The Effect of High Temperature on Styrene Monomer Migration from Polystyrene Cup

by

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Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Mechanical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(MECHANICAL ENGINEERING)

Approved by,

_____
(Dr Puteri Sri Melor bt Megat Yusoff)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2008

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

_____

MUHAMMAD SHAFIQ BIN MAT SHAYUTI

ABSTRACT

Polystyrene (PS) cup was characterized thermally and chemically before being tested for its styrene monomer migration behavior under the influence of temperature. The difference in thermal properties measured and the pure PS with PS cup may have been due to the additives employed during the manufacturing of the cup. Fourier transfer infrared spectroscopy (FTIR) test results showed the chemical compounds that made up the PS cup, such as aromatic compound and also substitution pattern of benzene ring. There were 2 types of stimulants employed in the study namely distilled water and cooking oil. PS cups containing the liquid stimulants were placed in an oven with temperature ranging from room temperature to 100°C with 25°C increment for each sample. Cooking oil was selected as a liquid stimulant in the study because oil simulated the fatty medium, while distilled water simulated the aqueous medium of beverages. Gas chromatography-mass spectrometry (GC-MS) detected styrene traces in the cooking oil and not in distilled water at all temperatures. In general as temperature increased, the migration of styrene from the PS cup into the cooking oil also increased. As the temperature increased, the molecules move faster due to higher kinetic energy and therefore collide more frequently. Thus, the proportion of collisions that could overcome the activation energy for the reaction increased with temperature, resulting in higher migration rate. However, at temperature above 75°C, the migration rate jumped relatively high, suggesting the possibility of the PS cup's wall damage, which could enhance and facilitate the styrene migration. In addition styrene solubility in the cooking oil may have increased significantly beyond 75°C, resulting in higher styrene migration. Arrhenius equation was used to analyze and model the relationship between temperature and the amount of styrene migration. From the experiment, the highest styrene migration resulted in styrene content in cooking oil of only 1.12×10^{-4} weight percent. This was well below the maximum allowable limit of 0.5 weight percent.

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CHAPTER 1
INTRODUCTION

1.1 Background

Polystyrene (PS) is a type of polymer made from styrene monomer, a liquid hydrocarbon that is manufactured from petroleum by the chemical industry. Polystyrene is widely used as food and beverages packaging material for many years because polystyrene has suitable properties such as low density, high thermal insulation, good strength, and easy to be formed. Besides that, other applications of polystyrene in non-food area are television and computer cabinets, compact disc "jewel boxes", and audiocassette cases.

PS cup is normally used to hold beverages, cold or hot because it has high thermal insulation ability, hence the ability to maintain the beverage's temperature for a considerable time. Many beverage companies and individual serve beverages in PS cup, be it water, coffee, tea, carbonated drinks, and many more. Even hot soup, instant noodles, and mashed potato are sometimes prepared and consumed in PS cup.

However, there is possibility that styrene monomers from polystyrene can migrate into beverages it holds. Styrene monomer is dangerous for human health. Short-term exposure can result in mucous membrane and gastrointestinal effects. Whereas long term exposure in humans results in negative effects on the central nervous system, causing headache, fatigue, weakness, depression, central nervous system dysfunction, hearing loss, and peripheral neuropathy. Although it has not yet been cited as carcinogenic, but several studies suggest there may be an association between styrene exposure and an increased risk of leukemia and lymphoma [1].

1.2 Problem Statement

Polystyrene (PS) cup has been used widely in the food industry due to its convenience and low cost. However, the possibility of chemical migration or leaching from the cup to the drink has caused panic on the consumer side as the chemicals may be carcinogenic. In addition, the effect of using PS cup to hold hot beverages also has been speculated to accelerate the chemical migration. Hence, this project was initiated to investigate further on the effect of high temperature on chemical migration and composition of PS cup.

A few lessons learnt from past research works were implemented in this research project. Although generally many past research works studied the styrene migration from PS cup/container, but none has taken temperature as the key parameter. Hence this project was focused on the effect of high temperature on the migration of styrene from the PS cup.

1.3 Objective

The objective of this project is to study the effect of high temperature on the styrene monomer migration from the PS cup. The relationship of styrene migration with respect to temperature will be investigated. The findings of this study will conclude whether or not PS cup is safe to hold beverages at high temperature.

1.4 Scope of Study

The range of temperature used in this project was between 25°C to 100°C. Since most all hot drinks prepared and served in PS cup are around 75°C to 100°C, hence it is not realistic to have a temperature higher than 100°C. Furthermore, PS cup is unstable at temperature higher than 100°C. The scope of study of this project is limited to find any trace of styrene monomers that might be migrated from PS cup into the liquid samples, under the influence of high temperature.

The brand of PS cup under studied was ‘Zhaori’, and it was assumed to be a standard PS cup available in the market. As for the liquid stimulants, only cooking oil and distilled water were used. The cooking oil was a palm oil of ‘Vesawit’ brand, and the distilled water was collected from a single source throughout the experiment.

Other parameters were kept constant throughout the experiment. For example, time duration, volume of cooking and distilled water used, area of PS cup exposed to liquid stimulants, and machines used. This was to ensure the accuracy of the results obtained.

CHAPTER 2
LITERATURE REVIEW

2.1 Polystyrene

Polystyrene is an aromatic polymer made from the aromatic monomer styrene. In terms of its chemical structure, it is a long chain hydrocarbon with every other carbon connected to phenyl group as shown in Figure 2.1 [2].

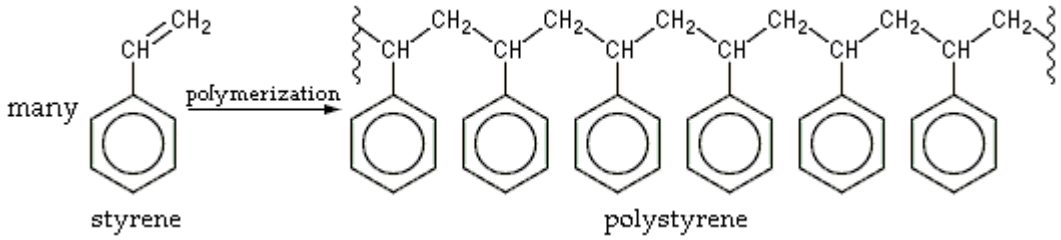

Figure 2.1: Chemical structure of polystyrene

The properties of the polystyrene are summarized in Table 2.1 [3].

Table 2.1: Properties of polystyrene.

Property	Value
Density	1050 kg/m^3
Specific gravity	1.05
Glass temperature, T_G	95 °C
Melting temperature, T_M	240 °C
Heat transfer coefficient	0.17 W/(m^{2}K)
Specific heat	1.3 kJ/(kg·K)

Polystyrene's most common use is as expanded polystyrene (EPS). Expanded polystyrene is produced from a mixture of about 90-95% polystyrene and 5-10% gaseous blowing agent, most commonly pentane or carbon dioxide. The solid plastic is expanded into foam through the use of heat, usually steam. Polystyrene cup is also made up of expanded polystyrene [4].

2.2 Styrene Monomer and Its Effects on Human Health

Polystyrene is manufactured by polymerization process of styrene monomers. Styrene is an organic compound with chemical formula $C_6H_5CH=CH_2$. This aromatic hydrocarbon is in a form of oily liquid under normal condition. It can evaporate into the air easily and has a sweet smell. In addition, styrene is soluble in lipid/fat, alcohol, and vitamin A [5].

Since the polymerization process is not 100% efficient, there will be some unprocessed styrene monomers left in the cup [2]. Styrene is categorized as possible carcinogenic and will affect one's health if exposed to consistently. Environment Protection Agency (EPA) claims short-term exposure will result in mucous membrane and eye-irritation, and gastrointestinal effects. While long-term exposure results in negative effects on the central nervous system such as headache, fatigue, weakness, and depression [6]. It will also lead to central nervous system dysfunction, hearing loss, and peripheral neuropathy. Furthermore, several epidemiologic studies suggested there might be an association between styrene exposure and an increased risk of leukemia and lymphoma [7].

Studies suggested that styrene mimics estrogen in the body and can therefore disrupt normal hormone functions, possibly contributing to thyroid problems, menstrual irregularities, and other hormone-related problems, as well as breast cancer and prostate cancer. The estrogenicity of styrene is thought to be comparable to that of Bisphenol A, another potent estrogen mimic from the world of plastics. Long-term exposure to small quantities of styrene is also suspected of causing low platelet

counts or hemoglobin values, chromosomal and lymphatic abnormalities, neurotoxic effects due to accumulation of styrene in the tissues of the brain, spinal cord, and peripheral nerves, resulting in fatigue, nervousness, difficulty sleeping, and other acute or chronic health problems associated with the nervous system. The International Agency for Research on Cancer listed styrene as a possible human carcinogen, though this conclusion was primarily based on studies of workers in styrene-related chemical plants. The Vallombrosa Consensus Statement on Environmental Contaminants and Human Fertility Compromise included styrene on its list of contaminants of possible concern [8].

2.3 Equipment and Samples

There were several equipments used in this research project. They were differential scanning calorimeter (DSC), fourier transform infrared spectroscopy (FTIR), and gas chromatography mass spectrometry (GC-MS).

2.3.1 Differential Scanning Calorimeter (DSC)

Differential scanning calorimeter (DSC) was used to determine the thermal properties of PS cup such as glass temperature (T_G) and melting temperature (T_M). This study employed differential scanning calorimetry, which is thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions [9], [10], [11]. The result of a DSC

experiment is represented as a curve of heat flux versus temperature or versus time as shown in the Figure 2.2.

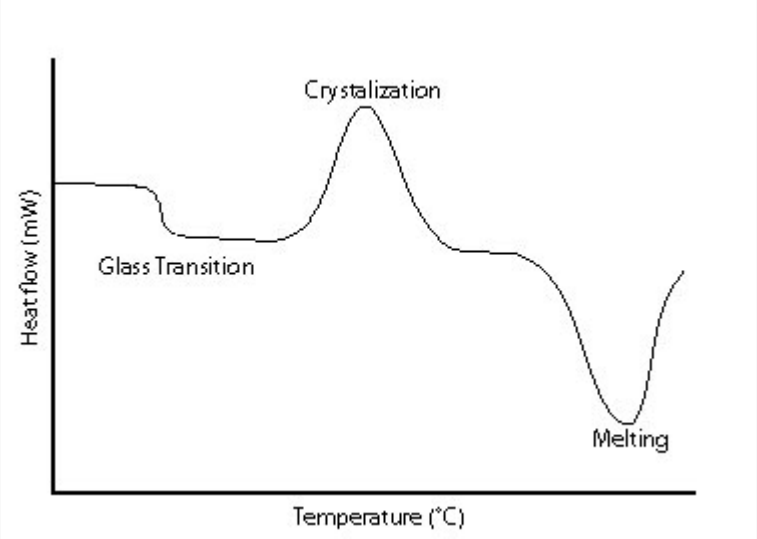

Figure 2.2: A schematic DSC curve demonstrating the appearance of several common features

It was important to characterize the PS cup in this study thermally to determine its glass transition and melting temperature, so the methodology for this project could be designed accordingly. The glass transition and melting temperature will determine the temperature range of liquid stimulants in the experiment. Generally, glass temperature of polystyrene is around 95^{o}C and its melting temperature is about 240^{O}C [12].

2.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a device that applies fourier transform spectroscopy measurement technique to a sample whereby spectra are collected. The spectra data then will be interpreted and the result shall give the chemical composition of the sample. In infrared spectroscopy, infrared radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission,

creating a molecular fingerprint of the sample. Like a fingerprint, no two unique molecular structures produce the same infrared spectrum [13], [14], [15]. Infrared spectroscopy is a popular method for identifying polymers. It may be used to identify the composition of polymers, to monitor polymerization process, to characterize polymer structure and many more [16]. With regard to his project, the chemical composition of PS cup will be obtained, and the rest of the experimental design will be based on that information.

2.3.3 Gas Chromatography Mass Spectrometry (GC-MS)

GC-MS is a machine that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances within a test sample. This equipment since was used to trace for any styrene monomer in liquid stimulants from the experiment [17].

GC-MS is composed of two major parts, the gas chromatograph and the mass spectrometer. The gas chromatograph utilizes a capillary column which depends on the column's dimensions (length, diameter, film thickness) as well as the phase properties. The difference in the chemical properties between different molecules in a mixture will separate the molecules as the sample travels the length of the column. The molecules take different amounts of time (called the retention time) to come out of (elute from) the gas chromatograph, and this allows the mass spectrometer downstream to capture, ionize, accelerate, deflect, and detect the ionized molecules separately. The mass spectrometer does this by breaking each molecule into ionized fragments and detecting these fragments using their mass to charge ratio. The schematic of GC-MS is shown in Figure 2.3 [18].

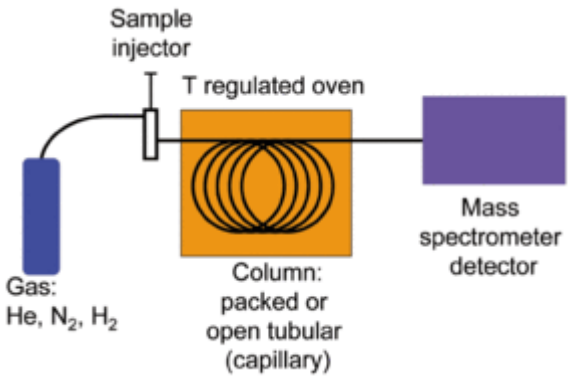

Figure 2.3: A schematic of GC-MS

2.4 Past Researches

There are a few past and on-going research works focusing on the possible migration of styrene monomer into beverages/food and the health affects it brings. One study indicated a migration of styrene from a polystyrene cup into the beverage it contained as high as 0.025 wt% for a single use [8]. That may seem like a very little amount, but if a person drinks beverages from polystyrene cups four times a day for three years, he/she may have consumed about one foam cup's worth of styrene along with the beverages. However, the existing regulation in the United States permits up to 1 wt-% or equal to 10,000 ppm by weight of the styrene monomer in food-grade PS, except that when used in contact with fatty foods not more than 0.5wt-% styrene monomer is allowed [19]. Hence the finding is still in accordance to the standard.

