Chapter III

Experiment

3.1 Instrument Settings

3.1.1 Thermal Desorption System (TDS)

Figure 10 shows the Gerstel Thermal Desorption System (TDS 2)/ Cold Injection system (CIS 4) coupled to an Agilent GCMS (6890/5973) that was used in this experiment. It is suitable to be used for online sampling for both volatile and semi-volatile gaseous and vapor samples. The system consists of an autosampler, TDS, CIS, liquid nitrogen and the controller. The autosampler is made of a magazine with 20 adsorbent tube slots; each slot has o-rings at both ends to seal the tube when it is loaded to the slot. The magazine is also covered to prevent cross contamination of compounds from the environment to the tubes.

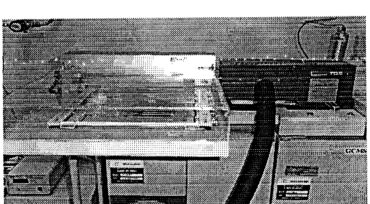
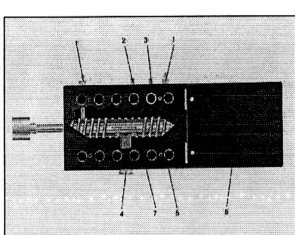


Figure 10. Gerstel TDS2/ CIS4

The liquid nitrogen is used to cool down the oven temperature to the initial temperature. Figure 11 shows the TDS front view. When the initial temperature (50 °C) is reached, the autosampler will load the adsorbent tube into the oven and oven temperature programming will be activated. The temperature will hold at initial temperature for initial time set (0.01 min); following by ramping to the final temperature 350 °C at 60 °C/ min. Helium is used to purge the desorped compounds from one end and flow through the transfer line to the cryogenic trap. The desorption process will end after 30 min and the TDS will be cooled to the initial temperature and the tube will be unloaded to the magazine. An empty tube will be loaded into the oven after the sample tube is unloaded. This prevents contaminants from entering the CIS.



1. Outlets for liquid nitrogen
2. Helium gas connection
3. Split outlet for TDS 2
4. Inlet for liquid nitrogen
5. Oven
6. Heated chamber for transfer line to CIS
7. Adsorbent tube

Figure 11. TDS Oven

When large amount of analyte is present in the samples, the split outlet enable users to choose the split mode. In Solvent Venting mode, the tube will be purged before the desorption process starts. This eliminates large amounts of

solvent flowing into the cryogenic trap and GC column. The TDS settings used for this experiment is summarized in Table 2.

Parameter	**Setting**
Sample Mode	Standard or Sample Remove
Flow Mode	Solvent Vent
Transfer Temp.	350 °C
Initial Temp	50 °C
Initial Time	0.01 min
1st Ramp Rate	60 °C
Final Temp	350 °C
Final Time	30 min

Table 2. TDS Setting

3.1.2 Cold Injection System (CIS)

The CIS serves as a cooled and/ or heated trap as an injector for focusing, concentrating and transferring the compounds to the GC capillary column. It is maintained at the initial temperature (-50 °C) by liquid nitrogen. A glass liner is placed in the CIS. When the TDS final time ends, the glass liner is flash heated to 350 °C at a very fast rate, 12 °C/ sec by the heater surrounding the CIS. GC ystem is activated when compounds are injected into the column. As shown in Figure 12, the CIS has a split vent valve which will split the sample according to the split ratio set in the GC front inlet split ratio.

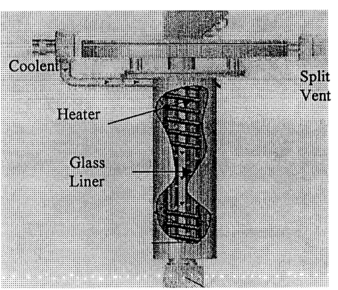


Figure 12. CIS

CIS parameters applied in this experiment are tabulated in Table 3.

