and was held in this position with a clamp. The heater temperature of the lab-built thermal desorption unit was set at the temperature-time control unit. The temperature inside the adsorbent tube, measured by the thermocouple, was read every 2 minutes for 30 minutes for each heater temperature setting. From this the temperature inside the adsorbent tube corresponding to a set heater temperature was obtained and used for further studies.

2.3.8.2 Preparation of vacuum vials

Vials, 10 ml, were cleaned by washing with detergent solution followed by sonicating in an ultrasonic bath for 1 hour. Then rinsed with distilled water and dried in an oven. A chlorobutyl rubber stopper was placed (slightly opened) at the neck of each cleaned and dried vials. The vials were arranged on the Stoppering Tray Dryer of the Freeze-Dreyer. By Freeze Drying technique, the pressure inside the vials was reduced to about 60-70 m torr. After this pressure was reached, the tray was raised in order to sealed the vials tightly in vacuum condition. Turned of the system and removed the vials from the tray, then capped with aluminum crimp top cap.

In thermal desorption, the important parameters need to be optimized were desorption temperature, desorption flow rate and desorption time.

2.3.8.3 Optimization of desorption temperature

The optimum desorption temperature for this system was investigated by injecting 1.0 µl of 20 µg of MTBE aqueous standard solution (MTBE content per sample in breakthrough volume study) into the front part of the conditioned adsorbent tube and kept at room temperature (25°C). After allowing for the adsorption time, MTBE was desorbed by the above procedure (2.3.8) using various desorption temperatures i.e. 70, 100, 120, 150, 180, 200 and 220°C. The desorption flow rate and desorption time were set at 50 ml/min and 20 minutes respectively. The responses were plotted *versus* the desorption temperatures. The optimum desorption temperature was the one given the highest response.

2.3.8.4 Optimization of desorption flow rate

The optimum flow rate was determined by directly injected 1.0 µl of an aqueous standard solution containing 20 µg of MTBE (MTBE content per sample in breakthrough volume study) into the front section of the conditioned adsorbent tube and stored for 4 hours (the optimum adsorption time). This adsorbent tube was desorbed by the above procedure (2.3.8) at 200°C for 20 minutes and varied the desorption flow rate at 20, 30, 40, 50 and 60 ml/min. The responses *versus* the desorption flow rate was obtained to determine the optimum desorption flow rate at the highest response.

2.3.8.5 Optimization of desorption time

Standard solution of MTBE, 1.0 µl, 20 µg, (MTBE content per sample in breakthrough volume study) was directly spiked at the front section of the adsorbent tube and left for 4 hours. Desorption time was

investigated by desorbing the adsorbent at 200°C with the flow rate of 50 ml/min (obtained by 2.3.8.2-2.3.8.3) and the desorption time was varied at 10, 15, 20, 25 and 30 minutes. The obtained responses were plotted *versus* the desorption time. The optimum desorption time was the time that gave the highest response.

2.3.9 Calibration curve

A series of 10-100 μg μl^{-1} MTBE were prepared by diluting the standard MTBE (2.1.1) with methanol. Each of these standard solutions, 1.0 μl, was directly spiked to the front section of the conditioned adsorbent tube and stored at room temperature (25°C). After 4 hours of adsorption time, it was desorbed by the desorption procedure described previously (2.3.8). A calibration curve was obtained by plotting the response (peak area) *versus* the MTBE content.

2.3.10 Correction factor

The adsorbed MTBE could be lost during desorption process, a correction factor for this must be accounted for in order to obtain the correct concentration of MTBE in the sample.

The correction factor was investigated by comparing the results from the previous calibration curve (2.3.9) to the results from the standard curve of the 100% desorption efficiency. This standard curve was determined using the MTBE standard solution, prepared in methanol, in the concentration range 10-200 μg μl^{-1}. 1.0 μl of each standard solution was directly injected into the 10 ml vacuum vial using a 10.0 μl syringe. This vial was placed in the in-house water bath to be equilibrated at 70°C for 20 min. One milliliter of gas in the vacuum vial was transfer by a gas-tight syringe to the gas chromatograph that was set at the optimum conditions (Table 2).

2.3.11 Qualitative and quantitative analysis of MTBE in air

2.3.11.1 Adsorbent holding unit

In order to sampling triplicate air samples by 3 adsorbent tubes at the same time, the adsorbent holding unit was designed. A glass tube, 8 mm (O.D.) x 80 mm, was connected to another 3 glass tubes (channels), 0.6 mm (O.D.) x 15 mm, as shown in Figure 6.
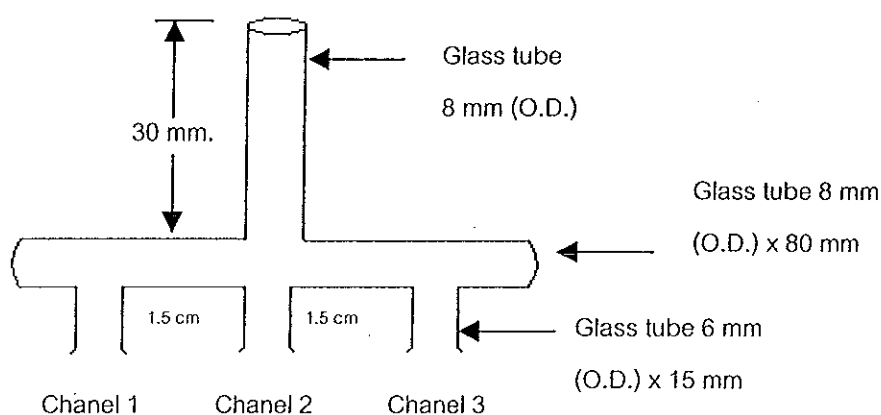
Figure 6 Adsorbent holding unit

2.3.11.2 Calibration of the flow rate for each channel

The different flow rate of each channel in the adsorbent holding unit was the source of error in triplicate sampling. The flow rate for each channel needed to be calibrated. This was done by first broke off the fused end of the adsorbent tube to give an opening of approximately half the inner diameter of the tube. This broken end was connected to a flow meter. The other end of the adsorbent tube was inserted into the arm (channel) of the adsorbent tube holding unit and sealed with parafilm. Connected the other side of the adsorbent tube holding unit to the tube holder of the sampling pump, and set the flow rate of the sampling pump. The flow rate of the air drawn through the

adsorbent of each channel was measured for 10 replicates and the average flow rate of each channel was determined.

2.3.11.3 The sampling sites

Three gas stations were selected as the sampling sites

Site 1: PTT gas station at Suppasarn-rungsun road, Hat Yai, Songkhla.

Site 2: Bangchak gas station in Prince of Songkla University, Hat Yai, Songkhla.

Site 3: Caltex gas station at Tambol Kor Hong, Hat Yai, Songkhla.

The air samples at each sampling site were collected twice each day (morning and evening) for 2 days.

2.3.11.3 Sample collection

The adsorbent tubes were broken at the fused end to provide an opening of approximately half the internal diameter of the tube. The other end of the adsorbent tubes were inserted into the three channels of the adsorbent tube holding unit, sealed with parafilm and attached to the tube holder of the sampling pump. The adsorbent tubes were position at 1.50 m above ground level and 30 cm away from the petrol pump, set the flow rate of the sampling pump and rechecked the sampling flow rate of each adsorbent tube before sampling. Sampling was performed by a Personal Sampling Pump Model I.H. PUMP (A.P.BUCK INC., Florida, USA) which drawn air through the adsorbent tubes at 100 ml/min for 2 hours and 34 minutes for an air sample volume of 15.4 liters (70 % of the breakthrough volume) (Torres *et al*, 1995). The adsorbent tubes were then removed and sealed with the plastic end caps and parafilm. These adsorbent tubes were kept in clean box and brought back to the laboratory for analysis.

While sampling, the air temperature and velocity were measured every 15 minutes. The number of vehicles refueling during the sampling time were also counted.

Chapter 3

Results and Discussion

The analysis of Methyl *tert*-Butyl Ether (MTBE) in air was studied using a gas-solid chromatographic technique (GSC). The system used nitrogen gas as the mobile phase and Super Q 80/100 mesh packed in a glass column (2.1m × 2.5 mm ID.) as the stationary phase. The flame-ionization detector was employed for MTBE detection. Several analysis conditions were optimized to obtain the best GSC performance.

3.1 Optimization of the GSC-FID analysis conditions

3.1.1 The carrier gas (N_2) flow rate

The optimum carrier gas flow rate was determined by considering its effect on the height equivalent to a theoretical plate (HETP). The HETP can be determined by the van Deemter equation.

$$HETP = A + B/\mu + C\,\mu \qquad (1)$$

where A = Eddy diffusion term: a constant that accounts for the effect of "eddy" diffusion in column

= $2\lambda d_p$; λ is a factor characteristic of the packing and d_p is the particle diameter of the packing.

B = longitudinal diffusion term: a constant that accounts for the molecular diffusion of the vapor in the direction of the column axis

= $2\lambda D_g$; D_g is the diffusion coefficients of the component in gas phase.

C = mass transfer term: a constant proportional to the resistance of the column packing to mass transfer of solute through it.

$= (8/\pi^2)[k'/(1+k')^2](d_f^2/D_1)$; k' is the capacity ratio, d_f is the effective thickness of the liquid film on the support and D_l is the diffusion coefficients of the component in the liquid phase.

$\mu =$ the linear velocity of carrier gas (mobile phase)

Equation (1) shows the dependence of HETP on carrier gas flow rate and this is a hyperbola with its minimum at velocity $\mu = \sqrt{B/C}$, and the minimum HETP value $HETP_{min} = A + 2\sqrt{BC}$ (Szepesy, 1970). Figure 7 shows the change in HETP versus average linear velocity of carrier gas.
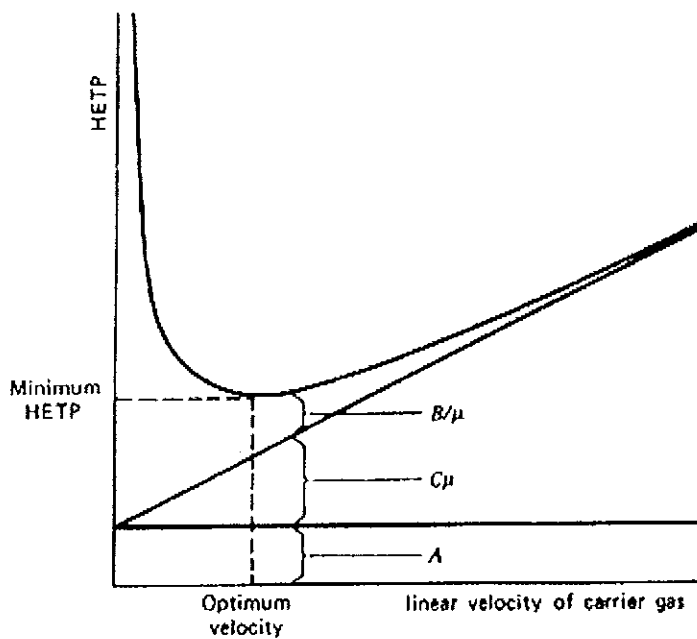
Figure 7 The van Deemter plot.