EPA National Human Adipose Tissue Survey for 1986 identified styrene residues in 100% of all samples of human fat tissue taken in 1982 in the United States. Styrene is used to make polystyrene plastic and is a contaminant in all polystyrene foam packages. A 1988 survey published by the Foundation for Advancements in Science and Education also found styrene in human fatty tissue with a frequency of 100% at levels from 8 to 50 nanograms/gram (ng/g) [20]. The 350 ng/g level is one third of the level known to cause neurotoxic symptoms. The cups apparently lost weight

during their use. The study showed that tea with lemon produced the most marked change in the weight of the foam cup.

In 1979, University of Connecticut reported a discovery that lemon tea erodes polystyrene cups. However no polystyrene could actually be detected in the lemon tea. Woodrow C. Monte later confirmed the findings. The study added that polystyrene dissolved in the lemon actually disappeared from the solution. Using polystyrene tagged with radioactive carbon in its molecular structure, it was found that the dissolved polystyrene stuck firmly to the walls of the container. After 20 minutes, up to 98 percent of the polystyrene experimentally introduced was found on the cup, which was apparently acting as an adsorbent for its solvent, the lemon oil [21].

The amount of styrene in the food is directly proportional to the fat content of the food and inversely proportional to the size of the container [8]. This is because larger containers would expose a lower percentage of the food to the container. The results of the experiment are shown in Table 2.2.

Table 2.2: Level of styrene detected on packaged food [8].

Processed Food	Styrene level (ppb)
Milk and cream	134
Yogurt	26
Desserts	22
Soft cheese	16

Styrene migration has been shown to be partially dependent on the fat content of the food in the PS cup. The higher the fat content, the higher the styrene migration into the food. Hence, soups, or beverages that are higher in fat will dissolve more of the styrene out of the polystyrene cup than water. Some compounds found in beverages,

like alcohol or the acids in "tea with lemon," may also raise the styrene migration rate. Styrene also appeared to migrate more quickly when foods or drinks are hot [8].

There are several reasons why styrene-based cups could be a source of contamination. First, the styrene monomer, a colorless or yellowish oily liquid, is the feedstock in the manufacture of polystyrene. Since the manufacturing process is not 100% efficient, polystyrene contains some residual styrene. Second, styrene is soluble in oil and ethanol, substances commonly found is foods and alcoholic beverages. In 1985, a study noted migration of monomers from low and high density polyethylene into milk, yogurt, and alcohol solutions. This means that ingestion could take place by using PS cups to drink alcoholic beverages, mixed drinks or perhaps even coffee with cream [20].

In packaged foods, vitamin A will decompose and produce m-xylene, toluene, and 2, 6-dimethylnaphthalene with the addition of heat such as microwave temperatures. Toluene will aggressively dissolve polystyrene. This renders polystyrene as an unsuitable package for containing or microwaving products that contain vitamin A [20].

CHAPTER 3
METHODOLOGY

The methodology of this project is represented by the flow chart shown in Figure 3.1. The detailed methodology and procedures of experimental works are explained and discussed further in this chapter. It includes equipment needed, sample preparation and procedures. The gantt chart is shown in appendix section.

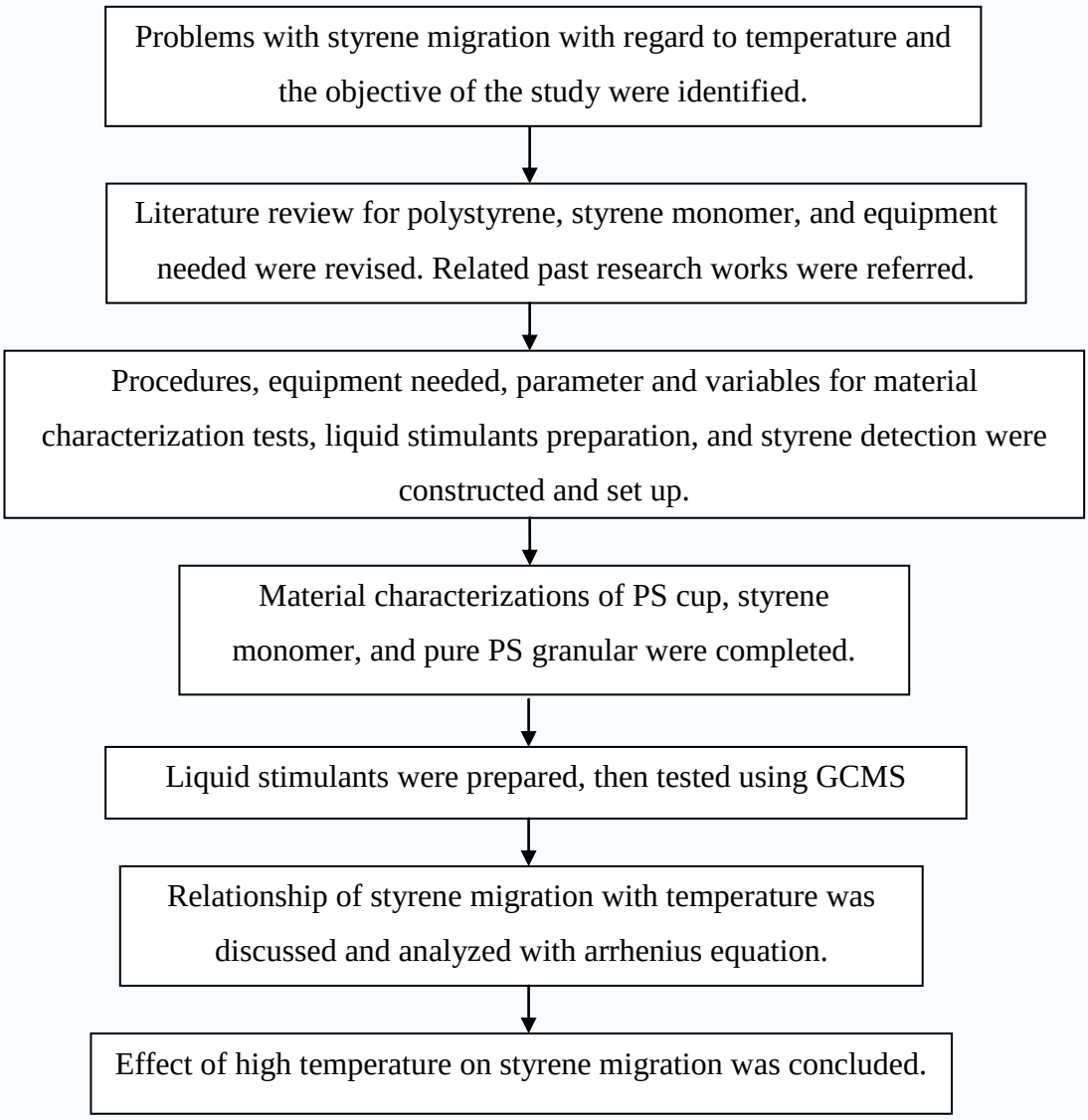

Figure 3.1: Process flow chart of methodology

3.1 Material Characterizations

3.1.1 Determination of Thermal Properties of PS Cup and Pure Polystyrene Granular

The objective is to get the thermal properties of polystyrene cup and pure polystyrene granular, particularly their glass transition temperature, T_G, and melting temperature, T_M. Besides, the behavior of those items with temperature change also will be observed.

For PS cup characterization, by using differential scanning calorimeter (DSC), firstly the temperature range for DSC was set to be between 50^{o}C and 240^{o}C. Standard polystyrene will start melting at 240^{o}C. After that a small piece of PS cup, weighted around 0.5g was prepared and put into a special metal case, and finally tested with DSC. At the same time, a reference sample that has a well-defined heat capacity over the temperature was used as a reference to the PS cup in the DSC. They were heated and DSC curve was obtained. The same procedure was repeated for pure polystyrene granular. From the curves, all the desired data such as glass transition temperature, T_G, and melting temperature, T_M were obtained.

3.1.2 Determination of Chemical Composition of PS Cup and Styrene Monomer

The equipment needed was fourier transform infrared spectroscopy. For sample preparation, polystyrene powder was processed from polystyrene cup by using grinder. Then the PS cup powder was added with additive, namely potassium bromide powder, KBr, and the mixture was pressed in a press machine to get a thin layer of film. The film then finally was put into the FTIR. As for styrene monomer, since it was already in the form of liquid, it was poured directly onto the feed input of FTIR to be tested. The styrene monomer used had 99% purity and was a stabilized one.

3.2 Liquid Stimulants Sample Preparation

Only 2 types of liquid stimulants were used in this experiment, distilled water and cooking oil. Styrene is most soluble in fat substance. Hence, this experiment utilized cooking oil which is rich in fat, as the liquid stimulant in this experiment. Cooking oil was assumed to be the strongest stimulant there is, hence will produce the 'worst-case' result. Fat is present in normal beverages such as milk and coffee with creamer. The distilled water in this experiment represented the aqueous medium of beverages. The distilled water used was taken from one same source throughout the experiment for standardization. Besides, tap water might contain additives and impurities that will affect and influence the result and getting in the way of result interpretation. Since the boiling temperature of distilled water is 100°C, the temperature experiment for water is only limited to that temperature.

150 ml of each of the liquid stimulant was placed in separate PS cups. The opening of each cup was covered with aluminum foil and tightened by rubber band prior to the heating process. This was to ensure no styrene monomer vapor could into the surrounding. Those stimulants samples were maintained at respective temperature for 1 hour period. After heating, the stimulants were left to cool naturally at ambient temperature for one day before being tested for any styrene monomer traces using GC-MS.

3.3 Method for Detection of Styrene Monomers in Liquid Stimulants

GC-MS was employed to measure the styrene content of the stimulants. The GC-MS used was Shimadzu model GC14AQP-1100 of direct injection type. The capillary column used in the GC-MS was SPB-5, which has 3.0 meter long x 0.32 mm internal diameter, with 0.5 micro meter film thickness [13], [14].

Firstly, stabilized pure styrene monomer with 99% purity was diluted with acetone to produce a solution of 1000, 500, and 1 part per billion (ppb) by volume. Those solutions were run using the GC-MS and a calibration curve with correlation coefficient, r, of 0.95 was constructed.

Then each of the liquid stimulants was injected into the GC-MS. Liquid stimulants stored in the closed tubes were shaken before a very small volume was injected into the GC-MS, by using a special syringe. GC-MS then processed the liquid stimulants and compared its findings with the calibration curve constructed earlier, to determine the concentration of styrene monomer contained in the liquid stimulants.

CHAPTER 4
RESULTS AND DICUSSION

4.1 Material Characterizations

4.1.1 Differential Scanning Calorimetry

The DSC analysis was done for two samples. The first sample was pure polystyrene granular. Pure polystyrene granular is used in feedstock of manufacturing polystyrene-based products. The graph obtained is as in Figure 4.1. From the graph, the pure standard polystyrene granular has a glass temperature, T_G value of 91.97 °C and melting temperature, T_M value of 240.12 °C. These values are very close to the theoretical value stated in the literature review. The glass temperature, T_G is detected from the first positive peak of the curve. The positive curve indicates an endothermic process, meaning the polystyrene granular required more heat, hence denoting a glass temperature, $T_{G.}$ At 237 °C an exothermic process denotes a crystallization temperature for the pure PS. Finally a clear positive peak 240 °C indicates an endothermic process, which is the melting temperature, $T_{M.}$ It is much easier to be detected compared to glass temperature, T_G, since in melting process, a larger amount of heat are required.

The second sample was powder form of a PS cup. The sample was prepared by blending small pieces of PS cup. Then the powder was tested under DSC. The result showed an inconclusive finding as can be seen in Figure 4.2. The graph plots as an increasing straight line and there is no peak at all. Hence, the glass temperature, T_G, and the melting temperature, T_M, of the sample cannot be determined. It is possible that the glass temperature, T_G, and the melting temperature, T_M, of PS cup are higher than 260 °C. Although pure polystyrene granules has glass temperature, T_G, value of 91.97 °C and melting temperature, T_M, value of 240.12 °C, since it has undergone

various manufacturing process and added with additives before turning into a PS cup, so the thermal properties of them are different. Polystyrene cup is made up of expanded polystyrene. Expanded polystyrene is produced from a mixture of about 90-95% polystyrene and 5-10% gaseous blowing agent, most commonly pentane or carbon dioxide. The solid plastic is expanded into foam through the use of heat, usually steam [4].

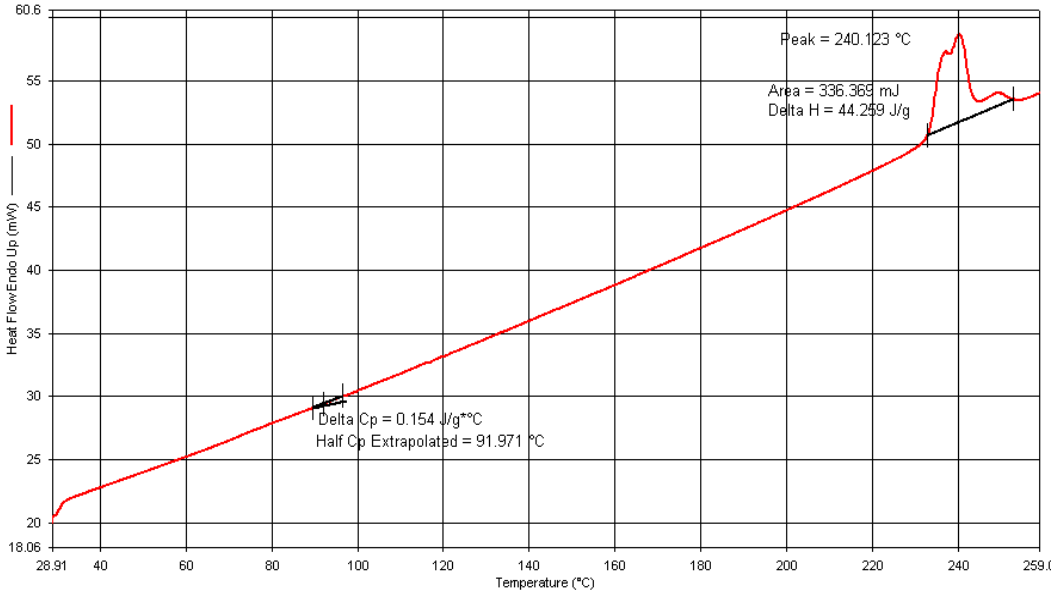

Figure 4.1: DSC analysis of pure polystyrene granular.