Parameter	Setting
Cryo Cooling	On
Equilib Time	0.2 min
Initial Temp	-50 °C
Initial Time	0.2 min
1st ramp Rate	12 °C/ sec
Final temp	350 °C
Final time	3 min

Table 3. Gerstel CIS Setting

3.1.3 GC-MS

The GCMS system was tuned (Standard Spectra Tune) and an air and water check was performed prior to sample run to ensure the system is in good condition. A parafinnic column 5%-Phenyl-methylpolysiloxane (HP-5ms) with dimension 0.25mm x 30m x 0.25μm was connected to the CIS 4 outlet and the other end to the mass spectrometer. Helium (99.999%) was used as the mobile phase and column flows with 1ml/min constantly. Since the samples contains large amount of compounds, the front inlet split ratio was set at 99:1. Parameters used for the GC-MS are tabulated in Table 4.

Parameter	Setting
Column Flow	1 ml/min Mode: Constant Flow
Front Inlet (CIS 4)	Temperature: 350 °C Mode: Split Split Ratio: 99: 1
GC Oven Temperature	Initial Temp: 50 °C Hold time: 1 min Ramp: 6 °C/ min Final Temp: 260 °C Hold time: 4 min Total Run Time: 40 min
MS Interface Temperature	280 °C
Ion Source	Mode: EI Temperature: 230 °C
Solvent Delay	4 min
MS analyzer setting	Quadrupole Mass Scan: 50-550 Scan: 2.94 scan/sec
MS detector	Electron Multiplier

Table 4. GCMS Method

3.2 Apparatus

The apparatus used are listed as follows:

- HP Electronic Flow Meter (for nitrogen, helium, hydrogen and argon)
- Calibrated Binder Oven
- 6 pieces of PTFE containers with PTFE gas tubing (inlet connected from needle valve and outlet for adsorbent tube connection)

Figure 13 shows the set up of the sampling containers in an oven.

Figure 13. DHS Sampling Container and Oven System

3.3 Standards & Materials

The standards and materials used as a benchmark are:

- 200 ppm Hexadecane-d34, 99% deuterated (CAS:15716-08-2)
- 200 ppm Surrogate Standard for Recovery Spike: Anthracene-d10 (CAS: 1719-06-8)
- 1000 ppm 2-Hydroxyethyl Methacrylate (99.7%) CAS: 868-77-9
- 1000 ppm Tetrahydrofurfuryl Acrylate (88.4%) CAS: 2399-48-6
- 1000 ppm Isobornyl methacrylate (tech 87.8%) CAS: 7534-94-3
- Graphitized carbon blacks: Carbopack B (Supelco Cat No. 20287) & Carbopack C (Supelco Cat No. 20309)
- Microbalance
- Purge gas: Nitrogen gas purity 99.99%
- Solvent for dissolving standard: Methylene Chloride, Ultra grade
- Liquid Nitrogen for cyrogenic trap of Gerstel

3.4 Standard Solution Preparation Procedure

3.4.1 Preparation of Semi Quantitative Standard

20 mg of $C_{16}D_{34}$ was weighed and dissolved into methylene chloride in a 100 ml volumetric flask. The flask was topped up to the mark with the same solvent and solution was mixed well by shaking the flask repeatedly.

3.4.2 Preparation of Quantitative Standard

100 mg of standard compound of 2-hydroxyethylmethacrylate, tetrahydrofurfuryl acrylate and isobornyl methacrylate were weighed respectively and dissolved into methylene chloride in 3 separate volumetric flasks. The flasks were topped up to mark and solution was mixed well by repeated shaking.

3.4.3 Preparation of Surrogate Spike Standard

20 mg of Anthracene-d10 standard was dissolved in methylene chloride in a 100 ml volumetric flask. The flask was topped up to the mark and solution was mixed well by shaking the flask repeatedly

3.4.4 Preparation of Adsorbent

Carbotrap B was weighted 150 mg and Carbotrap C was weighed 250 mg and packed in empty tubes (tube measurement 6 mm x 7"). These tubes were specially cleaned and silanized with an arrow to indicate sampling flow direction. The adsorbent was held by two frits at both ends of the tubes. These frits will not adsorb or decompose the analytes. The adsorbent was

packed in accordance to the heating zone of the TDS oven. Figure 14 shows the packed adsorbent tube.

Figure 14. Adsorbent tube

3.5 Test Procedure

3.5.1 Conditioning Adsorbent Tubes

All new and used adsorbent tubes were conditioned by subjecting them to the instrument test method as described in section 3.1. New tubes were conditioned for 2 to 3 times to ensure thorough removal of impurities in them.