From the plate theory, it can be assumed that the column is divided into a number of zones called " theoretical plates" and HETP is the zone thickness according to the equation

$$HETP = \frac{L}{N} \qquad (2)$$

where L is length of column in centimeters

N is the number of theoretical plates.

The column efficiency improves with an increase in the number of theoretical plates or a decrease the *HETP* in the van Deemter equation.

In practice it is difficult to obtain the terms A, B and C in equation (1), therefore, equation (2) is normally used to calculate the *HETP*. The number of theoretical plates (N) is determine by equation (3)

$$N = 16 \left(\frac{t_R}{W} \right)^2 \qquad (3)$$

where t_R is the retention time of the peak (Figure 8)

W is the base width of the peak
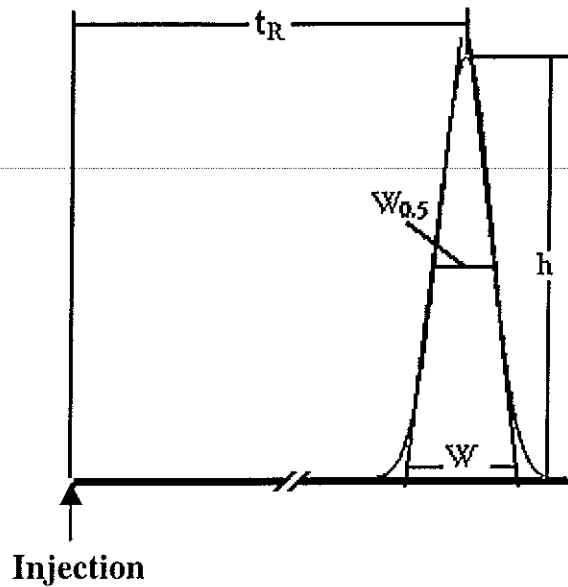
Figure 8 The characteristic data of the elution peak.

Since

$$W = \left(\frac{2}{\ln 2}\right)^2 W_{0.5} \tag{4}$$

where $W_{0.5}$ is the bandwidth at the half-height (Figure 8)

Therefore

$$N = 5.54 \left(\frac{t_R}{W_{0.5}}\right)^2 \tag{5}$$

In this study the HETP was calculated using equation (5) and equation (2). The results are shown in Table 5 and Figure 9. The optimum carrier gas flow rate 20 ml/min was obtained at the lowest HETP from the van Deemter plot (Figure 9).

Table 5 The height equivalent to a theoretical plate (HETP) of MTBE

(10 μg ml^{-1}, 3ml) at various carrier gas flow rate

Flow rate (ml/min)	HETP (mm)[*]
10	7.28
20	6.98
30	8.31
40	9.06
50	10.51
60	11.44

* 5 replications, RSD<4%
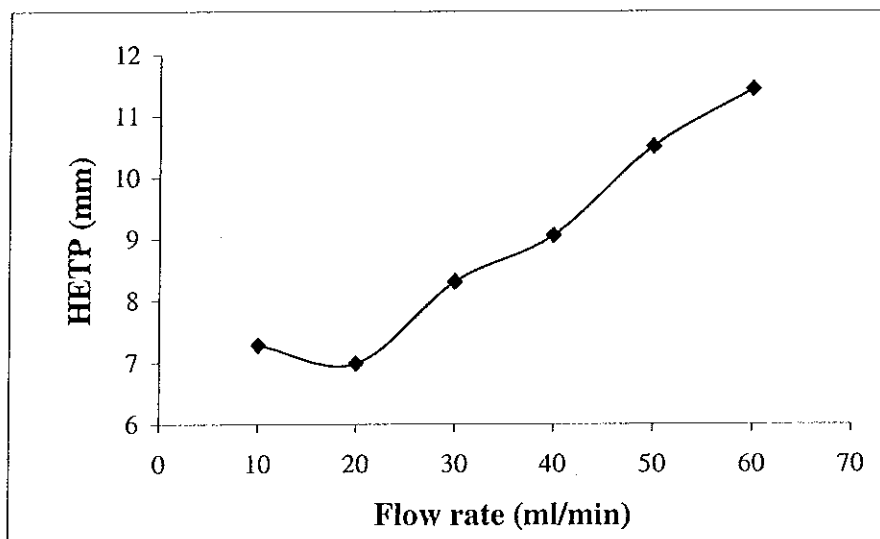
Figure 9 The van Deemter plot of MTBE

3.1.2 Fuel (hydrogen) flow rate

In this system the analyte eluted from the column was detected by a flame ionization detector (FID). This detector consists of a small hydrogen-air diffusion flame burning produced from oxidant and fuel gas. The oxidant gas was air and the fuel gas was hydrogen. Thus, the flow rates of air and hydrogen significant influence the noise level and the sensitivity of the detector.

The effect of hydrogen flow rate to the response is shown in Table 6 and Figure 10. The highest response was obtained at 20 ml/min, and this is selected as the optimum flow rate. This is similar to the finding of Szepesy (1970) where the adequate value of hydrogen flow rate was found to be between 15 to 50 ml/min.

Table 6 The effect of the hydrogen flow rate on the response of MTBE
$10 \ \mu g \ ml^{-1}$, 3 ml

Flow rate (ml/min)	Response $(\times 10^3)^*$, μV
10	4.77
20	6.65
30	5.73
40	5.37
50	4.85

* 5 replications, RSD<4%
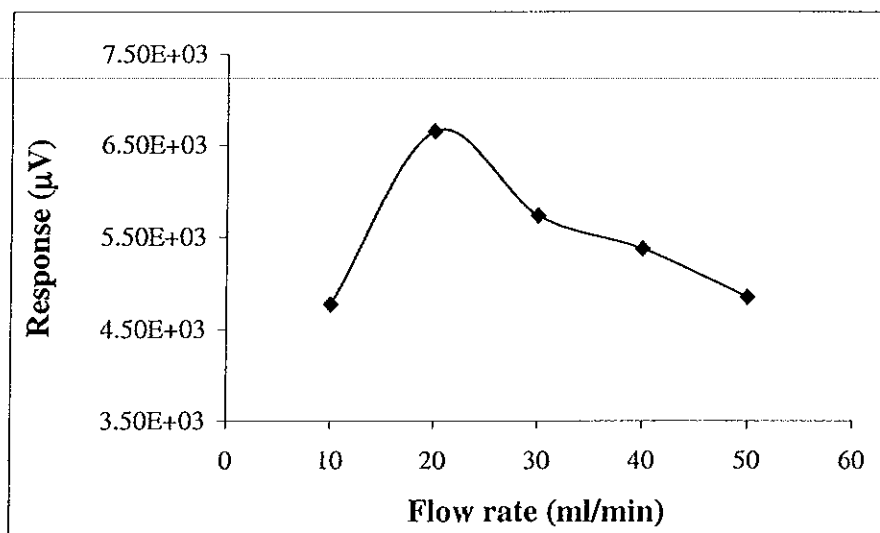
Figure 10 The effect of the hydrogen flow rate on the response of MTBE 10
$\mu g\ ml^{-1}$, 3 ml

3.1.3 Oxidant gas (air) flow rate

Table 7 and Figure 11 show the response obtained from experiment
2.3.3.2. The flow rate of 200 ml/min gave the highest response and this was
chosen as the optimum flow rate of air. From this study the optimum flow rate
ratio of fuel and air was 1:10 and this is similar to what found in most of the
GC-FID (Poole and Schuette, 1984).

Table 7 The effect of the air flow rate on the response of MTBE 10 $\mu g \, ml^{-1}$, 3 ml

Flow rate (ml/min)	Response $(\times 10^3)^*$, μV
100	5.79
200	5.94
300	5.93
400	5.91

* 5 replications, RSD<4%
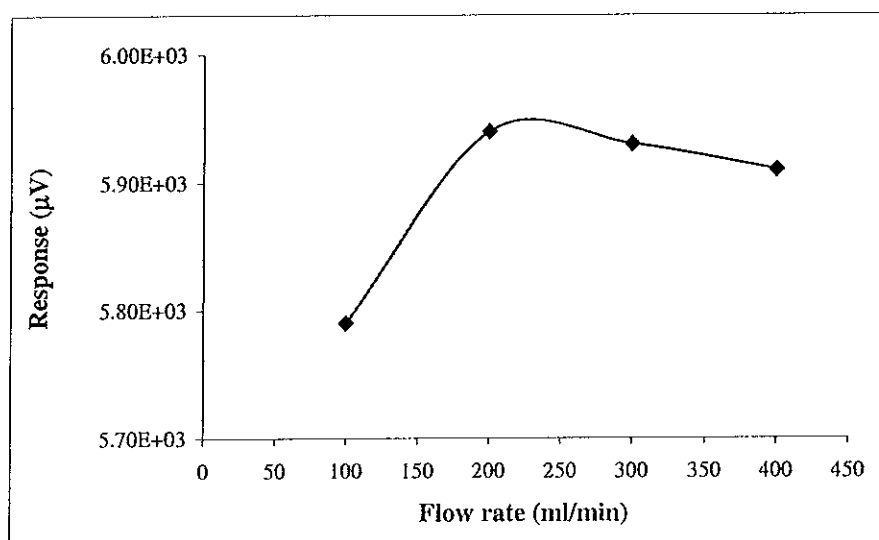
Figure 11 The effect of the air flow rate on the response of MTBE 10 $\mu g \, ml^{-1}$, 3 ml

3.1.4 Column temperature

The column temperature is one of the important parameters in gas chromatography technique, since it could minimize the time used for analyte elution, increase detectability and reduce analysis time. However, due to instrumental limitation in this study, the column temperature can only be used in an isothermal mode this was studied in experiment 2.3.3.4 and the results are shown in Table 8 and Figure 12. The optimum column temperature was obtained by considering the high response and short analysis time. In this case 220°C was the most suitable temperature.