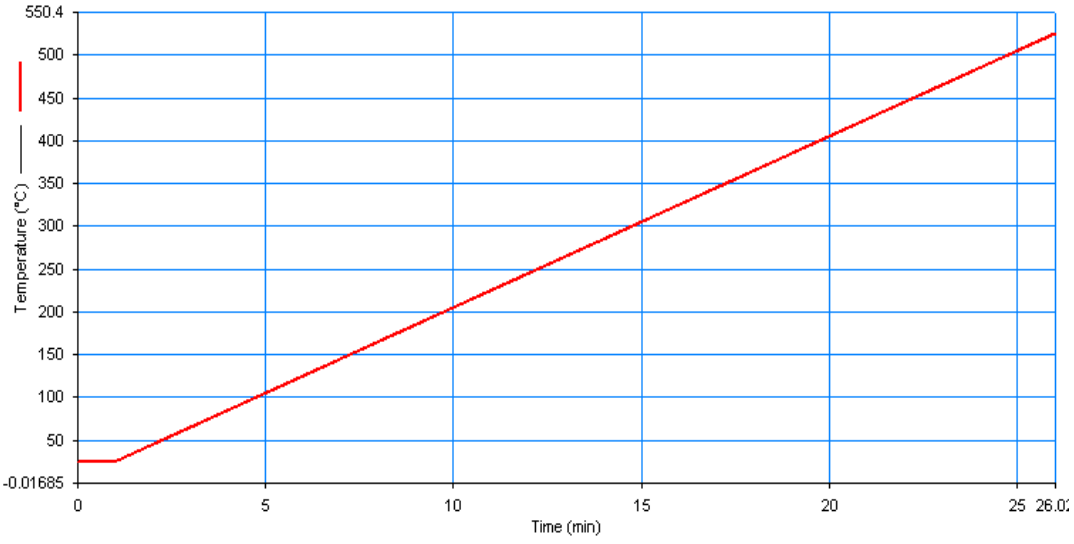

Figure 4.2: DSC analysis of PS cup.

From these results, the methodology of the study could be designed accordingly. The temperature at which the samples would be heated to should exceed the glass temperature, T_G value so that preferably more reaction could take place. Since the glass temperature, T_G of pure polystyrene granular is about 92 °C, the maximum temperature of this experiment was adjusted to be at 100 °C. Above this temperature, the PS cup will soften collapse as mentioned before. Furthermore, temperature of beverages does not normally exceed 100 °C.

4.1.2 Fourier Transform Infrared Spectroscopy

Chemical composition analysis of the PS cup and its monomer were conducted using FTIR. FTIR spectrum of the PS cup is shown in Figure 4.3.

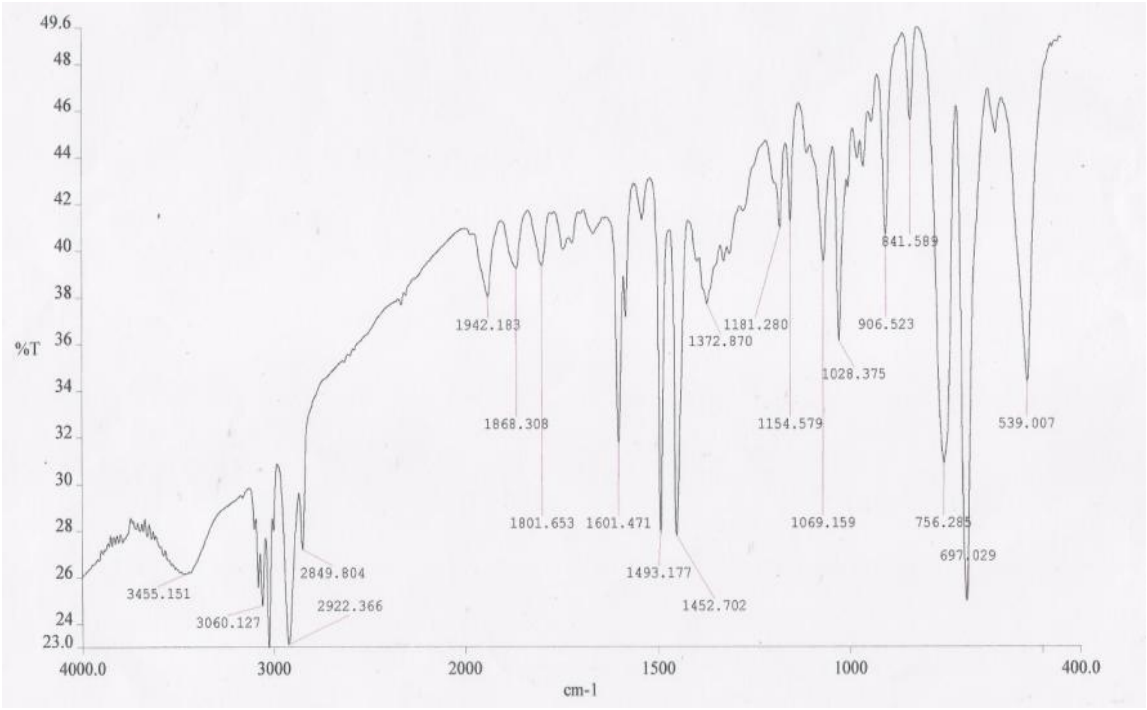

Figure 4.3: FTIR spectrum of the PS cup.

To analyze the graph, it is compared with the known infrared spectrum of standard polystyrene sample. Then a conclusion can be made whether the polystyrene is pure or has been mixed with other substance. The FTIR spectrum of a standard polystyrene sample is shown in Figure 4.4. This graph indicates an aromatic compound (polystyrene is an aromatic substance). Aromatic compounds show useful characteristic infrared bands in five regions of the mid-infrared spectrum (as in Appendix). The C–H stretching bands of aromatic compounds appeared in the 3100–3000 cm^{-1} range, so making them easy to differentiate from those produced by aliphatic C–H groups which appeared below 3000 cm^{-1}. In the 2000–1700 cm^{-1} region, a series of weak combination and overtone bands appear and the pattern of the overtone bands reflected the substitution pattern of the benzene ring. Skeletal vibrations, representing C=C stretching, absorbed in the 1650–1430 cm^{-1} range. The C–H bending bands were represented in the regions 1275–1000 cm^{-1} (in-plane bending) and 900–690 cm^{-1} (out-of plane bending). The bands of the out-of-plane bending vibrations of aromatic compounds are strong and characteristic of the number of hydrogen [22].

Besides, the graph also indicates that the substance is a polymer. This is shown when the bands in the graph are checked with the correlation table for the infrared bands of polymers (attached in appendix). As most polymers are organically based, the spectral assignments made for organic molecules are helpful when interpreting the infrared the infrared spectra of polymers [22].

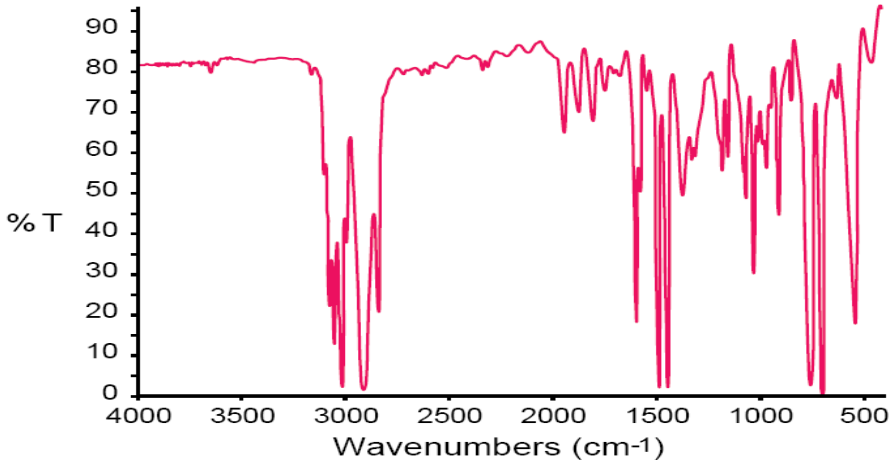

Figure 4.4: FTIR spectrum result of standard polystyrene.

By comparison, it is shown that the two samples were identical based on their FTIR results. They are both polystyrene. Polystyrene cup is classified as expanded polystyrene, meaning it has been further processed; hence it has a little difference chemical composition from the standard polystyrene. In Figure 4.3, the graph for polystyrene cup is a little more complex rather than the graph of standard polystyrene. It means the chemical composition of the cup is more complex due to the additives employed in its processing.

For analysis of pure styrene monomer using FTIR, the result is shown in Figure 4.5. From the result, the characteristic infrared bands showing a characteristic of aromatic compound (characteristic infrared bands of aromatic compounds are shown in appendix). This is because styrene monomer is an aromatic compound. The styrene monomer has a purity of 99% and was used later to calibrate the GC-MS. Figure 4.5 is the 'finger-print' of pure styrene monomer. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present [15].

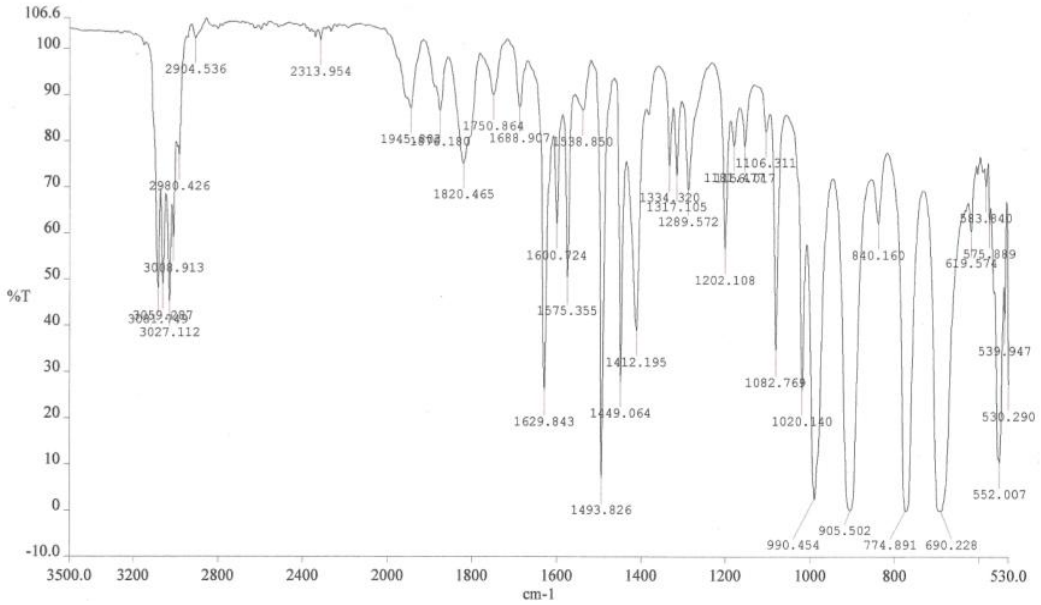

Figure 4.5: FTIR spectrum result of pure styrene monomer.

4.3 Styrene Detection by GC-MS

GC-MS was used to detect the presence in the liquid stimulants. It can detect the concentration of styrene in a solution through the construction of a calibration curve for styrene. Firstly, a standard stabilized styrene monomer of 99.9% purity was diluted with acetone as a solvent. 3 solutions of different concentration were produced, namely 1 ppb, 500 ppb, and 1000 ppb (1 ppm). The samples were run under GC-MS and the results are shown in Table 4.1, and a calibration curve is illustrated in Figure 4.6. The calibration curve was plotted in order to determine the concentration of styrene in the stimulant samples. The straight line of the calibration curve obtained has correlation coefficient, R, equal to 0.95, which represents a good fit of the data obtained.

Table 4.1: GC-MS results obtained for styrene-acetone solutions.

Concentration of styrene solution	GC-MS spectral area measured

1 ppb	451
500 ppb	4780
1000 ppb	14805

Then, all the liquid stimulants were tested by GC-MS. The results are summarized in Table 4.2. There was no styrene detected in the distilled water at all temperature studied. The temperatures of 25^{o}C to 100^{o}C have no significant influence on the styrene migration. However the concentration of styrene may be very low, and beyond the detection level of the GC-MS. This may be due to the low solubility of styrene in distilled water which is less than 1%. In conclusion, PS cup is safe to hold distilled water at any temperature between 25^{o}C to 125^{o}C without any significant amount of styrene leaching out from the cup.

