

**DETERMINATION OF DIFFERENT ORGANIC CONTAMINANTS
IN HARD DISK DRIVE COMPONENTS**

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ABSTRACT

The presence of organic contaminants in hard disk drive components is an issue as they may lead to drive operation failure. Various analytical instruments have been used to determine the organic contaminants. Determination of hydrocarbon contaminant in MBA and cover components was done by solvent extraction on the components, followed by GC-MS instrument analysis. For acrylate and methacrylate contaminant analysis, after sample collection through dynamic headspace sampling method, the extract was subjected to thermal desorption coupled with GC-MS. Hydrocarbon, acrylate, and methacrylate were quantified using internal standard technique, and recovery studied was carried out to assess the accuracy of the methods. Another organic contaminant, silicone, was also identified using ATR FT-IR technique. Silicone was determined at IR frequency region of 800 cm^{-1} with reference to a linear calibration curve obtained.

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LIST OF SYMBOLS AND ABBREVIATIONS

amu	Atomic mass unit
ATR	Attenuated Total Reflectance
DHS	Dynamic headspace
ESD	Electrostatic charge
eV	Electron volt
FT-IR	Fourier Transform Infrared
GC-MS	Gas chromatography-mass spectrometry
HDD	Hard disk drive
HP	Hewlett Packard
MBA	Motor base assembly
MCT	Mercury cadmium telluride
MFC	Mass flow control
n	Number
ND	Not detected
NIST	National Institute of Standards and Technology
ppm	Part per million
R ²	Coefficient of determination

U.K.	United Kingdom
U.S.A.	United States of America
USB	Universal Serial Bus

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CHAPTER 1

INTRODUCTION

1.1 Hard Disk Drives

Almost all personal computers come with a hard disk drive (HDD), or also known as a hard drive. It is mainly used for digital data storage and retrieval. Storage size has been the main advantage of HDDs in comparison to other data storage devices like flash memory drives and compact discs with much lower capacities. Nowadays, HDD can provide capacity up to 4 terabytes, developing from merely a few megabytes in the 1950s (Jacob *et al.*, 2010), due to the market demand in higher storage volume over the decades.

HDDs use read/write heads to retrieve or store data magnetically from or onto hard disks. The glass or metal disks are permanently sealed inside a HDD to prevent contamination that could lead to data lost or drive operation failure. Commonly, desktop computers use 3.5 inch HDDs while notebook computers use 2.5 inch HDDs. 1.5 inch HDDs are available for smaller digital devices (Morley and Parker, 2009). Figure 1.1 shows typical 3.5 inch and 2.5 inch HDDs.

HDDs can be divided into two categories - internal and external HDDs. An internal HDD is intended to be placed inside a system unit, whereas an external HDD, which is portable, usually connects to computers using a Universal Serial Bus (USB) port. In addition to computer industry, HDDs can be found in other digital products such as camera or video recorders, media players, game consoles, and many more.

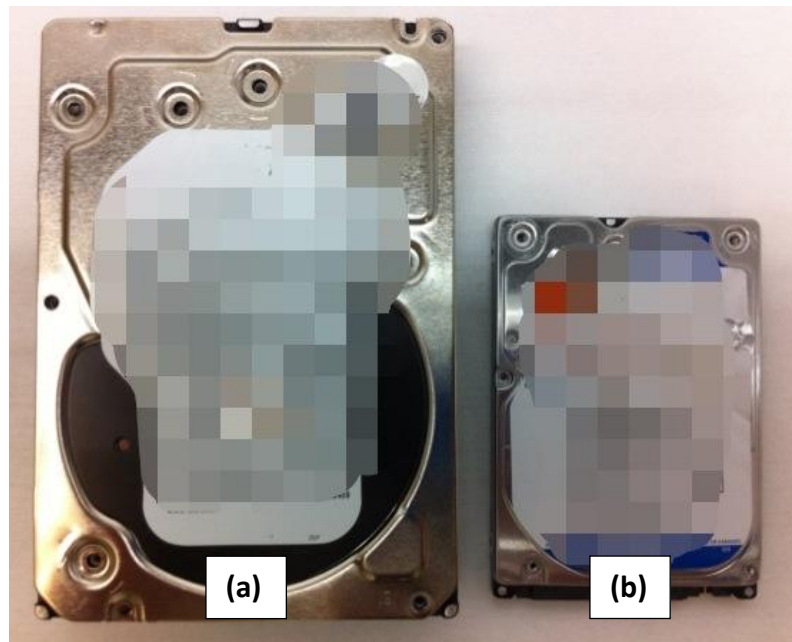


Figure 1.1 (a) 3.5 and (b) 2.5 inch HDDs

1.2 Hard Disk Drive Components

There are many mechanical and electronic components inside a HDD. Each component serves its specific function to build a complete HDD for digital data storage. Figure 1.2 illustrates the basic components inside a HDD.