The results indicated that the response increased as the column temperature increased, while the analysis time decreased. However, the lifetime of the stationary phase decreased when the column temperature increased. In order to prolong the lifetime of the stationary phase, the optimum column temperature should be lower than the maximum temperature of the stationary phase (250°C). This is the reason why the column temperature was only investigated up to 220°C.

Table 8 The relationship between the response and the analysis time of 10
$\mu g \ ml^{-1}$, 3ml MTBE at various column temperatures

Temperature (°C)	Response $(\times 10^4)^*$, μV	Analysis time (min)
150	0.94	17.08
180	1.12	15.43
200	1.48	12.15
210	1.52	10.38
220	1.63	8.23

* 5 replications, RSD<4%
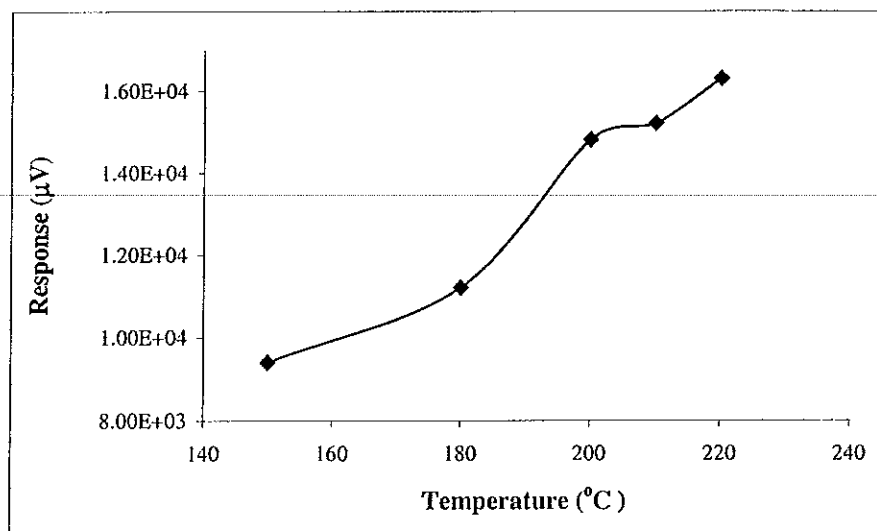
Figure 12 The relationship between the response of 10 μg ml^{-1}, 3ml MTBE at various column temperatures

3.1.5 Injector/Detector temperature

In a gas chromatography technique, the injector temperature must be set higher than the boiling point of the analyte in order to change the sample phase from liquid to vapor at the injector. In this study, however, the analyte was equilibrated into the gas phase before injected into the gas chromatograph. Therefore, MTBE analysis could be achieved at a relatively low injector temperature. On the other hand, the analysis time increased when the injector temperature decreased. Thus, the sensitivity and the analysis time were the main factors to be considered in order to obtained the optimum injector temperature.

For the temperature of the flame ionization detector (FID), there is no need to keep the detector temperature above the column temperature, as long as water does not condense. However, it is useful to keep the temperature of the detector stable since it has a slight effect on the detection mechanism (Grob, 1985).

In the GC-8A Gas chromatograph, the injector and detector have the same temperature control. Thus, their temperatures needed to be optimized at the same time (2.3.3.5). To prevent water condensation, the optimum injector and detector temperature must be equal or lower than 220°C (the optimum column temperature). Therefore, the injector and detector temperature was only investigated in the range from 150 (the analysis time lower than 20 min) to 220°C. The results are shown in Table 9 and Figure 13. The relationship between injector/detector temperature indicated that the response increased as temperatures increased. The optimum of the injector and detector temperature was selected by considering the sensitivity, analysis time and the lifetime of the stationary phase. The highest response and the lowest analysis time was obtained at 220°C. Thus, the optimum injector/detector temperature was 220°C.

Table 9 The response of 10 µg ml^{-1}, 3ml MTBE at different injector/detector temperature

Temperature (°C)	Response ($\times 10^3$)[*], µV	Analysis time (min)
150	5.42	18.65
180	5.69	12.54
200	5.87	8.21
210	7.59	8.09
220	8.32	7.82

[*]5 replications, RSD<4%
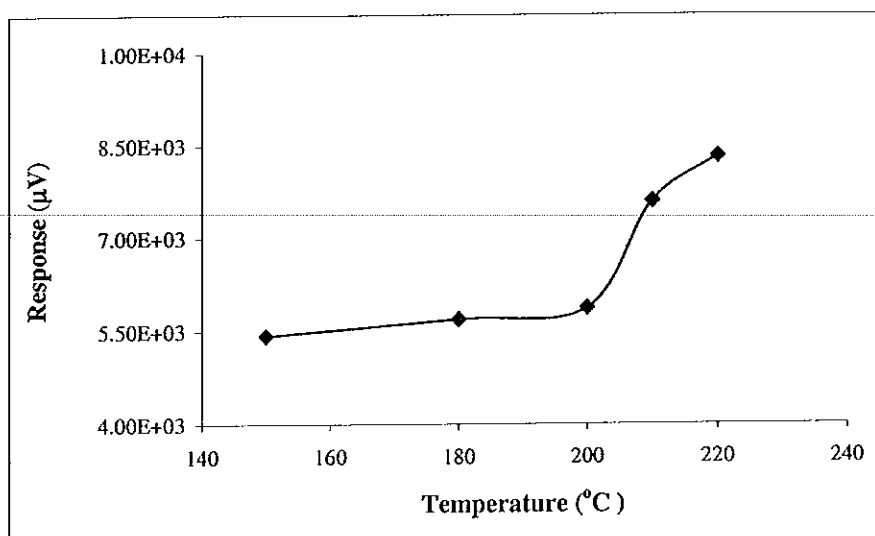
Figure 13 The response of 10 μg ml⁻¹, 3ml MTBE at different
injector/detector temperature

3.2 Optimization of the headspace analysis conditions

Gas chromatography is an analytical technique suitable for the investigation of volatile organic compounds. It is easy to introduce the sample into the analytical column if it is gas, but if the sample is liquid or solid sample preparation is required before introduction into the analytical system. To determine MTBE in air, the calibration of standard MTBE in gas phase must first be investigated. To transform the standard MTBE in the liquid form into a gas form the headspace technique was used as the sample preparation technique and the headspace parameters were optimized.

3.2.1 The equilibration time

In a headspace technique, standard MTBE solution is placed in closed container (vial) to establish an equilibrium condition between the standard solution and the gas phase above it (Figure 14). The volatile MTBE in the standard solution would be presented in the gas phase in contact with the solution. Its relative concentrations in the gas phase would depend on the

partial pressure which in turn could be influenced by the selection of temperature and time (Kolb and Ettre, 1997).

The equilibrate temperature and time were the main parameters influencing the headspace sensitivity. The equilibration time depended on the diffusion of the volatile components from and into the sample. This was optimized in experiment 2.3.4.1 and the results are shown in Table 10 and Figure 15. It can be seen that the response increased as the equilibration time increased from 10 to 20 min. During this time the MTBE in condense (liquid) phase was still partitioned into the gas phase, since the response increase as the time increase. After 20 min the response became steady. This is because when equilibrium is reached, the partition in gas phase is equal to the condense phase and the response will not change with longer time. This indicated that 20 min was the time the MTBE in the sample evaporated into the gas phase and reached the equilibrium. Therefore, 20 min was selected to be the optimum equilibration time.
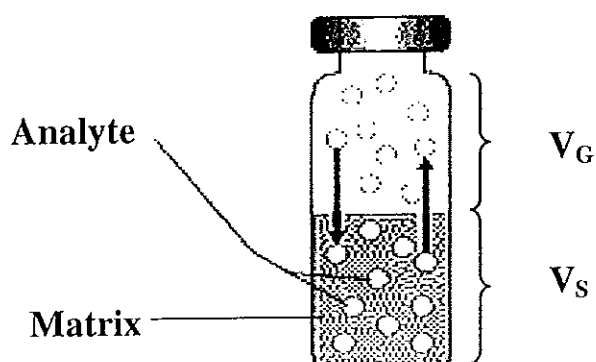
Figure 14 The headspace vial: V_G = volume of the gas phase and V_S = volume of the liquid sample

Table 10 The influence of the equilibration time on the response of

MTBE 10 $\mu g \ ml^{-1}$, 3 ml

Equilibration time (min)	Response $(\times 10^4)^*$, μV
10	1.18
15	1.19
20	1.22
25	1.22
30	1.21
40	1.22

* 5 replications, RSD< 4%
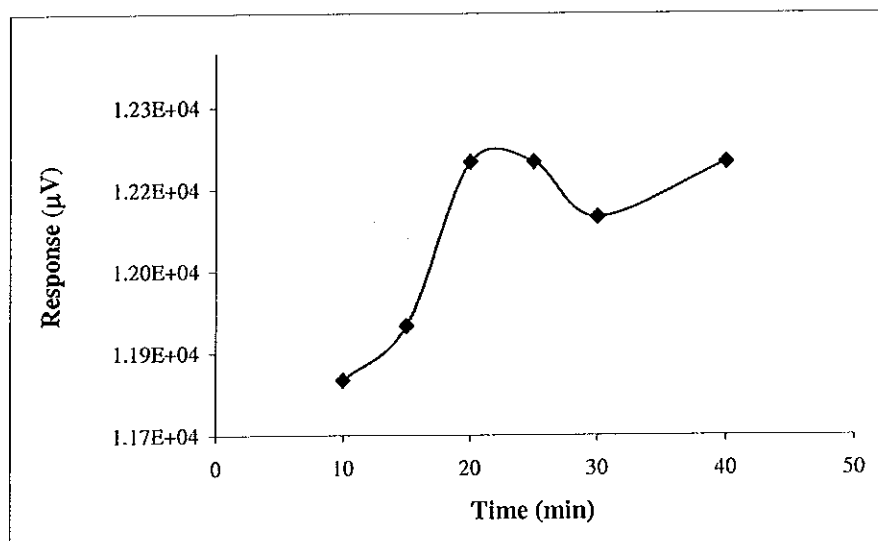
Figure 15 The relationship between the equilibration time and the response of

MTBE

3.2.2 The equilibration temperature

The effect of equilibration temperature was studied in experiment 2.3.4.2. The main criterion that must take account for is to avoid the sample decomposition. There are some samples that are sensitive to the high temperature and could either be decomposed or oxidized by the air in the headspace vial (Kolb and Ettre, 1997). Moreover, in static headspace analysis the increasing equilibration temperature that enhanced the evaporation of analyte into the gas phase could cause condensation problem. Hence, the equilibration temperature should be selected at the lowest temperature possible to avoid the condensation.