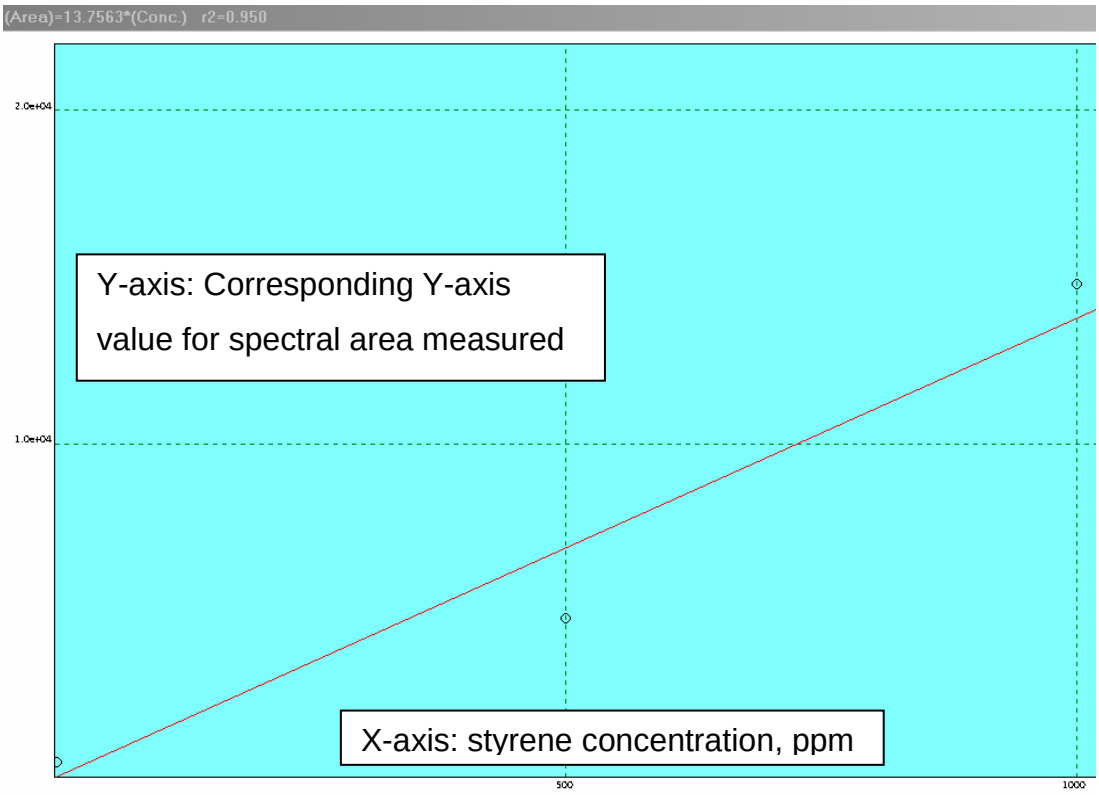

Figure 4.6: Calibration curve of the standard pure styrene.

Table 4.2: Concentration of styrene measured in the liquid stimulants.

Temperature	Concentration of styrene	
	Distilled Water	Cooking oil
25^{o}C	0	44.05 ppb
50^{o}C	0	64.99 ppb
75^{o}C	0	88.90 ppb
100^{o}C	0	1097.10 ppb
125^{o}C	0	-

In the meanwhile, all cooking oil stimulants showed traces of styrene under the influence of temperature. The higher the temperature of cooking oil, the higher the concentration of styrene detected in the cooking oil. This could be explained as the solubility of styrene in fatty medium depends on temperature. The dependence of styrene migration on temperature is illustrated in Figure 4.7. The rate of a reaction depends on the temperature at which it is run. As the temperature increases, the molecules move faster and therefore collide more frequently. The molecules also possess higher kinetic energy. Thus, the proportion of collisions that can overcome the activation energy of the reaction increases with temperature, which in this case, resulted in higher amount of styrene migration.

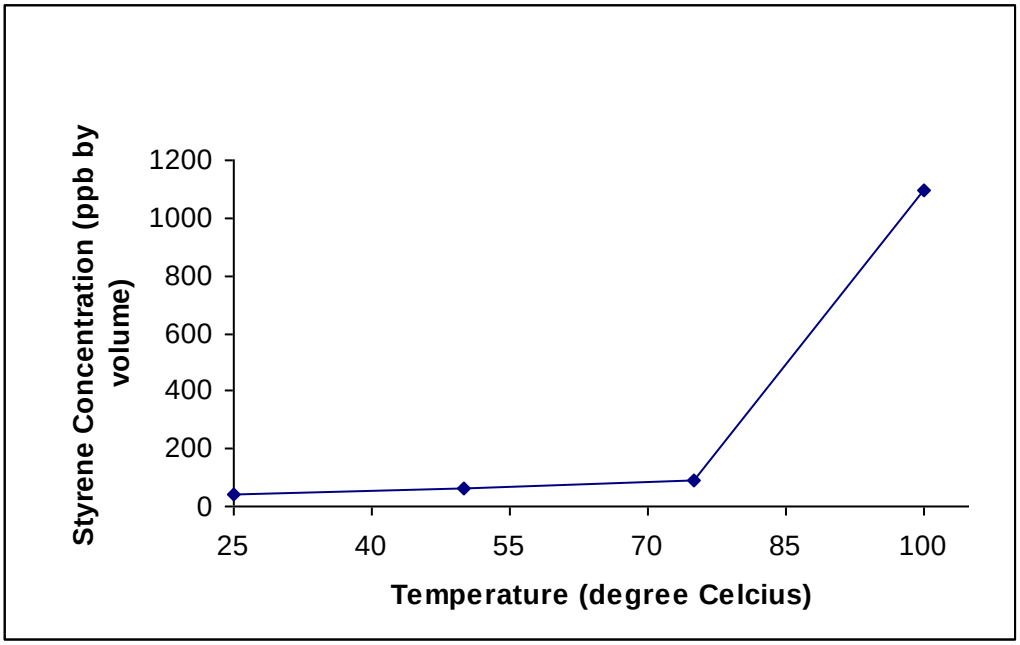

Figure 4.7: Styrene concentration in the cooking oil vs temperature

As can be observed, the concentration of styrene in the cooking oil at 100^{o}C showed a very high concentration of styrene compared to that at 75^{o}C. A step pattern or behavior is shown. After 75^{o}C, the concentration of styrene measured increased abruptly, indicating a 'threshold' temperature for styrene migration at temperature beyond 75^{o}C. It is possible that at a temperature beyond 75^{o}C, the PS cup wall started to 'break' and facilitate higher rate of styrene migration from the wall into the stimulants. Moreover, the solubility of styrene in the cooking oil may increased significantly beyond 75^{o}C. As mentioned in the literature review, styrene is highly soluble in oil, and the higher temperature has further increased the amount styrene migration. Overall, all the heated cooking oil including those at 25^{o}C has promoted the styrene migration from the PS cup. Hence drinks that are fat or lipid based such as milk, coffee with creamers are not recommended to be consumed in PS cup, especially at high temperature. This is due to the incomplete polymerization process of PS cup which resulted in residual monomers left in the cup.

A concentration unit of ppm in volume was used earlier in this experiment to simplify the dilution calculation of pure styrene monomer in acetone used in constructing the calibration curve. The styrene concentration measured can also be converted to ppm by weight percent as shown in Table 4.3.

Table 4.3: Concentration and weight % of styrene monomer in cooking oil at various temperatures.

Temperature (^{o}C)	Styrene concentration (ppm by weight)	Weight %
25^{o}C	0.0448	4.48×10^{-6}
50^{o}C	0.0661	6.61×10^{-6}
75^{o}C	0.0904	9.04×10^{-6}
100^{o}C	1.1158	1.1158×10^{-4}

Existing regulation in the U.S. permits up to 1 wt-% or equal to 10,000 ppm by weight of the styrene monomer in food-grade PS, except that when used in contact with fatty foods not more than 0.5wt-% styrene monomer is allowed [19]. The results obtained in the study showed that the amount of styrene detected in the cooking oil stimulant is well below the maximum values allowable. However, since styrene can accumulate in human body and cause health problems, the use of PS cup at high temperature must be cautioned.

4.4 Analysis of the Effect of Temperature on Chemical Migration of PS Cup

When the PS cup containing cooking oil was being heated in the oven, a chemical reaction occurred between the cooking oil and the PS cup which resulted in the migration of styrene monomer from PS cup into the cooking oil. The rate of a reaction depends on the temperature at which it is occuring. As the temperature increases, the molecules move faster and therefore collide more frequently. The

molecules also possess more kinetic energy. Thus, the proportion of collisions that can overcome the activation energy for the reaction increases with temperature.

Arrhenius equation may be used to represent temperature dependent processes such as styrene migration. At higher temperature, the probability that two molecules will collide is higher. This higher collision rate results in a higher kinetic energy, which has an effect on the activation energy of the reaction. The activation energy is the amount of energy required to ensure that a reaction happens. The effect of temperature on reaction rates can be determined by using Arrhenius equation,

$$k = A * \exp(-Ea/R*T) \qquad (1)$$

where k is the rate coefficient in s^{-1}, A is a constant in unit of s^{-1}, E_a is the activation energy, R is the universal gas constant (8.314×10^{-3} kJ $mol^{-1}K^{-1}$), and T is the temperature in Kelvin. According to this equation, a plot of ln *k* versus 1/*T* should give a straight line with a slope of - E_a/R. The Arrhenius equation can be used to determine the activation energy for a reaction. By taking natural logarithm on both sides of the equation, the Arrhenius equation can be rearranged be plotted as a straight line.

To find the activation energy, ln k versus 1/temperature has been plotted, and from it the activation energy is determined. Rate constant, k, at each temperature of reaction is calculated from number of mole of styrene migrated from PS cup into cooking oil in 1 hour period. All the related calculations are shown in the appendix. The calculated parameters are shown in Table 4.4. Based on these information ln k versus 1/temperature is plotted in Figure 4.8. The reaction at 100^oC is left out in this calculation. This is because if it is included in the analysis, there will be 2 activation energies present. Although it is possible for a few chemical reactions to have 2 activation energies due to changing mechanism in their reactions, but for this project concrete and evident data are lacking to support and justify the claim of existence of

2 activation energies. Thus, only temperatures between 25^{o}C to 75^{o}C are used and covered in this analysis.

Table 4.4: Related parameters in Arrhenius equation.

Temperature, T (K)	Rate constant, k (sec^{-1})	1/Temperature, (1/K)	ln k	Point No.
298.15	1.19486E-11	0.003354016	-25.1504070	1
323.15	1.76295E-11	0.003094538	-24.76144748	2
348.15	2.41105E-11	0.002872325	-24.44837369	3

From the graph in Figure 4.8, linear line is obtained from point 1 to point 3. It indicates the activation energy for the reaction is constant throughout the temperature range. Activation energy is given by slope of the straight lines multiply by ideal gas constant, R. Hence activation energy from point 1 to point 3 (25^{o}C to 75^{o}C) is 12.117 kJ/mol.

The value of constant A can be calculated from the obtained values of activated energies. It is assumed that the value of A will be constant for temperature from 25^{o}C until 75^{o}C. From the calculation, A is equal to$1.59x10^{-9}$ s^{-1}. In summary, the reaction from 25^{o}C until 75^{o}C is governed by the equation

$$k = (1.59x10^{-9})*\exp^{[-12.117 / (8.314*T)]} \quad (2)$$

The rate of reaction at any temperature can simply be obtained by replacing T with the temperature of a reaction.

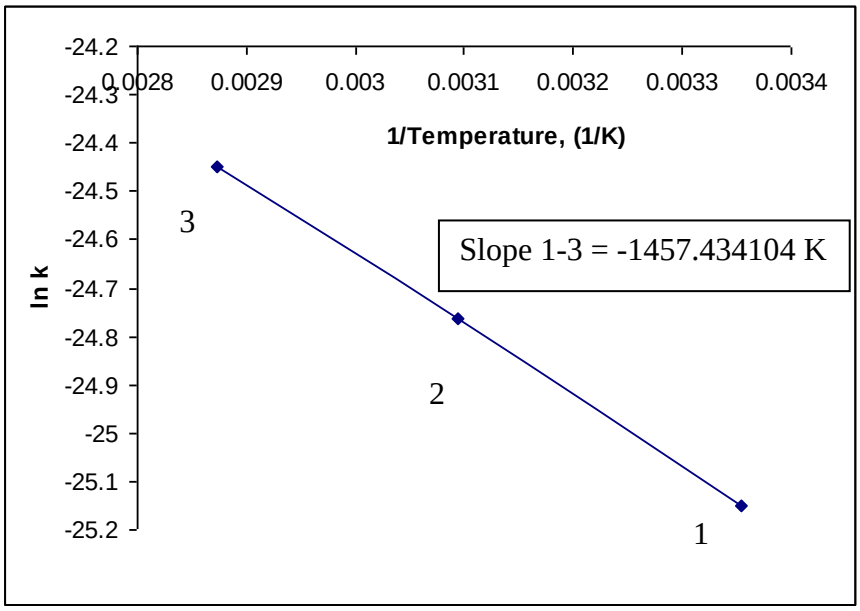

Figure 4.8: Ln k versus 1/temperature for the styrene migration process.

Generally, the rate of the reaction will be higher as temperature increases. A step pattern was shown, where the rate suddenly rises after 75^{o}C. After 75^{o}C, the reaction suddenly jumps, resulting in more styrene migration into the cup. The possible causes of the increment in rate are first, the solubility of styrene in the cooking oil increases significantly after 75^{o}C, thus promoting higher styrene migration. This is due to the fact that the rate of styrene migration increases as it's solubility in a specific medium (in this case cooking oil) increases. The second cause is it could be at a point between 75^{o}C and 100^{o}C, the wall of PS cup starts to fail and break, causing the migration of styrene relatively high. The combination of the two causes arelikely the reasons for the relatively high styrene migration after 75^{o}C.

4.5 Physical Observation on the Effect of Temperature on Polystyrene Cup

All PS cups containing oil stimulants showed oil seepage through the cups at the end of 24 hours. There was oil penetrating through the PS cup's wall, as demonstrated in Figure 4.9. However that was not the case with distilled water. This suggests that PS

cup is permeable to cooking oil, hence unable to hold or contain oily solution except for a very short time.

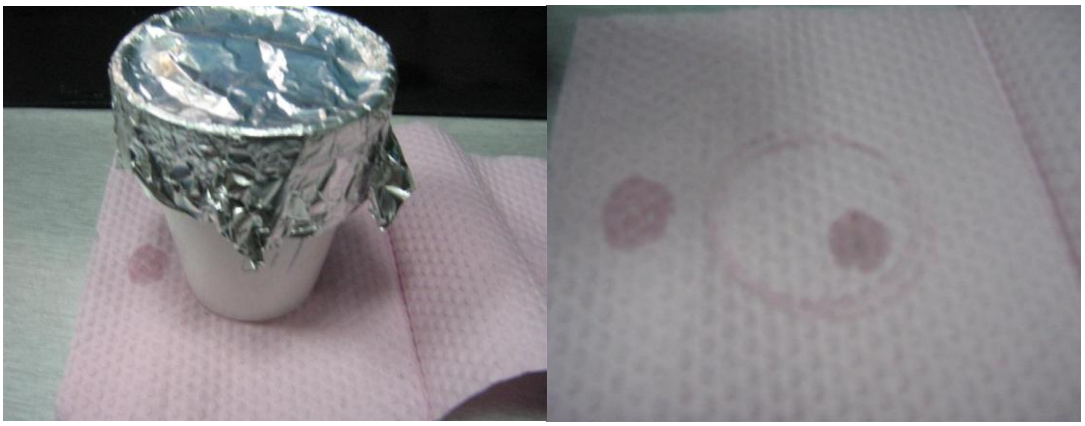

Figure 4.9: Oil marks on tissue paper, indicating cooking oil penetrating through the PS cup.