The main HDD components are the heads and the disks. There may be one or a stack of disk(s) inside, with a read/write head flying on each surface of the disk(s). Spindle motor spins the disk(s) when the HDD is performing data reading and writing. Spindle motor is attached to a base casting, which houses all components inside a HDD. Spindle motor, together with the base casting, is referred to as a motor base assembly (MBA). Disk clamp is used to hold the disks onto the spindle motor. The disks are separated by disk spacer to allow head placements.

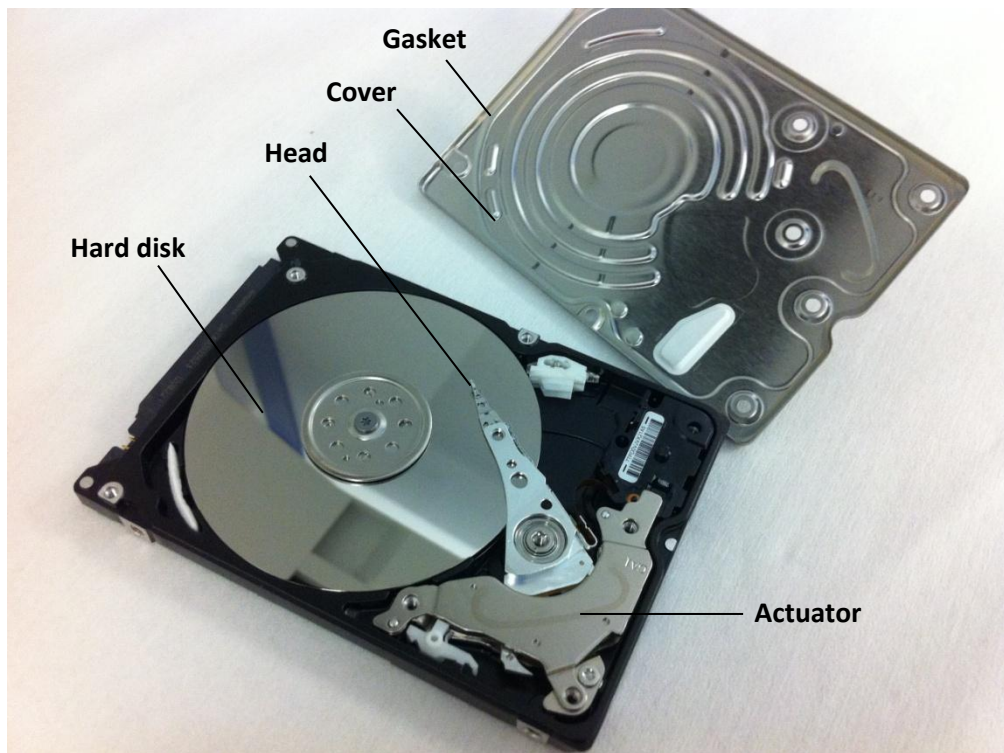


Figure 1.2 Basic HDD components

On the other hand, an actuator, with two high powered magnets, holds the heads on the disk surfaces freely to avoid head-disk direct contact. HDD is sealed completely by a cover with gasket on it so that all components are protected from contamination.

There are other smaller components like plastic parts, filters and seals, as well as some other electronic components that play important roles in overall drive operations.

1.3 Micro Contamination in Hard Disk Drive Components

Contamination control of HDD components and assembly process is essential to prevent contamination related HDD failures. Organic, particulate, and ionic are the general types of contaminants found in HDD and its components. Hard disk damage, disk scratch, and head crash can be caused by particulate contamination. Particularly, magnetic particles would lead to permanent data erasure (Nagarajan, 1997). Organic

contamination causes stiction failure. When this happens, a head cannot be lifted by the motor current and it will stick onto the disk upon landing. Some volatile organic contaminants tend to outgas and condense on the head surface as droplets, causing head flying instability and drive operation failure (Sonoda, 2012). Ionic contamination may result in corrosion of the metal components.