Table 11 and Figure 16 were the results of the effect of the equilibration temperature on the response of MTBE. The response increased as the equilibration temperature increased. At $80^{\circ}C$ the relative standard deviation (RSD) was much higher than the rest and this was due to two sources. One was because in this study the headspace system was done in an open water bath system. When operated at a high temperature setting the temperature of the water was not as steady as at lower temperature and the relative standard deviation increased. The other being the condensation in the syringe which was caused by the uncontrolled temperature of the syringe. To avoid this problem the ASTM standard practice recommended that the syringe should be put in an oven at $90^{\circ}C$ before sampling (Kolb and Ettre, 1997). However, this problem still occurred. Therefore, in this study the optimum equilibration temperature was chosen to be $70^{\circ}C$.

Table 11 The relationship of the equilibration temperature and the response of MTBE 10 $\mu g\ ml^{-1}$, 3 ml

Temperature (^oC)	Response (%RSD)[*], μV
40	9708 (2.0)
50	11807 (3.1)
60	13990 (3.0)
70	17234 (3.0)
80	26067(7.5)

[*]5 replications
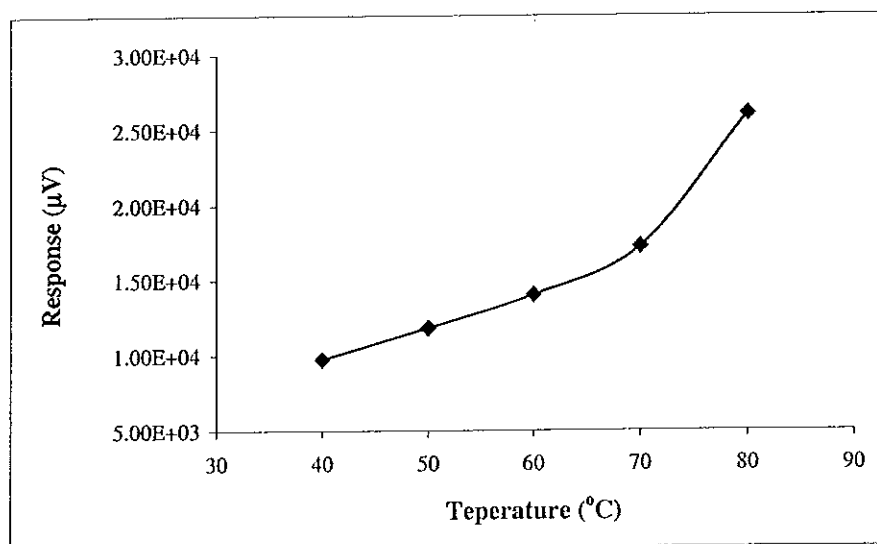
Figure 16 The relationship of the equilibration temperature and the response of MTBE 10 $\mu g\ ml^{-1}$, 3 ml

3.2.3 The phase ratio and the vial (volume) size

The phase ratio is the relative volumes of the two phases in the vial and can be expressed as

$$\beta = \frac{V_G}{V_S} \tag{6}$$

where V_G = volume of the gas phase

V_S = volume of the sample phase

V_V = total volume of the vial

Since

$$V_V = V_S + V_G \tag{7}$$

equation (6) can be expressed as

$$\beta = \frac{V_V - V_S}{V_S} \tag{8}$$

and

$$V_S = \frac{V_V}{1 + \beta} \tag{9}$$

From equation (8), the phase ratio decreases when the sample volume increases.

In a headspace analysis technique, the response or peak area obtained from the GC-FID is directly proportional to the concentration of the analyte in the headspace as follow

$$A \propto C_G = \frac{C_0}{K + \beta} \qquad (10)$$

where A = the peak area or response

     C_G = the headspace concentration

     C_0 = the original concentration of the analyte in the sample

     K = the distribution (partition) coefficient

     β = the phase ratio

According to equation (10), the headspace sensitivity (the obtained peak area) depends on the distribution coefficient (K) and the phase ratio (β). The headspace sensitivity increases as the distribution coefficient and the phase ratio decreases.

Experiment 2.3.4.3 investigated the effect of the phase ratio and the vial (volume) size and the results are shown in Table 12 and Figure 17. The sensitivity decreased as the phase ratio increased and the optimum phase ratio is at 0.5.

For the influence of the vial volume on the response of MTBE the results showed that the responses of the two difference size of vial, i.e. 60 ml and 10 ml, at the same phase ratio were not significant different. These results agreed well with Kolb and Ettre (1997), i.e. the headspace sensitivity was only depended on the concentration of the gas phase and not the vial volume. This was in contrast to the finding by Kotcharit (2002) who studied the relationship between the phase ratio and the vial volume and reported the decrease of the phase ratio (the headspace sensitivity increased) when the vial (volume) size decreased.

The optimum conditions for MTBE analysis on 2.1 m $\times$ 2.5 mm I.D. glass column packed with Super Q, 80/100 mesh are summarized in Table 13.

The chromatogram obtained using these optimum conditions is shown in Figure 18.

Table 12 The effect of phase ratio and the vial (volume) size of the response of MTBE 10 µg ml^{-1}

Phase ratio	Response ($\times10^4$)*, µV	
	Vial 60 ml	Vial 10 ml
0.5	1.66	1.76
1.0	1.54	1.55
1.5	1.47	1.43
2.0	1.38	1.40
3.0	1.37	1.39

*5 replications, RSD<4%
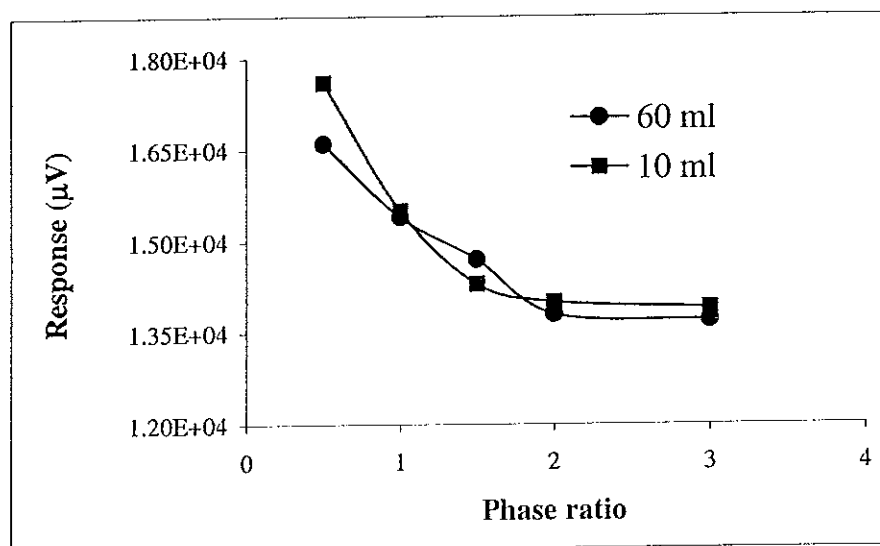
Figure 17 The effect of phase ratio and the vial (volume) size of the response of MTBE 10 µg ml^{-1}

Table 13 The optimum conditions of Headspace GC

Carrier gas flow rate	20 ml/min
Fuel gas (H_2) flow rate	20 ml/min
Oxidant gas (air) flow rate	200 ml/min
Column temperature	$220^{\circ}C$ (isothermal)
Injector/Detector temperature	$220^{\circ}C$
Equilibration time	20 min
Equilibration temperature	$70^{\circ}C$
Phase ratio	0.5
Vial (volume) size	10.0 ml
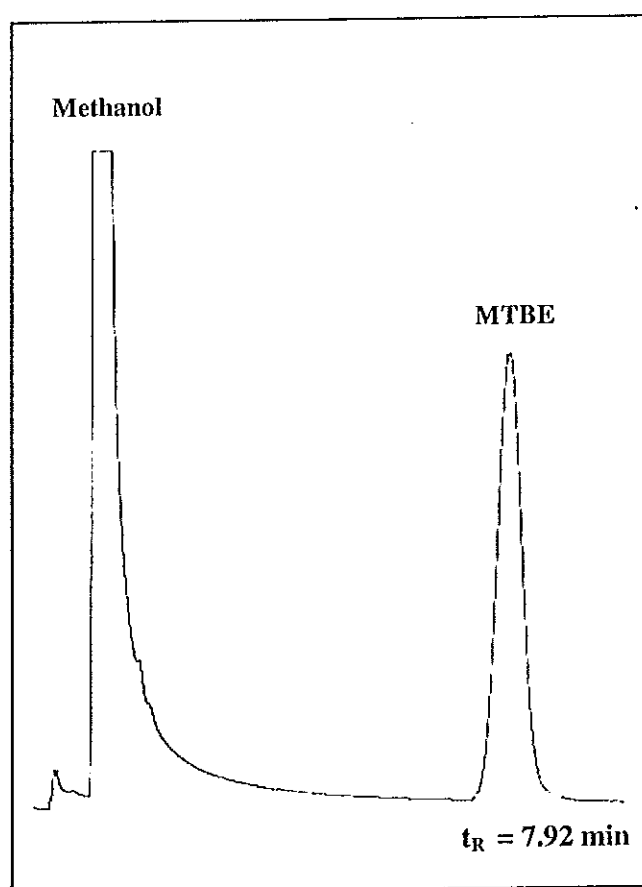
Figure 18 The chromatogram of MTBE, 10 μg ml^{-1} at the optimum conditions.

3.3 Linear dynamic range (linearity)

The linear dynamic range of MTBE was investigated by experiment 2.3.5 and the responses of various concentrations of standard MTBE were obtained (Table 14, Figure 19). Five replications were done for each concentration and the results showed high precision, with all relative standard deviations lower than 4%. The system provided a wide linear dynamic range from 2 to 1000 μg ml^{-1} with a very good correlation coefficient, $R^2 > 0.999$. This is better than that obtained by Lemley et al (1999) where the analysis was done by DB-FFAP column (30 m $\times$ 0.25 mm ID., film thickness 0.25 μm) with direct aqueous inject-GC-FID mode. The linearity in their work was in the range of 2.5-500 μg ml^{-1} with $R^2 = 0.949$.