PS cup's wall texture changed after heating at 125^{o}C for water containing and 100^{o}C for cooking oil containing cup. They exhibited grainy surface texture as shown in Figure 4.10 instead of a smooth texture before being heated. Physical changes normally mean there is a change in its properties as well. Hence, PS cup's integrity to hold high temperature drinks is questionable.

Ultimately, the PS cup filled with cooking oil subjected to a temperature of 125^{o}C in the oven failed. The PS cup has deformed plastically, before it failed and ruptured, as shown in Figure 4.11. This implies that PS cup unsuitable and unstable to hold beverages of more than 100^{o}C.

Figure 4.10: Grainy texture of PS cup after heating process.

Figure 4.11: Ruptured PS cup at 125^{o}C.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

In general, as temperature of the liquid stimulant increased, the rate of styrene migration from the PS cup into the liquid stimulants also increased. This is expected because the rate of a reaction depends on the reaction temperature. The relationship however, is not linear. From the results, after 75^{o}C, the rate of styrene migration increased significantly compared to the rate of migration at 75^{o}C and below. The possible causes were that the solubility of styrene in the cooking oil increased significantly at high temperature and because the PS cup's wall started to fail after 75^{o}C. The relationship between styrene migration and temperature can be modeled by using Arrhenius equation. However, even at the highest rate of styrene migration, the weight percent of styrene content detected in the cooking oil was still within the allowable limit as stipulated in the regulation. Although the styrene concentration measured was below the limit, it could accumulate in human body and caused long-term effect to human's health. The findings also indicated that fatty substance could enhanced the migration of styrene from PS cup with the greatest effect at higher temperature. Distilled water did not promote any significant amount of styrene migration although heated up to 125^{o}C.

5.2 Recommendations

To further improve this study, one can reduce the temperature increment set up for the experiment. This could give the exact temperature point at where the migration of styrene starts to increase vigorously, hence gives more accurate and detail relationship between temperature and styrene migration. The migrated chemical the study should also not be limited to styrene only, as many other possible chemical that made up a PS cup can also be migrating.

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APPENDICES

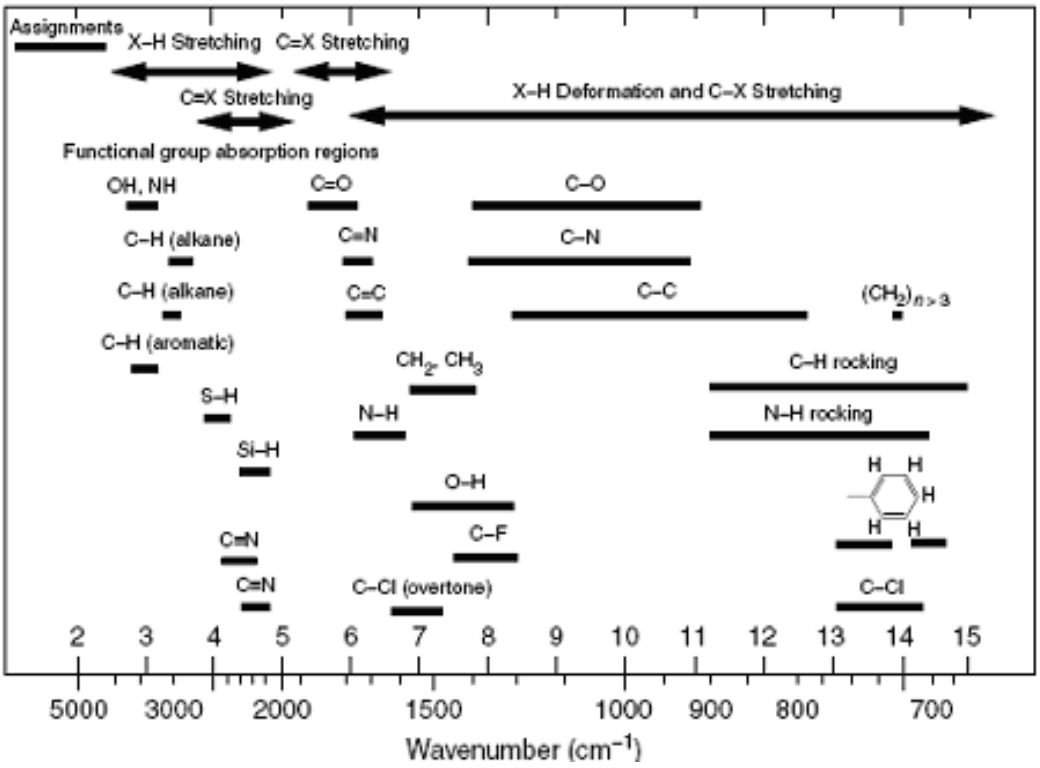
Appendix 1: Characteristic infrared bands of aromatic compound

Wavenumber (cm^{-1})	Assignment
3100–3000	C–H stretching
2000–1700	Overtone and combination bands
1600–1430	C=C stretching
1275–1000	In-plane C–H bending
900–690	Out-of-plane C–H bending

Appendix 2: Characteristic infrared bands of oxygen-containing compound

Wavenumber (cm^{-1})	Assignment
	Alcohol and phenols
3600	Alcohol O–H stretching
3550–3500	Phenol O–H stretching
1300–1000	C–O stretching
	Ethers
1100	C–O–C stretching
	Aldehydes and ketones
2900–2700	Aldehyde C–H stretching
1740–1720	Aliphatic aldehyde C=O stretching
1730–1700	Aliphatic ketone C=O stretching
1720–1680	Aromatic aldehyde C=O stretching
1700–1680	Aromatic ketone C=O stretching
	Esters
1750–1730	Aliphatic C=O stretching
1730–1705	Aromatic C=O stretching
1310–1250	Aromatic C–O stretching
1300–1100	Aliphatic C–O stretching
	Carboxylic acids
3300–2500	O–H stretching
1700	C=O stretching
1430	C–O–H in-plane bending
1240	C–O stretching
930	C–O–H out-of-plane bending
	Anhydrides
1840–1800	C=O stretching
1780–1740	C=O stretching
1300–1100	C–O stretching

Appendix 3: Correlation table for the infrared bands of polymers.

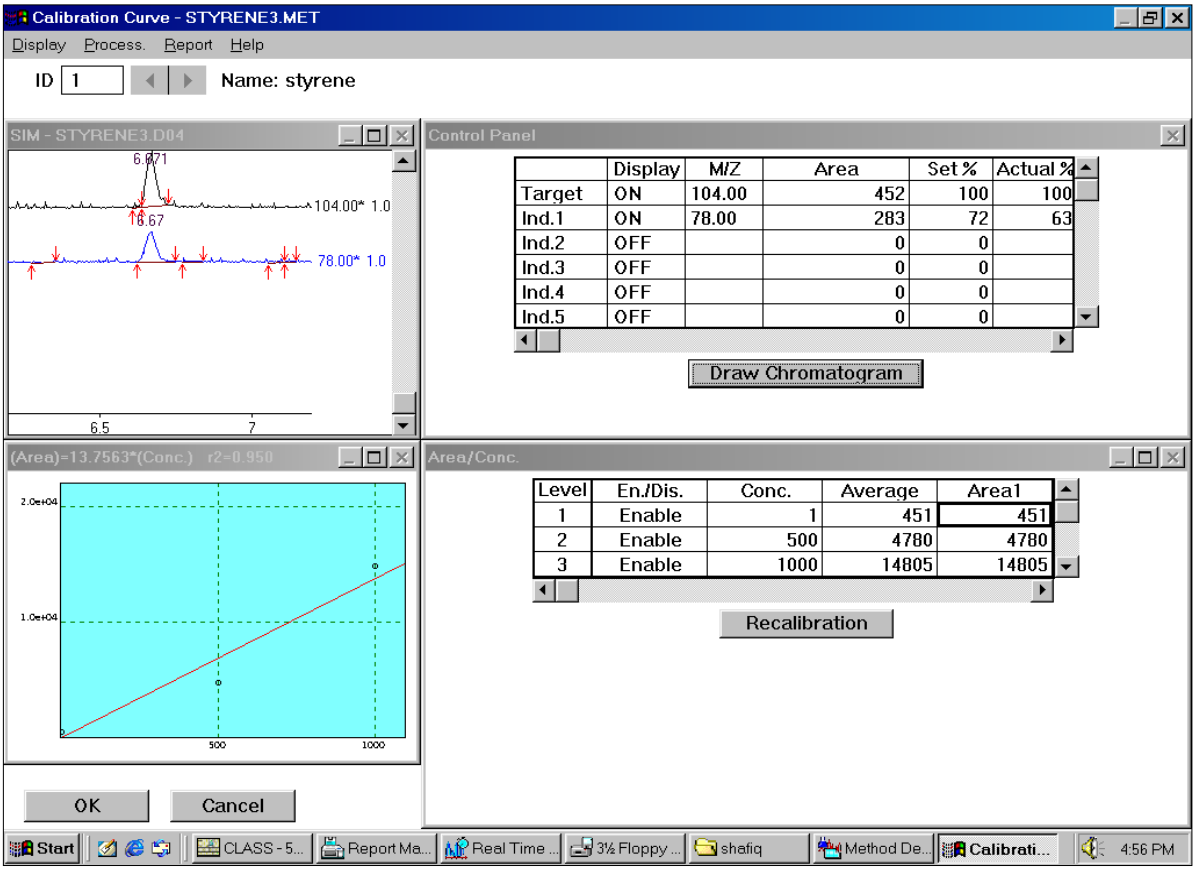

Assignments
X–H Stretching
C≡X Stretching
C=X Stretching
X–H Deformation and C–X Stretching
Functional group absorption regions
OH, NH
C=O
C–O
C–H (alkane)
C≡N
C–N
C–H (alkane)
C=C
C–C
(CH2)n>3
C–H (aromatic)
CH2, CH3
C–H rocking
S–H
N–H
N–H rocking
Si–H
O–H
C≡N
C–F
C=N
C–Cl (overtone)
C–Cl
2 3 4 5 6 7 8 9 10 11 12 13 14 15
5000 3000 2000 1500 1000 900 800 700
Wavenumber (cm−1)

Appendix 4: Project Gantt chart

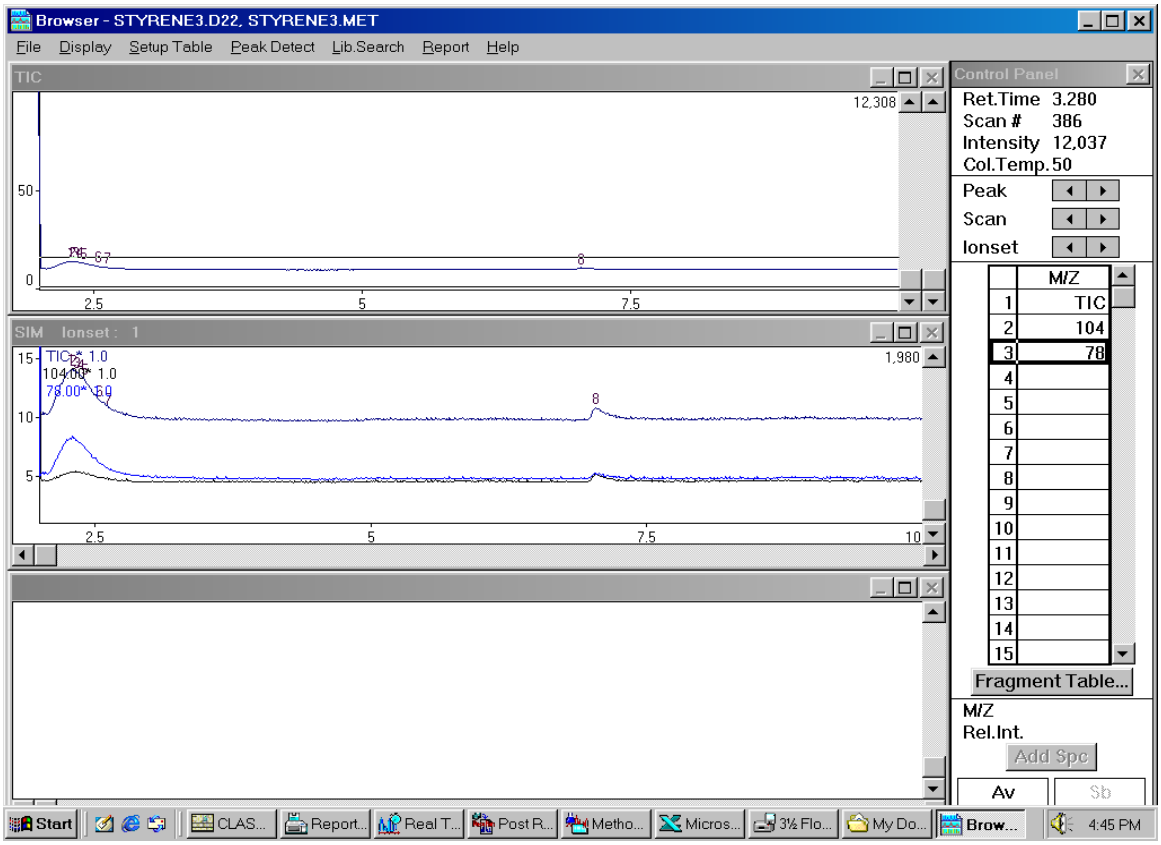
No.	Detail/ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	Continue experiment (DSC)																		
2	Project work continues																		
3	Order styrene monomer																		
4	Progress report 1																		
5	GC-MS samples preparation																		
6	Continue Experiment (GC-MS)																		
7	Project work continues																		
8	Exposition																		
9	Dissertation draft																		
10	Oral presentation																		
11	Hardbound Dissertation																		