1.3.1 Organic Contaminants

Organic contaminants can be categorised into volatile and non-volatile organic contaminants. Volatilization of organic contaminants is facilitated by the heat generation via disk rotation controlled by the spindle motor. Typical volatile organic contaminant sources of HDDs include adhesives that contain acrylates and methacrylates, elastomers, oils, greases, and organic coatings (Akamatsu and Ohtani, 2002).

Although non-volatile organic contaminants or residues are not volatilized but these contaminants can still lead to drive failure. Uncured adhesive, silicone-containing mould release agents, plasticisers, oils, greases, and packaging materials used in HDD components are the sources of non-volatile organic contaminant.

Moreover, the presence of hydrocarbons, no matter volatile or not, in both metal and plastic HDD components is possible due to usage of various organic chemicals during manufacturing and cleaning processes.

1.3.2 Particulate Contaminants

Particulate contaminants can be organic, inorganic, metallic, and magnetic particles. Sources of organic and inorganic particles are glove powders, finger cot powders, human debris, and make up powders. HDD components that are made from metal may contain metallic particulate contamination. For instance, steel components contain steel particles. Magnetic particles could come from spindle motor and actuator magnet.

1.3.3 Ionic Contaminants

With the presence of moisture, ionic contaminants could corrode metal components in HDD. The examples of ionic contaminants are chloride, sulphate, and phosphate. There are many possible sources of these ionic contaminants. Sulphate and phosphate may present if the ionic surfactants used to wash HDD components remain on the parts. Cleaner components often can be obtained by aqueous cleaning system, but ineffective removal of the surfactants might introduce ionic contaminants onto HDD components.

Other sources of ionic contaminants include gloves, finger cots, cotton Q-tips, foam swabs, packing materials, and the presence of humans in the cleanroom during component or HDD manufacturing processes. It is known that almost all latex gloves have certain amount of chloride while some electrostatic discharge (ESD) gloves contain sulphate (IDEMA Standards, 1998).

1.4 Cleanliness Measurement Approaches

Nagarajan (1997) has summarized a number of published cleanliness measurement approaches to identify and quantify the micro contamination in HDD and its components. Non-volatile organic residue analysis involves extraction of organic contaminants from a component surface with the aid of an organic solvent. The extract can then be subjected to weight difference determination and Fourier Transform Infrared (FT-IR) spectroscopy analysis. HDD components outgassing compounds was quantified using Gas Chromatography-Mass Spectrometry (GC-MS).

Thus far, various analytical techniques have been developed for the cleanliness measurement. For example, determinations of acrylates and methacrylates have been carried out using dynamic headspace outgassing procedure coupled with GC-MS (Pua, 2004). 2-hydroxyethyl methacrylate, tetrahydrofurfuryl acrylate, and isobornyl methacrylate from spindle motors have been quantified using both semi and full quantitative methods in the study. Quantification of X-1P additive that presents in hard disks was performed by solvent vapour extraction coupled with GC-MS (Koay, 2004). The additive was successfully quantified and the extraction method has been proven effective based on good recovery obtained. Similarly, silicone extraction from cover via solvent extraction method coupled with Attenuated Total Reflectance (ATR) FT-IR spectroscopy as quantification technique has been studied (Ng, 2004).

A major approach for particulate contamination measurement is liquid particle counting. This method has been widely accepted in HDD industry because of its effectiveness and low detection limit (2 to 5 μm) (Nagarajan, 1997). Further assessment can be carried out by filtering the extract solution after component extraction, followed by subjection of the filtrate to microscopic analyses. Tape testing was used for surface

cleanliness assessment. Particles can be picked up and examined via microscope or scanning electron microscope for particulate contaminants identification.

Ionic contaminants are normally identified using ion chromatography and the ions detected can be quantified by a conductivity detector (Nagarajan, 1997).

1.5 Objectives

In this study, the main objective was to determine different organic contaminants in HDD components using various analytical techniques. The components selected are MBA and cover. Two suppliers were chosen for each of the component for comparison purpose. Hydrocarbon level in the components was analysed using GC-MS with organic solvent extraction. Acrylate and methacrylate amounts in the components were quantified using GC-MS with dynamic headspace sampling method. Silicone in the components was determined using ATR FT-IR analysis.