Table 14 The relationship between the response and the various

MTBE concentration (μg ml^{-1})

Concentration (μg ml^{-1})	Response [*], μV
2.0	2186
4.0	5045
6.0	6653
8.0	7954
10.0	17529
30.0	52831
50.0	91056
100.0	176348
400.0	692465
800.0	1358012
1000.0	1654219

[*]5 replications, RSD<4%
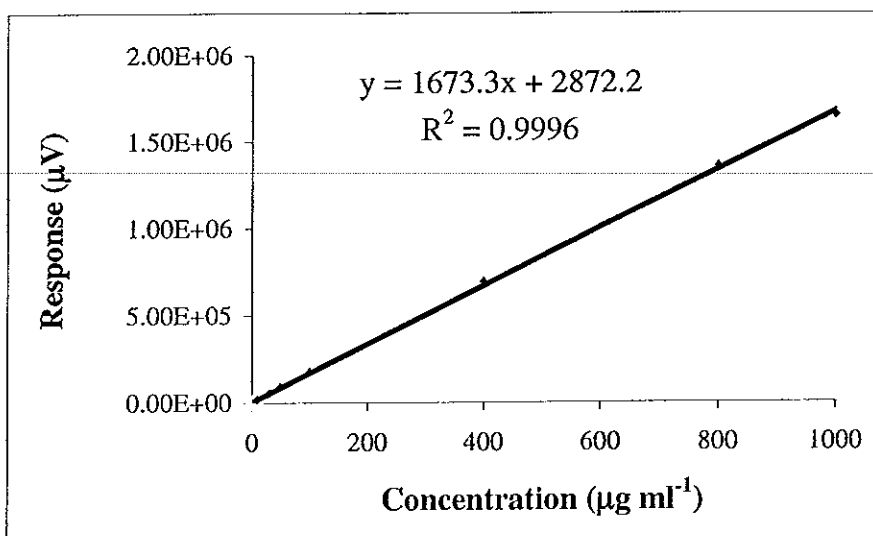
Figure 19 The linear dynamic range of MTBE

3.4 The limit of detection

The limit of detection is the lowest concentration or the weight of analyte which can be measured at a specific confidence limit (Kebbekus and Mitra, 1998).

The method used to investigate the limit of detection was the Taylor method (1987). The relationship between the standard deviation and the concentration of the standard solution (Table 15) was plotted as shown in Figure 20. The linear equation from this relationship was used to extrapolate the standard deviation at the concentration closed to 0 (S_0). The limit of detection was then defined as $3|S_0|$. The linear equation obtained from Figure 20 was $y = 9.71x-1.12$, i.e. $|S_0| = 1.12$, and the limit of detection of MTBE was 3.36 $\mu g\ ml^{-1}$

Table 15 The relationship between the standard deviation (SD) and the various MTBE concentration ($\mu g\ ml^{-1}$)

Concentration ($\mu g\ ml^{-1}$)	Standard deviation (SD)[*]
2.0	15.0
4.0	40.3
6.0	59.0
8.0	78.3
10.0	93.1

[*] 5 replications, RSD<4%
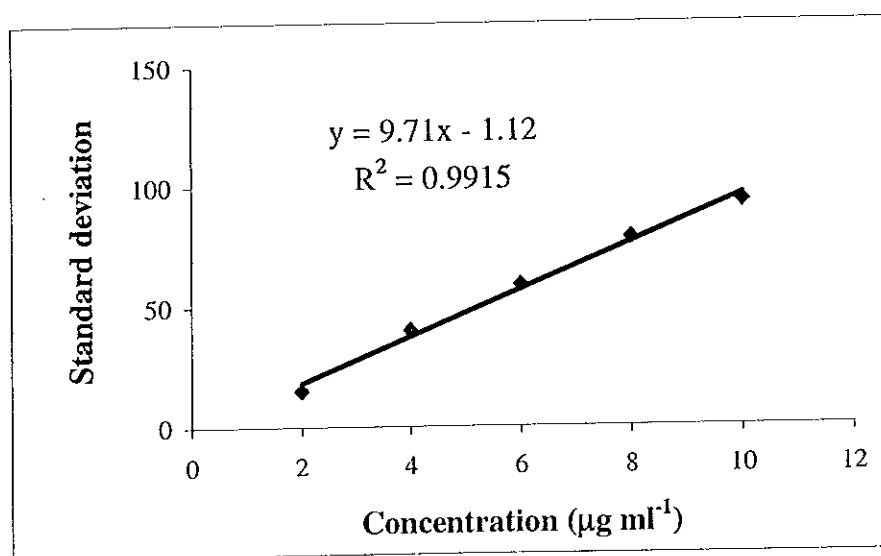
Figure 20 The limit of detection of MTBE with the optimum conditions

3.5 Sample preconcentration

Because the concentration of VOCs in ambient air was in the trace level, a preconcentration step is required for the instrumental determination. In this study MTBE in air was preconcentrated by adsorption in an adsorbent tube in an active sampling process. This was followed by thermal desorption. Chromosorb 106 was chosen as the adsorbent for MTBE analysis due to its property, *i.e.* it does not adsorb water vapour (Price and Saunder, 1984).

3.5.1 Conditioning of the adsorbent

Chromosorb 106, 60/80 mesh was conditioned in a lab-built apparatus in experiment 2.3.7.1. The conditioning process was done by purging nitrogen at 100 ml/min through the adsorbent under heat at 230°C for 1 hour. While conditioning, the adsorbent container (the round-bottom flask) was gently shaken occasionally to prevent the temperature gradient in the apparatus. The chromatogram obtained from the conditioned Chromosorb 106 (Figure 21) showed that the conditioning temperature of 230°C was enough to remove contamination that had retention time higher than 6 which could interfere with MTBE (retention time of MTBE was 7.92). This conditioning process (230°C, 100 ml/min) could removed the contaminant to a level lower than the condition recommended by the EPA compendium method TO-17 (250°C, 100 ml/min) (EPA, 1997).

$t_R = 5.17$ min
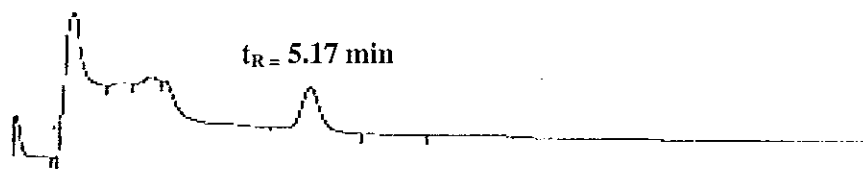
Figure 21 The chromatogram of the conditioned Chromosorb 106

3.5.2 Breakthrough volume

In the sampling process, the amount of analyte is directly proportional to the air sample volume. When using the adsorbent tube for sampling, the amount of the analyte from the atmosphere that could be concentrated in the adsorbent without being loss (called "sampling capacity") must be evaluted. The breakthrough volume (BTV), which generally considered as a parameter related to the sampling capacity, was defined as the volume sample when amount of analyte collected in the back section of sorbent tube reaches a certain percentage (typically 5%) of the amount collected in the front section (OSHA, 1997).

In this study, the air sample containing MTBE was generated by the lab-built apparatus. The air sample with MTBE in the headspace was drawn through the adsorbent tube by a calibration pump at room temperature as described in 2.3.7.3. The relationship between the percent breakthrough volume and the sampling volume is shown in Table 16 and Figure 22. The results indicated that the breakthrough volume of MTBE with Chromosorb 106, 60/80 mesh (100 mg) was 22 liters.

Table 16 The relationship between the % breakthrough volume of MTBE and the sampling volume with Chromosorb 106, 60/80 mesh (100 mg) [a]

Sampling volume (L)	% Breakthrough volume [b]
12.0	1.02
16.0	2.1
20.0	3.5
22.0	5.2
24.0	8.5

[a] Sample was 200 ng ml^{-1}, 100 ml MTBE spiked water

[b] 5 replication ,RSD < 10%
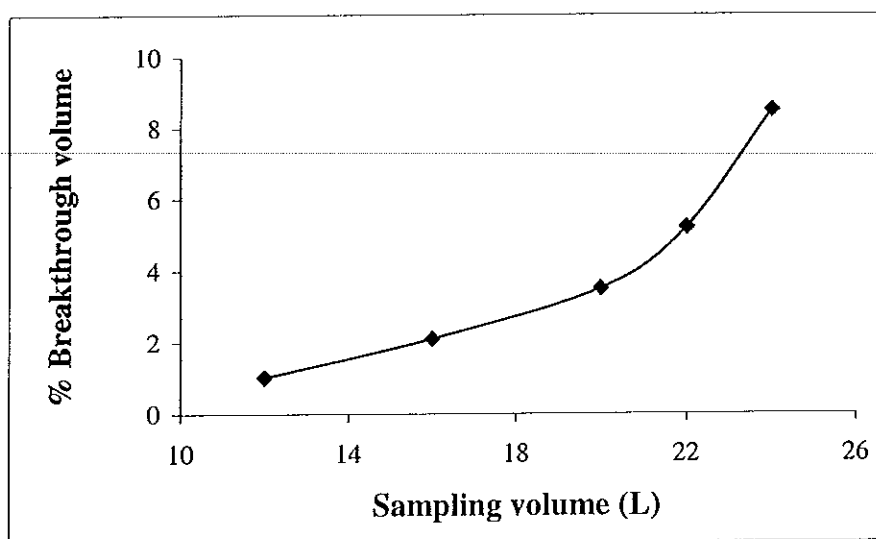
Figure 22 The % Breakthrough volume of MTBE with Chromosorb 106, 100 mg

3.5.3 Optimization of the flow rate through adsorbent

The flow rate through adsorbent (sampling flow rate) was an important parameter in sampling process because it would affect the adsorption efficiency of the adsorbent to MTBE. To optimize this the volatiled MTBE was drawn through the adsorbent tube (Chromosorb 106) with different flow rates *i.e.* 70, 100, 150, 200 ml/min (2.3.7.4). The influence of the flow rate on the response was shown in Table 17 and Figure 23. The highest response was obtained at 100 ml/min. After this flow rate the response decreased. At higher flow rate the retaining time of MTBE in the adsorbent tube decreased and this decreased the adsorption efficiency.