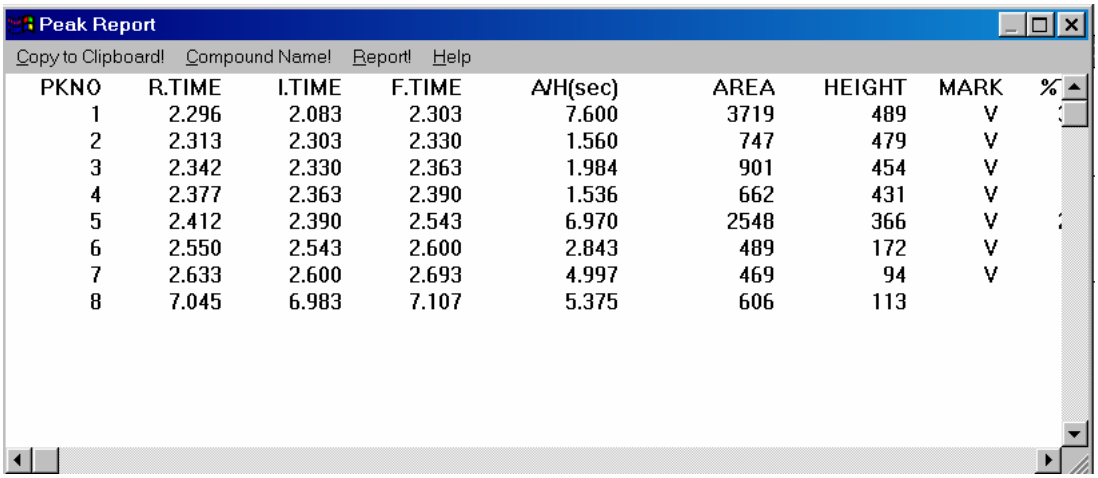
Appendix 5: GC-MS Result

Calibration curve obtained,



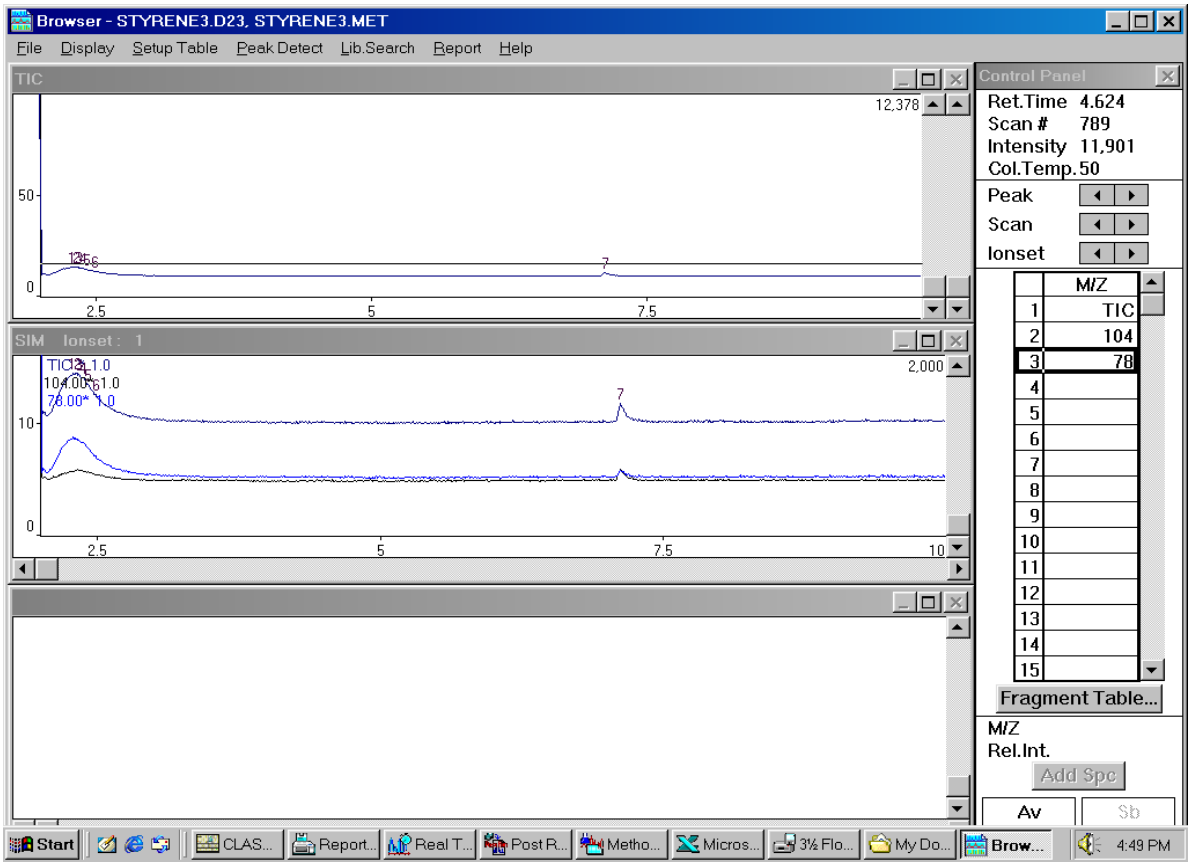
Cooking oil at 25°C

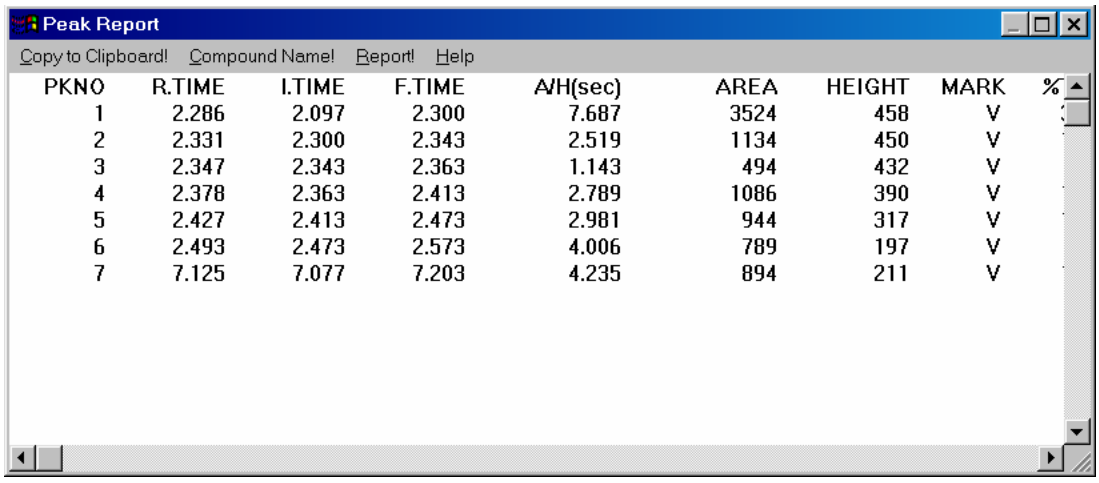




PKNO	R.TIME	I.TIME	F.TIME	A/H(sec)	AREA	HEIGHT	MARK	%
1	2.296	2.083	2.303	7.600	3719	489	V	
2	2.313	2.303	2.330	1.560	747	479	V	
3	2.342	2.330	2.363	1.984	901	454	V	
4	2.377	2.363	2.390	1.536	662	431	V	
5	2.412	2.390	2.543	6.970	2548	366	V	
6	2.550	2.543	2.600	2.843	489	172	V	
7	2.633	2.600	2.693	4.997	469	94	V	
8	7.045	6.983	7.107	5.375	606	113		

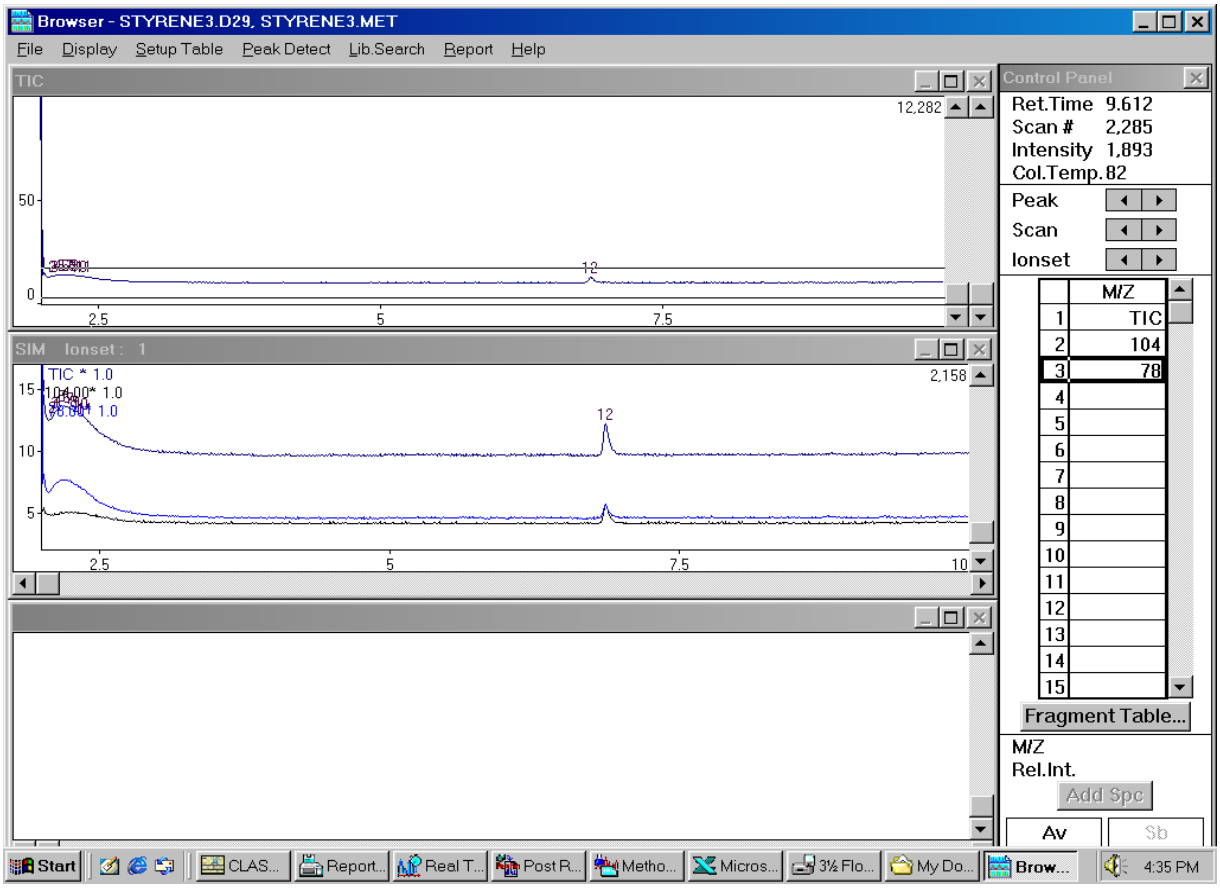
Cooking oil at 50°C

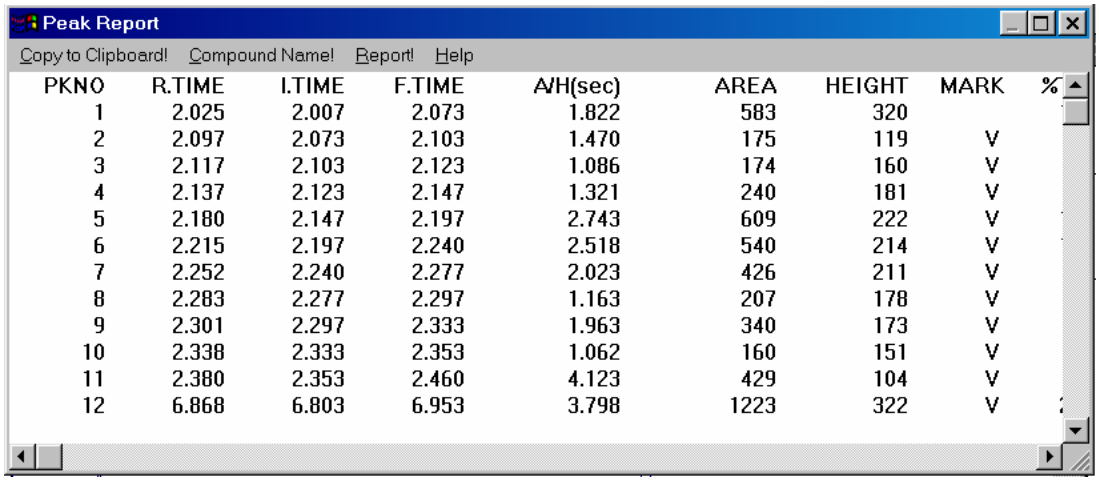




PKNO	R.TIME	I.TIME	F.TIME	A/H(sec)	AREA	HEIGHT	MARK	%
1	2.286	2.097	2.300	7.687	3524	458	V	
2	2.331	2.300	2.343	2.519	1134	450	V	
3	2.347	2.343	2.363	1.143	494	432	V	
4	2.378	2.363	2.413	2.789	1086	390	V	
5	2.427	2.413	2.473	2.981	944	317	V	
6	2.493	2.473	2.573	4.006	789	197	V	
7	7.125	7.077	7.203	4.235	894	211	V	