3.5.2 Container Cleanliness Check

The containers were baked at 120 °C and the impurities/ contaminants were purged with nitrogen gas to waste adsorbent tubes. This purging procedure was performed for 5 hours. In order to ensure the cleanliness of the sampling containers, a 'container cleanliness check' test was performed prior to the sample test.

3.5.3 Sampling Procedure

6 clean adsorbent tubes were connected to each PTFE container outlet by their respective nitrogen gas tubing. The oven was preheated to 85 °C. 5 samples from the same source were subjected to the test each time where 1 piece of motor was placed in a sampling container. 5 µl of Anthracene-d10 (200 ppm) was spiked into each container by using a 10 µl syringe. All containers were sealed tightly and nitrogen gas flow was turned on. The gas flow for each container was measured by the electronic flow meter and adjustment on the needle valves was made to obtain flow rate of 65 (±2) mL/ min. The oven timer was set to 3 hours.

After 3 hours, the nitrogen gas flow was turned off. Then, adsorbent tubes were disconnected from the containers. Each tube was injected with 5 µl of hexadecane-d34 (200 ppm).

3.5.4 Sample Run

The tubes were loaded to the TDS magazine for sample analysis by using method as described in section 3.1. Procedure 3.4.1 to 3.4.4 were repeated for the other motor samples.

3.6 Data Analysis Method

3.6.1 Semi-quantitative analysis

From the GCMS chromatograms obtained, peak integration was performed with Chemstation Integrator at threshold 20. The amount of each peak was calculated with reference to the peak area of 1 μg hexadecane-d34:

Amount of compound (ng/pc) =
Peak Area of compound/ hexadecane-d34 peak area * 1000

The NISK98k and the in-house mass spectrum libraries were used for identification of the compounds. Mass spectrum for each peak was examined to ensure that they matched with the library identity. A list of compound identities with their retention time (Rt), integrated peak area and the semi quantitative amount was tabulated. Classification of the compounds were carried out where 4 groups of compounds were identified:

- Acrylate/ methacrylates (ester of acrylic acid which is the main ingredient of the adhesive)
- Hydrocarbon (including all aliphatic, aromatic and cyclic hydrocarbon)
- Alcohol
- Others (which do not belong to the mentioned groups, including those unidentified compounds)

3.6.2 Quantitative Analysis Method

3.6.2.1 Calibration Plot

In order to quantified the acrylate and methacrylate accurately, the compounds standard calibration plots were established. Since TDS response to the amount of solute present (not concentration), the calibration plot was established by injecting different volume of the 1000 ppm standard solution into the adsorbents.

2-hydroxyethyl methacrylate calibration plot was established at range 10 to 50 μg as indicated in Table 5.

Volume of 1000 ppm Standard (μL)	Amount of Solute (μg)
10.0	10
20.0	20
30.0	30
40.0	40
50.0	50

Table 5. HEMA Standard Calibration Range

Tetrahydrofurfuryl acrylte (THFA) calibration plot was established at range 2 μg to 20 μg as tabulated in Table 6.

Volume of 1000 ppm Standard (μL)	Amount of Solute (μg)
2.0	2.0
5.0	5.0
10.0	10.0
15.0	15.0
20.0	20.0

Table 6. THFA Standard Calibration Range

Isobornyl methacrylate (IBM) calibration plot was established at range 2.0 μg to 10.0 μg, as indicated in Table 7.

Volume of 1000 ppm Standard (μL)	Amount of Solute (μg)
2.0	2.0
4.0	4.0
6.0	6.0
8.0	8.0
10.0	10.0

Table 7. IBM Standard Calibration Range

3.6.2.2 Check Standard

25 μg of 2-hydroxyethyl methacrylate, 10 μg of tetrahydrofurfuryl acrylate, 5 μg of isobornyl methacrylate and 1 μg of hexadecane-d34 were injected into an adsorbent tube. The adsorbent tube was subjected to the sample run method as described in section 3.5.4. Then, the peak area obtained for each compound was quantified via 2 methods, the respective calibration curve and the semi-quantitative standard. Total of 3 check standard runs were performed.