Table 17 The influence of the flow rate through adsorbent on the
response of MTBE

Adsorption flow rate (ml/min)	Response ($\times 10^4$)[*], μV
70	1.17
100	1.52
150	1.36
200	1.25

[*] 5 replications, RSD< 10%
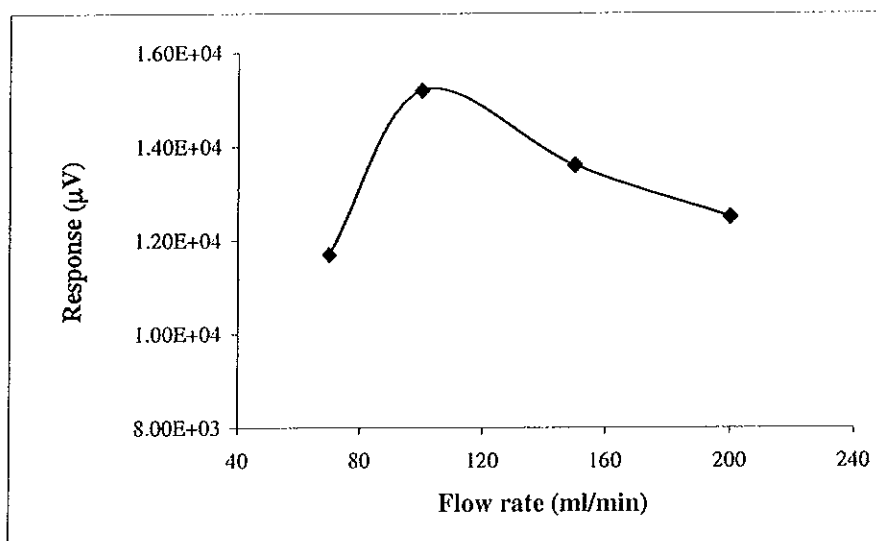
Figure 23 The influence of the flow rate through adsorbent on the response of
MTBE

3.5.4 Optimization of the adsorption time

To avoid the complication of generating the volatile MTBE (2.3.7.4-2.3.7.5) the spiked method was used to investigate the adsorption of MTBE in the adsorbent tube. Spiked liquid sample was prepared with an amount of MTBE equivalent to the adsorbed masses obtained from the study of the breakthrough volume (20 μg).

The adsorption time was the appropriate time for the spiked liquid MTBE to be completly evaporated and adsorbed in the front section of the adsorbent tube. By comparing the loss of analyte into the back section with the analyte adsorbed in the front section of adsorbent tube, the optimum adsorption time can be obtained. The effect of the adsorption time to the adsorption by the two sections of the adsorbent tube is illustrated in Table 18 and Figure 24. The response in the front section initially increased with the adsorption time and reached the highest response in 4 hours. After this time, the response in the front section decreased while the response in the back section increased. This indicated that when this test started, the spiked liquid MTBE became volatile and was adsorbed in the front section and the process was completed in 4 hours. After that MTBE diffused into the back section. Therefore, the optimum adsorption time for MTBE to be completely adsorbed in the front section with minimal loss to the back section was chosen as 4 hours.

Table 18 The effect of the adsorption time to the MTBE response in
each section of Chromosorb 106, 60/80 mesh adsorbent tube

Adsorption time (hour)	Response ($\times 10^4$)[*], μV	
	Front section	Back section
2.0	2.06	0.18
4.0	2.29	0.20
5.0	2.27	0.23
6.0	1.77	0.26
8.0	1.69	0.35
10.0	1.93	0.58
16.0	1.87	0.60

* 5 replications, RSD < 10%
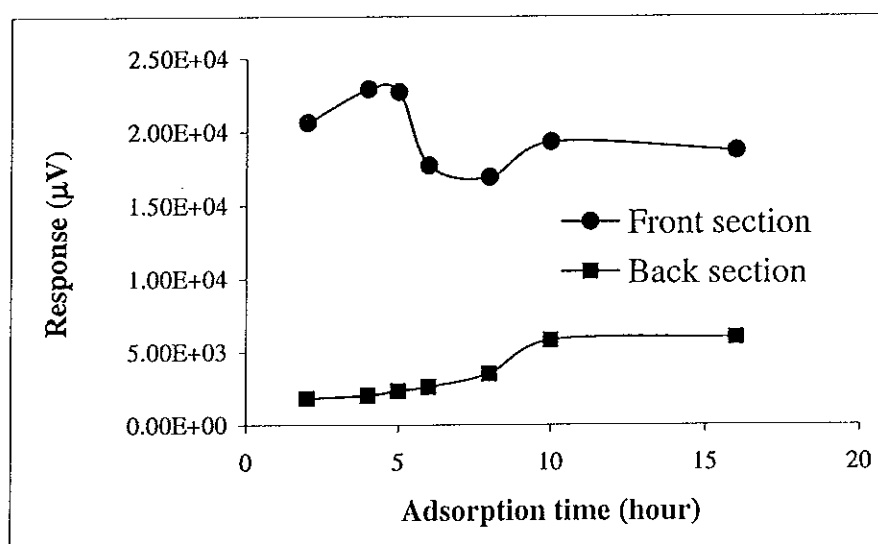
Figure 24 The effect of the adsorption time to the MTBE response in each
section of Chromosorb 106, 60/80 mesh adsorbent tube

3.5.5 The storage time of the adsorbent tube

After sampling, where the analyte was adsorbed by the adsorbent in the adsorbent tube, there may be a lag period before the analysis is carried out. This experiment was to determine whether there would be any loss of the analyte during storage. This was done by comparing the response of the adsorbed sample at 3 days intervals. Table 19 shows the response to MTBE at different storage time at ambient temperature and in the refrigerator. It can be seen that there is no significant decrease in the MTBE response during the storage of up to 15 days. This showed that MTBE adsorbed on Chromosorb 106, 60/80 mesh adsorbent bed is highly stable.

Table 19 The effect of the storage time of the adsorbent tube to the response of MTBE (average of 3 tubes, 5 replications/tube)

Storage time (day)	Average response ($\times 10^4$)[*], μV	
	Room temperature	Refrigerator
0	1.53	1.51
3	1.59	1.49
6	1.48	1.54
9	1.57	1.54
12	1.55	1.57
15	1.49	1.52

* 3 replications, RSD < 10%

3.6 The lab-built thermal desorption unit

In the previous study, trapped MTBE was desorbed by headspace technique. In the headspace desorption technique, the loss of adsorbed analyte can occur during the removal of the adsorbent from the tube. Also to re-use the adsorbent, the complicated process of re-conditioning and re-packing the adsorbent have to be carried out. Therefore, a lab-built thermal desorption unit was designed to thermally desorb the trapped MTBE in the adsorbent tube without removing the adsorbent from the tube. This desorption unit was operated as described in 2.3.8.

3.6.1 Calibration temperature of the lab-built thermal desorption unit

Prior to analysis, the temperature of the lab-built thermal desorption unit was calibrated to obtain the actual temperature. The calibration method was described in experiment 2.3.8.1 and the results are shown in Table 20.

For thermal desorption, several parameters must be optimized *i.e.*, the *desorption temperature, desorption flow rate* and *desorption time*. These parameters were optimized as described in experiments 2.3.8.2-2.3.8.4, respectively.

Table 20 The relationship between the set temperature and the actual
temperature of the lab-built thermal desorption unit

Set temperature at temperature control unit (^{o}C)	Actual temperature read from multimeter (SD)*, (^{o}C)
65	67 (1)
70	70(2)
100	97(1)
105	100(1)
110	105(1)
120	113(1)
125	116(1)
130	120(1)
165	150(1)
200	180(1)
226	200(3)
250	220(4)
260	230(4)

*10 replications after reached actual temperature

3.6.3 Optimization of the desorption temperature

To optimize the desorption temperature, the maximum allowable temperature of the adsorbent must be taken into consideration in order to prevent the damage to the adsorbent and to prolong its lifetime. The maximum temperature of Chromosorb 106 quoted by the manufacturer is 250°C and the conditioned temperature is at 230°C, then the desorption temperature must be lower than 230°C. In addition, the boiling point of the analyte is also an important parameter for the optimization the desorption temperature.

Therefore, in this study the desorption temperature was started from 70°C, higher than the boiling point of MTBE in order to ensure that MTBE could be complete eluted from the trap, and ended at 220°C.

The influence of the temperature on MTBE desorption is shown in Table 21 and Figure 25. The optimum temperature was taken as the minimum temperature that achieved the highest response and this was obtained at 200°C.

Table 21 The relationship between the desorption temperature and the response of MTBE

Desorption temperature (°C)	Response*($\times 10^4$), μV
70	1.25
100	1.70
120	2.60
150	2.94
180	3.66
200	3.83
220	3.54

* 5 replications, RSD < 10%
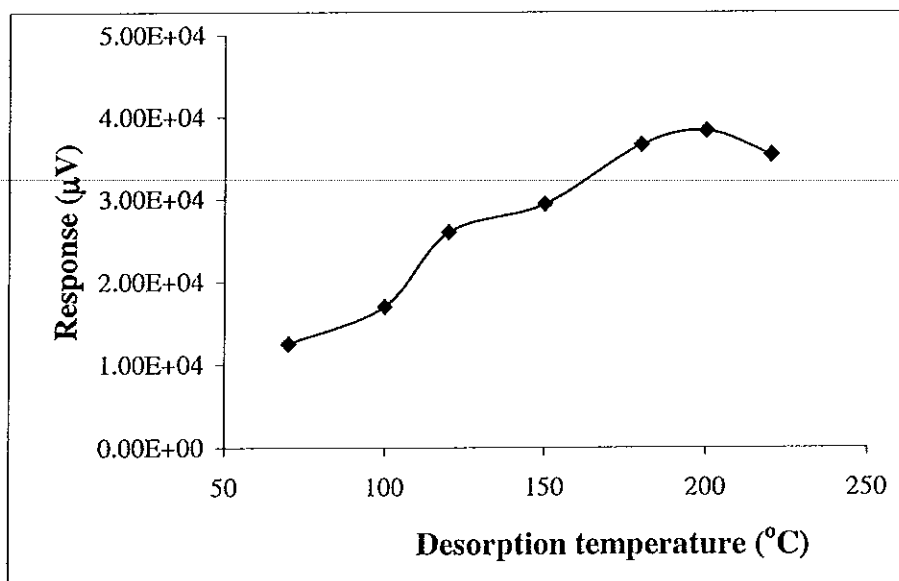
Figure 25 The relationship between the desorption temperature and the
MTBE response

3.6.4 Optimization of the desorption flow rate

The effect of the desorption flow rate on the elution of MTBE was
evaluated by running the system at different flow rates as indicated in
experiment 2.3.8.3. The results are shown in Table 22 and Figure 26 and it
could be observed that the desorption process increased with the desorption
flow rate up to 50 ml/min, and then declined. Therefore, the optimum
desorption flow rate was taken as 50 ml/min. This value agreed with Esteban *et
al.* (1993) who found that a high desorb flow rate would lead to a complete
elution of analyte from sample cartridge for both high and low volatility
compounds.