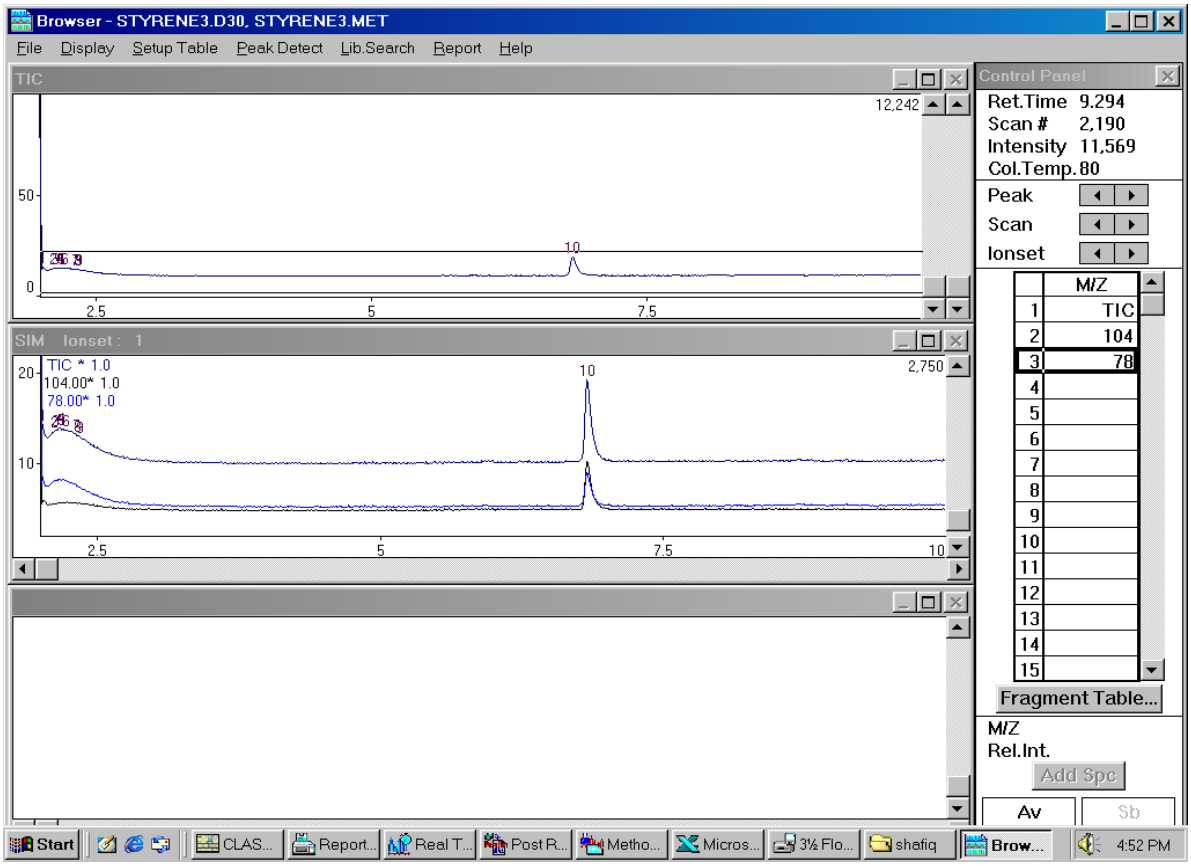
Cooking oil at 75°C

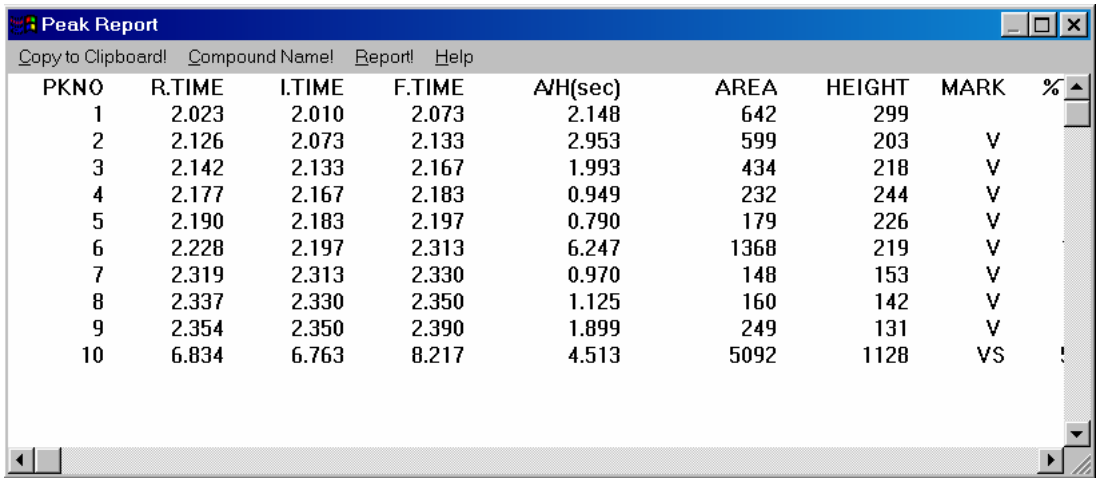




PKNO	R.TIME	I.TIME	F.TIME	A/H(sec)	AREA	HEIGHT	MARK	%
1	2.025	2.007	2.073	1.822	583	320		
2	2.097	2.073	2.103	1.470	175	119	V	
3	2.117	2.103	2.123	1.086	174	160	V	
4	2.137	2.123	2.147	1.321	240	181	V	
5	2.180	2.147	2.197	2.743	609	222	V	
6	2.215	2.197	2.240	2.518	540	214	V	
7	2.252	2.240	2.277	2.023	426	211	V	
8	2.283	2.277	2.297	1.163	207	178	V	
9	2.301	2.297	2.333	1.963	340	173	V	
10	2.338	2.333	2.353	1.062	160	151	V	
11	2.380	2.353	2.460	4.123	429	104	V	
12	6.868	6.803	6.953	3.798	1223	322	V	

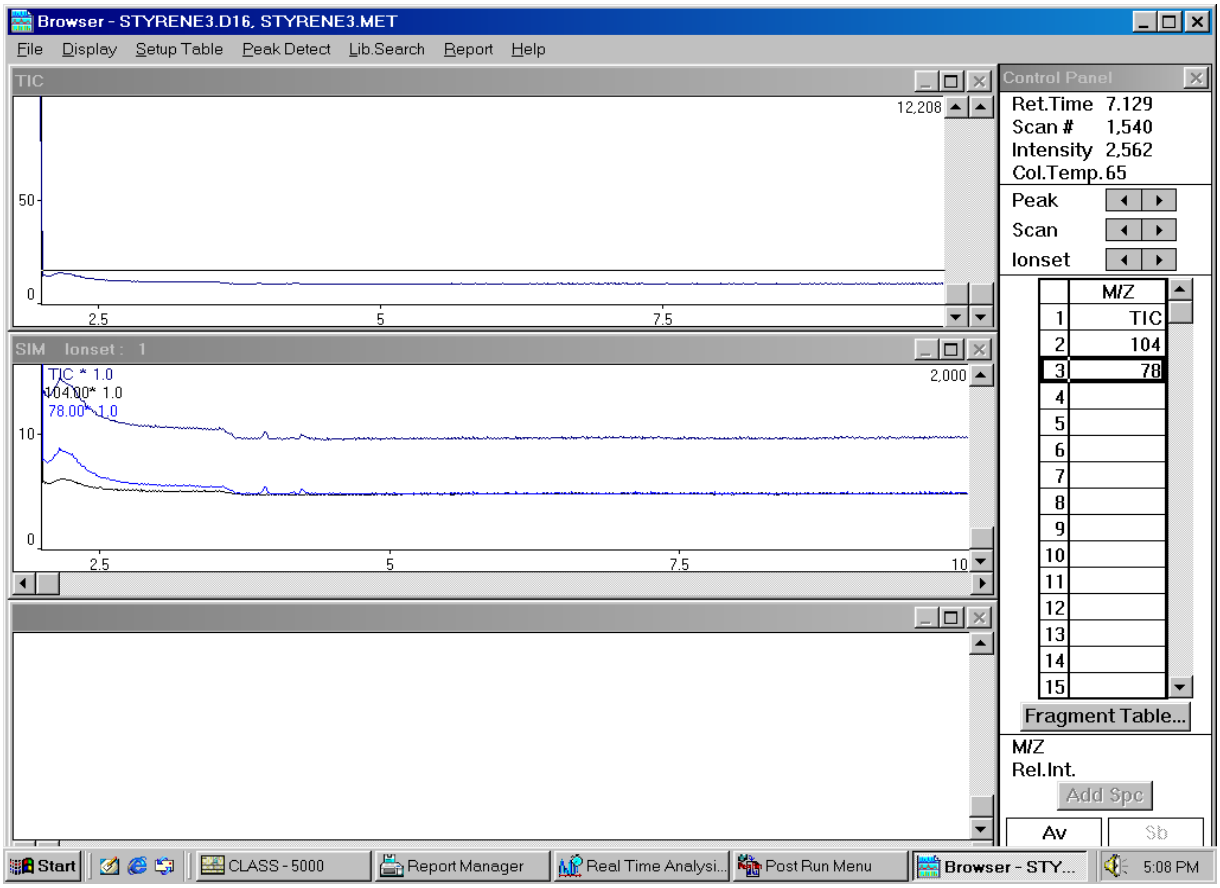
Cooking oil at 100^{o}C



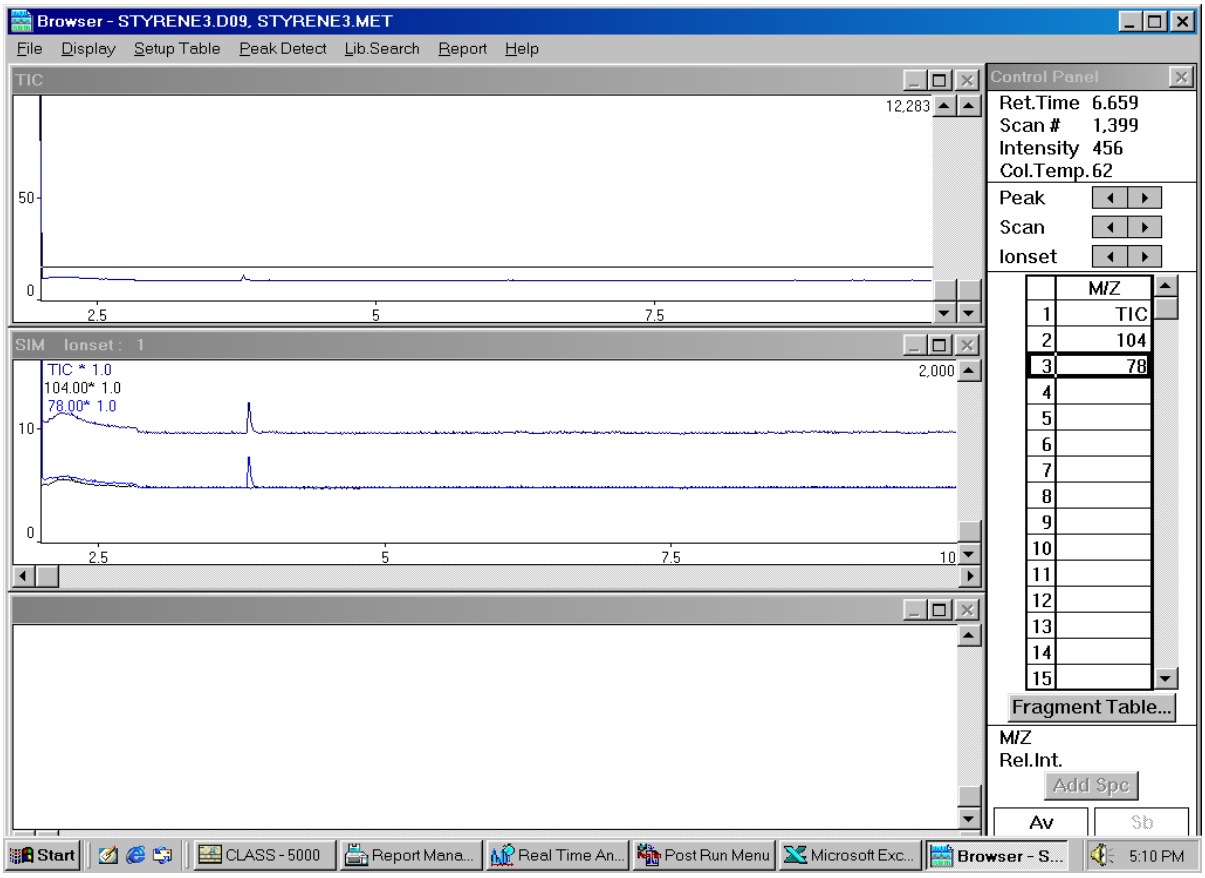


PKNO	R.TIME	I.TIME	F.TIME	A/H(sec)	AREA	HEIGHT	MARK	%
1	2.023	2.010	2.073	2.148	642	299		
2	2.126	2.073	2.133	2.953	599	203	V	
3	2.142	2.133	2.167	1.993	434	218	V	
4	2.177	2.167	2.183	0.949	232	244	V	
5	2.190	2.183	2.197	0.790	179	226	V	
6	2.228	2.197	2.313	6.247	1368	219	V	
7	2.319	2.313	2.330	0.970	148	153	V	
8	2.337	2.330	2.350	1.125	160	142	V	
9	2.354	2.350	2.390	1.899	249	131	V	
10	6.834	6.763	8.217	4.513	5092	1128	VS	