Table 22 The influence of desorption flow rate on the response of MTBE

Desorption flow rate (ml/min)	Response($\times 10^4$) *, μV
20	1.15
30	1.23
40	1.52
50	1.95
60	1.84

* 5 replications, RSD < 10%
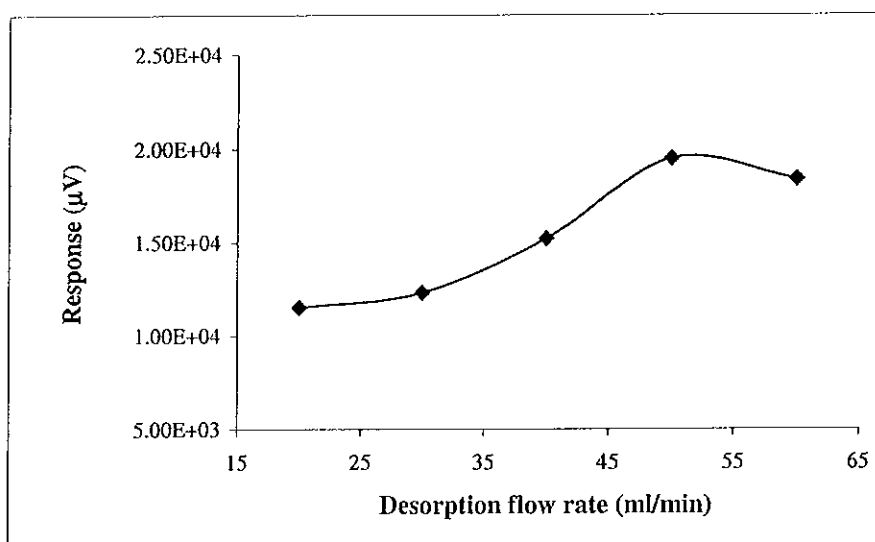
Figure 26 The influence of the desorption flow rate on the MTBE response

3.6.5 Optimization of the desorption time

The optimum desorption time was investigated between 10 to 30 minutes (2.3.8.4) and these are shown in Table 23 and Figure 27. The results showed that the response increased when the desorption time increased from 10 to 20 min, after which the response slightly declined. This indicated that the complete desorption process occurred at 20 minutes. Therefore the optimum desorption time was chosen as 20 minutes.

Table 23 The influence of desorption time on the response of MTBE

Desorption time (min)	Response($\times 10^4$)*, μV
10	1.75
15	1.86
20	2.07
25	1.98
30	1.96

* 5 replications, RSD < 10%
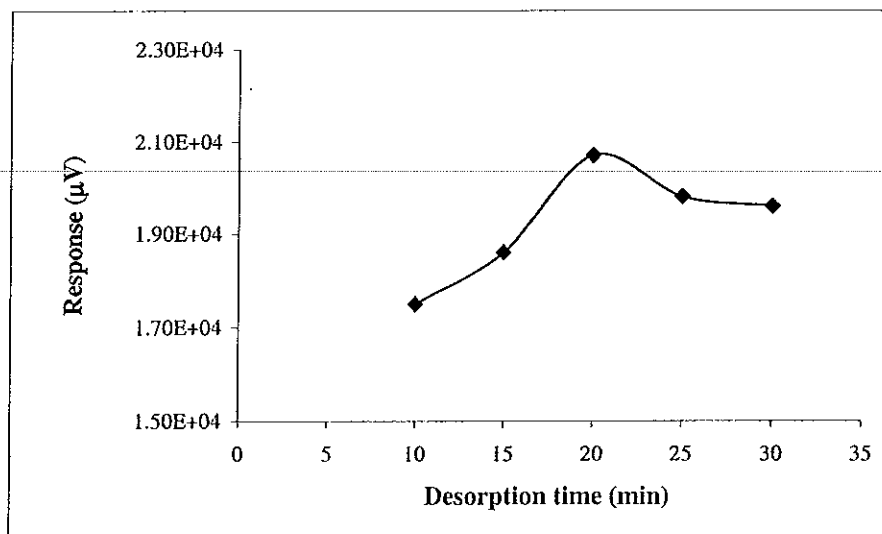
Figure 27 The influence of desorption time on the response of MTBE

3.7 The method calibration curve of Methyl *tert*-Butyl Ether (MTBE)

The standard MTBE solutions were prepared as described in experiment 2.3.9 and the calibration was investigated using micro-gram (μg) unit of eluted MTBE. The calibration curve was obtained by plotting the response against the weight of MTBE as shown in Table 24 and Figure 28.

Table 24 The relationship between the response and the various weight of MTBE (μg)

Weight of MTBE (μg)	Response($\times 10^4$) *, μV
10	1.34
20	2.41
50	5.58
80	8.43
100	10.02

* 5 replications, RSD < 10%
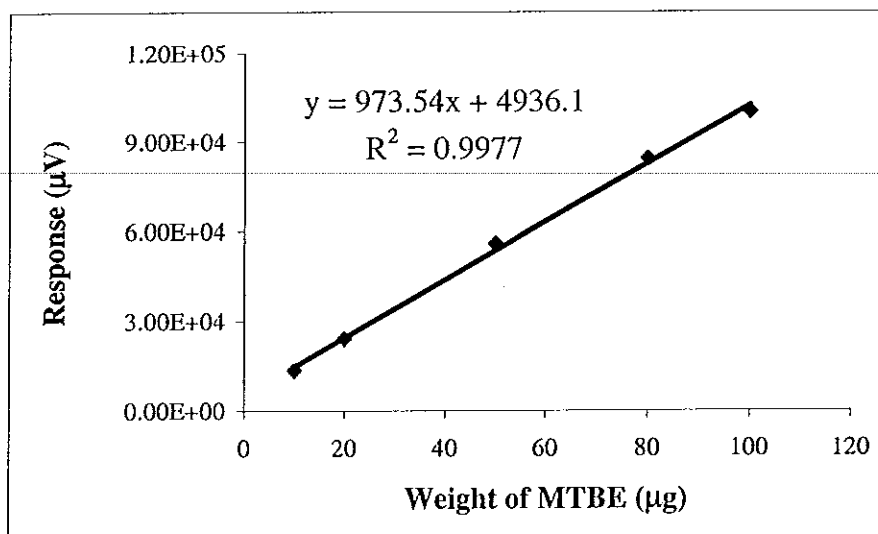
Figure 28 The method calibration curve

3.8 The correction factor

In order to account for the MTBE concentration that may have been lost during the adsorption-desorption process, the correction factor need to be determined (2.3.10). The MTBE standard curve of 100% adsorption - desorption efficiency was prepared and the results are shown in Table 25 and Figure 29. The comparison between the method calibration curve (Figure 28) with the standard curve of 100% adsorption-desorption efficiency is presented in Table 26. The results indicated that the highest recovery (48.57%) was obtained from 20 μg of MTBE, *i.e.* 51.43% of MTBE was lost during the adsorption-desorption process. To achieve the correct concentration of MTBE, the correction factor was determined by equation (11) and this was found to be 2.06. The correct concentration of MTBE was then obtained by multiplying the weight of MTBE determined from the method calibration curve (Figure 28) with 2.06.

$$\text{Correction factor} = 100/ \% \text{ of highest recovery} \qquad \textbf{(11)}$$

Table 25 The relationship between the response and the various

weight of MTBE (μg)

Weight of MTBE (μg)	Response($\times 10^5$)*, μV
10	0.29
20	0.48
30	0.69
50	1.47
100	2.45
200	5.17

* 5 replications, RSD < 10%
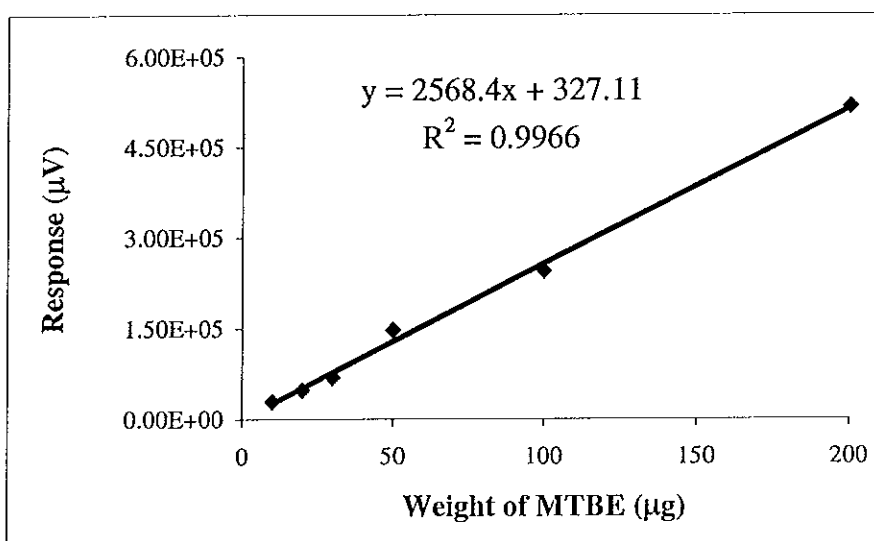
Figure 29 The standard curve of 100% adsorption-desorption efficiency

Table 26 The % recovery of MTBE

Weight of MTBE (μg)	% Recovery[*]
10	45.63
20	48.57
50	40.03
100	40.52

[*]5 Replications, RSD<10%

3.9 Qualitative and quantitative analysis of MTBE in air

3.9.1 Calibration of the flow rate for each channel of the adsorbent tube holding

The flow rate of each of the three channels of the adsorbent tube holding was calibrated as described in experiment 2.3.11.2 and the results are shown in Table 27. The differences of the average flow rate of each channel was about 5% with the %RSD of less than 2% for ten replications. The results indicated that this adsorbent tube holder has enough precision for triplicate sampling.

Table 27 Flow rates of the three channels of the adsorbent tube holding

Replication	Adsorbent tube holding flow rate (ml/min)		
	Channel1	Channel 2	Channel 3
1	102.86	101.98	98.63
2	103.75	101.12	99.44
3	106.51	100.28	97.56
4	104.96	101.98	98.36
5	105.88	100.28	98.36
6	103.75	104.05	101.12
7	103.75	103.75	100.27
8	102.86	101.98	97.83
9	106.51	103.75	101.12
10	105.88	101.98	99.45
Average	104.67	102.12	99.22
%RSD	1.39	1.34	1.30

3.9.3 The sampling sites

The sampling sites were selected by considering from the location and the number of vehicle refueling at each sampling site. The three selected sampling sites were:

Site 1: PTT gas station at Suppasarn-rungsun road, Hat Yai, Songkhla. This station located on the way to Hat Yai city, where the traffic was heavy with a lot of refueling vehicle. The station has twelve petrol pumps.

Site 2: Bangchak gas station in Prince of Songkla University, Hat Yai, Songkhla. There are four petrol pumps

Site 3: Caltex gas station at Tambol Kor Hong, Hat Yai, Songkhla. This station also located along the road with a heavy traffic. There are eight petrol pumps but there are very few vehicles refueling at this site.

3.9.4 The sample collection

The sample collections were done as described in experiment 2.3.11.3. The collected samples in the adsorbent tubes were analysed using the optimum conditions. The parameters at all sampling sites are shown in Table 28 and results from the analysis are shown in Table 29.

Table 28 Parameters at all sampling sites

Sampling site/ Date	Time*	Temperature (°C)	Wind velocity (km/hr)	Car	Motorcycle
1/17 Oct.	AM	29.8-33.9	1.0-2.5	51	104
2002	PM	29.8-31.8	0.0-3.8	51	245
1/18 Oct.	AM	27.4-31.8	0.0-0.7	52	132
2002	PM	31.7-34.4	0.0-2.0	54	203
2/22 Oct.	AM	25.7-29.3	1.0-2.4	44	61
2002	PM	26.4-30.1	0.9-2.3	51	72
2/23 Oct.	AM	26.8-32.5	0.0-2.3	24	34
2002	PM	25.7-27.3	0.0-4.1	34	50
3/24 Oct.	AM	27.3-31.5	0.0-3.4	12	10
2002	PM	25.5-28.2	0.0-2.0	11	17
3/25 Oct.	AM	25.8-29.7	0.0-3.0	11	26
2002	PM	29.3-31.3	0.0-3.6	9	20

* AM : In the morning between 7.00 and 9.34 am

PM : In the evening between 4.00 and 6.34 pm

Table 29 The MTBE concentration in three gas station sampling sites

Sampling site/ Date	Time	MTBE $(mg/m^3)^a$
1/17 Oct. 2002	Morning	N.D.[b]
	Evening	1.63
1/18 Oct. 2002	Morning	1.47
	Evening	1.51
2/22 Oct. 2002	Morning	0.97
	Evening	1.02
2/23 Oct. 2002	Morning	0.78
	Evening	0.82
3/24 Oct. 2002	Morning	0.36
	Evening	0.45
3/25 Oct. 2002	Morning	0.47
	Evening	0.39

[a] 3 Replications, %RSD <10

[b] N.D. = Not detectable

From the analysis, MTBE concentration was ranging from not detectable (N.D.) to 1.63 mg/m^3 (Table 29).

The highest concentration (1.63 mg/m^3) was detected at sampling site 1 on the day with highest refueling vehicles (51 cars + 245 motorcycles) and the lowest concentration (0.36 mg/m^3) was detected at sampling site 3 where refueling vehicles were the lowest (12 cars + 10 motorcycles). From this, it could be concluded that the concentration of MTBE was directly related to the number of refueling vehicles (Table 28).

Since the ambient temperatures between the morning and evening (Table 28) were not significant different. It did not play an important part in the

amount of MTBE detected (Table 29) like that reported by Periago, *et al.* (1997).

The nondetectable concentration of MTBE at site 1 on the first morning (17 Oct. 2002) was possibly due to two main factors:

- Uses of different adsorbent tubes. On that occasion the adsorbent tubes used to calibrate the sampling flow rate were not the same as the ones used during sampling. To prevent diffusion of MTBE into the real adsorbent tube before sampling, the sampling flow rate through adsorbent tubes were calibrate in the lab prior to sampling to a value of 100 ml/min. Different tubes were then used during sampling at the same pump setting. It was later found out that the flow rate through the sampling tubes was significantly lower than the calibrated 100 ml/min. That is less air was passing through the tube and, hence, less MTBE was adsorbed.

- Sampling position. The position of the sampling unit was placed near a petrol pump. However, it just happened that there were very few vehicles refueling at the petrol pump where the sampling unit was located since it was a diesel pump. These, in effect, reduced the amount of MTBE in the air. Since MTBE concentration depended on the number of refueling vehicles or volumes of gasoline sold (Vainiotalo, 1998).

To get over the first problem, in other samplings the same tube was used to calibrate the sampling flow rate and for the sampling. The calibration was done at the sampling site immediately before sampling. The sampling point was also shifted to the petrol pump that had more refueling vehicles (benzene 95 pump). This new sampling point was used for the next three samplings at sampling site1 where high concentrations of MTBE were detected.

In order to confirm that the amount of MTBE detected was related to the number of the refueling vehicles at the sampling point, the number of vehicles refueling at the sampling petrol pump was counted (on a

later date) and compared to the total number of vehicles refueling in each gas stations. The results were shown in Table 30-32.

Table 30 The number of vehicles refueling at PTT gas station (sampling site 1) on 15 January 2003, at the two sampling points compared to the total number of vehicles

Time	Total number of vehicle	At benzene 95 pump		At diesel pump	
		Number of Vehicle	$\%^*$	Number of vehicle	$\%^*$
Morning[a]	198	110	55.56	3	1.5
Evening[b]	230	123	53.47	1	0.43

$^*\%$: The percentage of the number of vehicles refueling at the sampling point compared to the total number of vehicles refueling in this sampling site.

[a]: 7.00 - 9.34 am

[b]: 4.00 - 6.34 pm

Table 31 The number of vehicles refueling at Bangchak gas station (sampling site 2) on 16 January 2003, at the sampling point compared to the total number of vehicles refueling in this sampling site

Time	Total number of vehicle	At sampling point	
		Number of vehicle	$\%^*$
Morning[a]	136	80	58.82
Evening[b]	195	125	64.10

$^*\%$: The percentage of the number of vehicles refueling at the sampling point compared to the total number of vehicles.

[a]: 7.00 - 9.34 am

[b]: 4.00 - 6.34 pm

Table 32 The number of vehicles refueling at Caltex gas station (sampling

site 3) on 17 January 2003, at the sampling point compared to the

total number of vehicles

Time	Total number of vehicle	At sampling point	
		Number of vehicle	%[*]
Morning[a]	41	23	56.10
Evening[b]	48	27	56.25

[*]%: The percentage comparison between the number of vehicles refueling in

the sampling point and all number of vehicles refueling in this sampling

site.

[a]: 7.00 - 9.34 am

[b]: 4.00 - 6.34 pm

It can be seen from Table 30 that the percentage of vehicles refueling at the diesel pump, which gave non detectable result, was very much lower that at the Benzene 95 pump that gave high values of MTBE (Table 29).

Table 30-32 also show that, the number of vehicles refueling at all the sampling points are high and were in the range of 54-64 % of the total number of refueling vehicles. This confirmed that the concentrations of MTBE in all sampling sites were directly correlated to the number of refueling vehicles.

Chapter 4

Conclusions

A method for MTBE analysis was developed. The analysis was carried out using a gas-solid chromatographic coupled with a headspace techniques. Samples were preconcentrated by active sampling using adsorbent tubes with thermal desorption. The results demonstrated that qualitative and quantitative analysis of trace level of MTBE in air could be obtained with high precision.

In the gas-solid chromatographic technique, MTBE standard gas was prepared by a headspace technique using an in-house water bath and was analyzed with a packed glass column of 2.1 m × 2.5 mm ID., Super Q, 80/100 mesh and a flame ionization detector (FID). The optimum conditions for the GC technique were, carrier gas flow rate 20 ml/min, column temperature 220°C (isothermal), injector/detector temperature 220°C, and flow rate ratio of hydrogen and air 20:200 ml/min. For the headspace technique, the optimum conditions were, equilibrium time 20 minutes, equilibrium temperature 70°C, phase ratio 0.5, and vial volume 10 ml. These optimum conditions provided a short analysis time (10 minutes), low detection limit (3.36 μg ml^{-1}), and a wide linear dynamic range (2-1000 μg ml^{-1}) with a linear regression (R^2) of more than 0.999. However, the detection limit of this system was not low enough to analyze the MTBE in air that was normally lower than ppm level.

To improve the detection limit of this system MTBE in air was preconcentrated in an adsorbent tube and thermally desorbed. The sampling, preconcentrating and desorbing were all done by the lab-built systems. These simple and low cost lab-built systems allowed MTBE in air to be analyzed. Air sampling and MTBE preconcentration could be done in a single step, directly at the sampling site. MTBE in air was preconcentrated in an adsorbent tube packed with conditioned Chromosorb 106, 60/80 mesh. This non-polar

adsorbent minimized the water vapor interference, the main problem for air analysis. Conditioned Chromosorb 106 also showed low contamination and good storage stability.

In the thermal desorption step, the trapped MTBE in the adsorbent tube was desorbed at 200°C for 20 minutes with a desorption flow rate of 50 ml/min. In this procedure there was no significant interference that affected the MTBE analysis. However, some MTBE was lost during the adsorption-desorption process. A correction factor of 2.06 was obtained from the comparison between the method efficiency with the 100% adsorption-desorption efficiency and this was used to calculate the correct MTBE concentration.

For qualitative and quantitative analysis of MTBE in real sample, the air sample was collected from three sampling sites (gas stations in Hat Yai, Songkhla) by using lab-built adsorbent tube holding for triplicate sampling. MTBE concentrations were in the range of 0.36 mg/m^3 to 1.63 mg/m^3 with the relative standard deviation (% RSD) lower than 10%. There was a significant relationship between the number of refueling vehicles and MTBE concentration.

In conclusion, this developed method, with the lab-built sampling and preconcentration systems, provided both qualitative and quantitative analysis of MTBE. The advantages of these systems are, the sample can be analyzed without the use of organic solvent, low cost and simple to use for analysis MTBE in air.

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