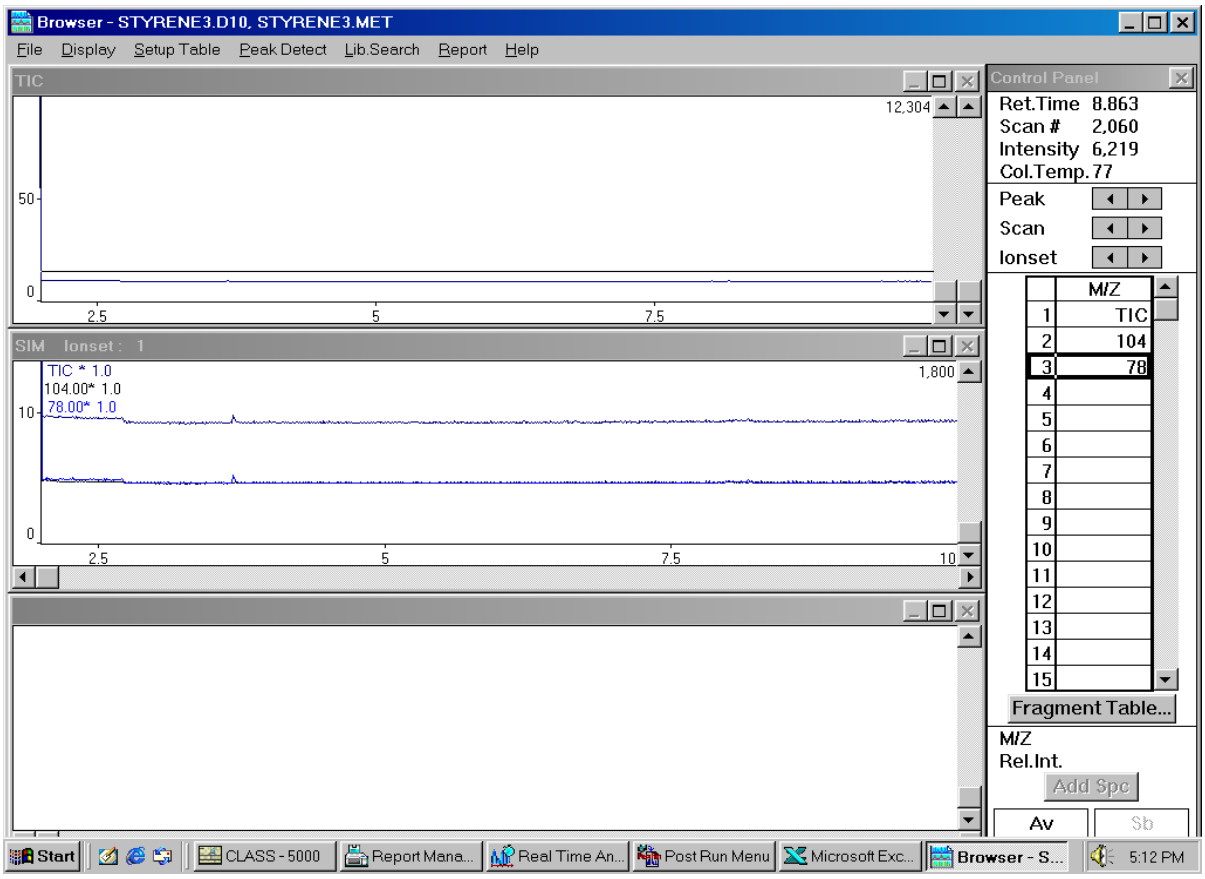
Distilled water at 25^{o}C



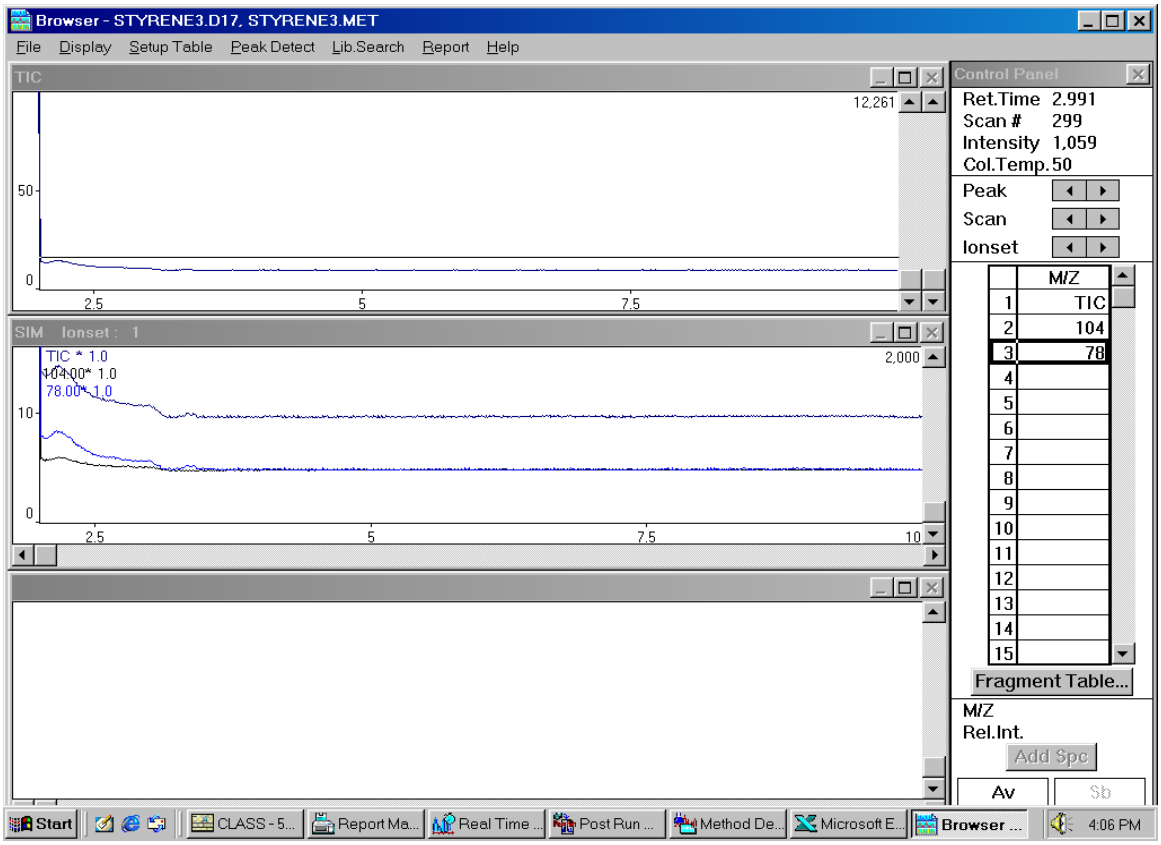
Distilled water at 50°C



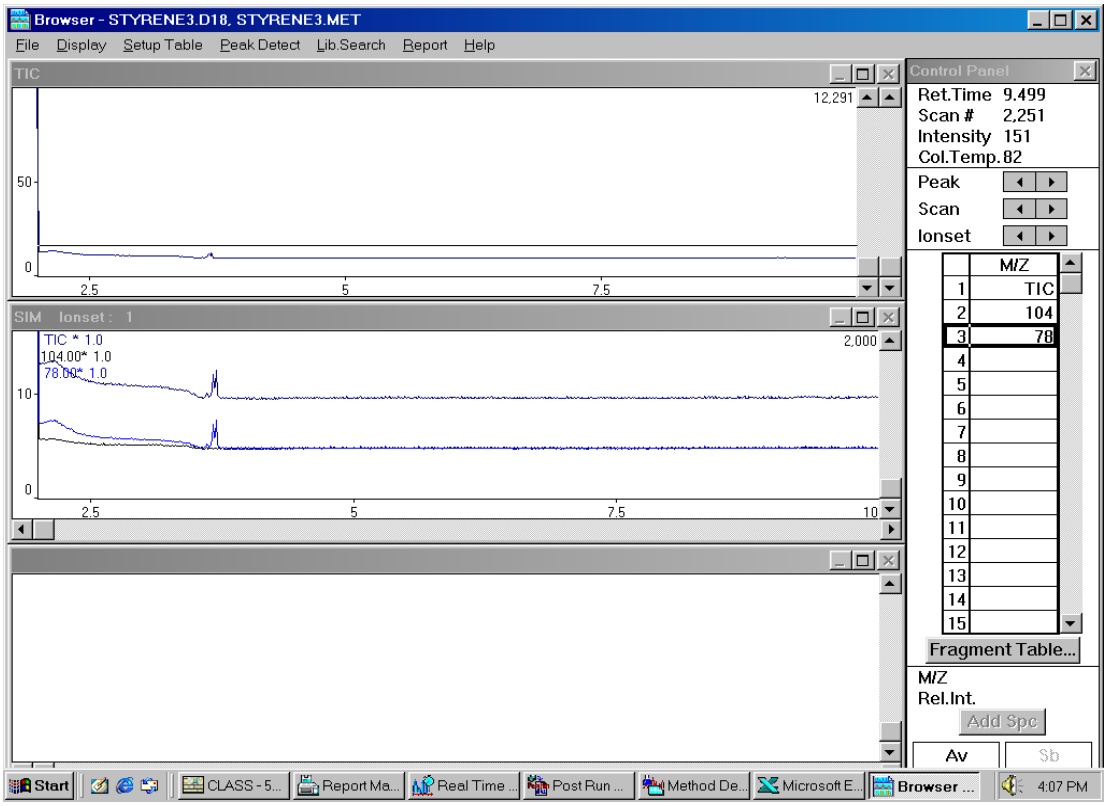
Distilled water at 75^{o}C



Distilled water at 100^{o}C



Distilled water at 125^{o}C



Appendix 6: Calculation

Concentration in part per million (ppm) by volume needs to be converted into part per million (ppm) by weight to compare with the existing regulation. At 100^{o}C, the concentration of styrene monomer in cooking oil is 1.0971 ppm by volume. To convert to ppm by weight easily, first find the conversion factor, which is what 1 ppm by volume is equivalent to in 1 ppm by weight. The density of styrene is 0.909g/ml and the average density of cooking oil is 0.894g/ml. 1 ppm by volume of styrene in cooking oil means, if there is 1ml of styrene in a solution, there are also 999, 999 ml of cooking oil in that solution. Hence for styrene weight,

$$= 1ml \times \frac{0.909\,g}{1ml}$$
$$= 0.909\,g$$

For cooking oil weight,

$$= 999{,}999\,ml \times \frac{0.894\,g}{1ml}$$
$$= 893{,}999.106\,g$$

Weight summation of those two,

$$= 0.909\,g + 893{,}999.106\,g$$
$$= 894{,}000.015\,g$$

The part of styrene in the solution is given by,

$$= \frac{0.909\,g}{894{,}000.015\,g}$$
$$= 1.017 \times 10^{-6}$$

Hence 1 ppm by volume of styrene in cooking oil is equal to 1.017 ppm by weight. So at 100^{o}C, where the styrene concentration in cooking oil was 1.0971 ppm per volume,

$$= 1.0971\, ppmv \times \frac{1.017\, ppmw}{1 ppmv}$$
$$= 1.1158\, ppmw$$

Repeat the same calculation for styrene concentration at other temperatures. To get the weight percent of styrene monomer in cooking oil, 1ppm by weight is equal to 1 x 10^{-4} weight percent, hence

$$= 1.1158\, ppmw \times \frac{1 \times 10^{-4}\, wt\%}{1 ppmw}$$
$$= 1.1158 \times 10^{-4}\, wt\%$$

Rate constant, k, at each temperature of reaction was calculated from number of mole of styrene migrated from PS cup into cooking oil in 1 hour period. The weight percent of styrene is taken for mole calculation. For instance, at 100^{o}C after 1hour, given the weight percent of styrene in cooking oil is 1.1158 x 10^{-4} and the molar mass of styrene is 104.5g/mole,

$$= 1.1158 \times 10^{-4}\, g \times \frac{1 mol}{104.15 g}$$
$$= 1.07134 \times 10^{-6}\, mol$$

Repeat calculation for other temperatures. Rate constant is given by

$$k = \frac{Mole}{time}$$

$$k = \frac{1.07134 \times 10^{-6} mol}{3600 \sec}$$

$$k = 2.97594 \times 10^{-10} s^{-1}$$

Notice that the mole unit in disappears in final k value. This is because the purpose of calculating k value is to get the rate of reaction, it does not matter what measurement or variables that is being used at the nominator part of the fraction. For example, instead from mole, other parameters that could be used are such as weight or volume. Mole is chosen because some other variables in arrhenius are in mole-based unit, for example the universal gas constant, R, in which the unit is kJ mol^{-1} K^{-1} , so mole is used in calculating rate constant, k, for consistentcy.

The calculation of activation energy, Ea, for the reaction requires plotting of ln k versus 1/temperature to obtain the slope. The equation that relates the slope with activation energy is,

$$slope = -\frac{Ea}{R}$$

Along point 1 until point 3, the calculated slope is equal to 1457.434104 and the supposed unit of the slope is Kelvin. The universal gas constant, R is equal to 8.314 x 10^{-3} kJ mol^{-1} K^{-1}. Hence,

$$Ea = -[slope \times R]$$

$$Ea = -[-1457.434104\, K \times 8.314 \times 10^{-3} \frac{kJ}{mol.K}]$$

$$Ea = 12{,}117.10741 \frac{J}{mol}$$

Meanwhile along point 3 to point 4, with calculated slope is equal to -13059.20143, following the same equation as before,

$$Ea = -[slope \times R]$$

$$Ea = -[-13{,}059.20143\,K \times 8.314 \times 10^{-3}\,\frac{kJ}{mol.K}]$$

$$Ea = 108{,}574.2007\,\frac{J}{mol}$$

Hence,

Activation energy along point 1-3 = 12 117.10714 J/mol

Activation energy along point 3-4 = 108 574.2007 J/mol

Finally, to calculate the value of constant, A, in arrhenius equation, assume the value of A_1 is constant for temperature between 25°C to 75°C, and another value which is A_2, is constant for temperature between 75°C to 100°C. Just substitute the value of rate constant, k, activation energy, Ea, and universal gas constant, R, into the initial arrhenius equation, and the value of constant A will be obtained. For A_1,

$$k = A_1 * \exp(-Ea/R*T)$$

$$1.19486 \times 10^{-11} s^{-1} = A_1 * \exp[-(12\,117.10714\ J\ mol^{-1}) / (8.314 \times 10^{-3}\ kJ\ mol^{-1}\ K^{-1} * 298.15K)]$$

$$A_1 = 1.585844026985617 \times 10^{-9}$$

For A_2,

$$k = A_1 * \exp(-Ea/R*T)$$

$$2.97594 \times 10^{-10}\ s^{-1} = A_2 * \exp[-(108\,574.2007\ J\ mol^{-1}) / (8.314 \times 10^{-3}\ kJ\ mol^{-1}\ K^{-1} * 373.15K)]$$

$$A_2 = 47\,0663.64082201617$$