CHAPTER 2

METHODOLOGY

2.1 Materials

Samples obtained were base casting and cover. Two suppliers were selected for each component as shown in the table below:

Table 2.1 MBA and cover suppliers

Component	Supplier
MBA	Supplier A
	Supplier B
Cover	Supplier C
	Supplier D

Chemicals used include analytical grade hexane, methylene chloride, and isopropyl alcohol from J.T. Baker (U.S.A.). Anthracene-d10, hexadecane-d34, and dimethylpolysiloxane standards were purchased from Sigma-Aldrich (U.S.A.).

2.2 Standard Solutions

All hexadecane-d34 and anthracene-d10 standard and dimethylpolysiloxane calibration solutions were made and mixed thoroughly by shaking and inverting the volumetric flasks repeatedly. The standard solutions were sealed and stored under refrigeration at 4 °C. The standard solutions were not kept more than three months to prevent deterioration.

2.2.1 Preparation of Internal Standard

200 ppm of internal standard was prepared by dissolving 20 mg of hexadecane-d34 in 100 mL of methylene chloride in a volumetric flask.

2 ppm of internal standard was then prepared by diluting 1 mL of 200 ppm hexadecane-d34 solution with 100 mL of hexane in a volumetric flask.

2.2.2 Preparation of Spike Standard

200 ppm of spike standard was prepared by dissolving 20 mg of anthracene-d10 in 100 mL of methylene chloride in a volumetric flask.

2 ppm of spike standard was then prepared by diluting 1 mL of 200 ppm anthracene-d10 with 100 mL of hexane in a volumetric flask.

2.2.3 Preparation of Silicone Calibration Standard

Approximately 25 mg of dimethylpolysiloxane was weighed into a 25 mL volumetric flask. By making up the volume to 25 mL with hexane, a stock solution of 1 mg/mL was prepared.

1 mL of the stock solution was pipetted into a 10 mL volumetric flask. 0.1 mg/mL dimethylpolysiloxane standard solution was prepared by topping up the flask to the mark with hexane. Finally, dimethylpolysiloxane standard solution with the concentration of 0.01 µg/mL was prepared by diluting 0.1 mg/mL dimethylpolysiloxane with 10 mL of hexane.

2.3 Determination of Hydrocarbon

2.3.1 Sample Preparation

Extraction of hydrocarbon was performed using hexane as solvent. Hexane was chosen due to its ability to dissolve hydrocarbons. A total of 50 mL of hexane was used to rinse the sample directly using a glass dropper. The rinsing was covered the exposed sample surface and each surface was rinsed for at least two times. With the hexane rinse, any hydrocarbons present in the sample can be extracted. The extract was collected into an evaporating dish, which was placed at an angle for collection of the residue in a localised area during solvent evaporation in a fume hood to dryness.

The residue was then re-extracted with 1 mL of hexane. Before transferring the extract to a 5 mL centrifuge tube, the solvent in the evaporating dish was swirled so that the residue was completely transferred. The extract in the centrifuge tube was evaporated to dryness by nitrogen gas purging.

100 μ L of hexane was added in the dried centrifuge tube to re-dissolve the residue, and the solution was transferred completely to a 250 μ L GC vial. Nitrogen gas purging was performed again to dry the extract in the GC vial. Finally, 40 μ L of 2 ppm hexadecane-d₃₄ internal standard was added into the GC vial, followed by GC-MS analysis.

A total of four samples with five replicates each were prepared as shown in Table 2.2. A method blank was prepared following the same procedure, but without any sample for extraction. For MBA samples, extraction at spindle motor area was excluded to prevent motor oil from being extracted. All samples were spiked with 40 μ L of 2 ppm anthracene-d₁₀ standard prior to sample extraction for recovery study.

Table 2.2 Sample for hydrocarbon analysis

Component	Supplier	Number of Replicate
MBA	Supplier A	5
	Supplier B	5
Cover	Supplier C	5
	Supplier D	5

2.3.2 Instrumentation

Analytical instrument employed for the hydrocarbon analysis was GC-MS system from Hewlett Packard (HP) 6890 GC system coupled to 5973 mass selective detector, and equipped with 7673 auto injector. Standard spectra tuning was performed prior to sample run to ensure the system was in good condition with low air and water percentages. Poly(5%-diphenyl-95%-dimethylsiloxane) fused silica column (HP-5MS from Agilent Technologies) with 30 m length, 0.25 mm inner diameter and 0.25 μm film thickness was used for separation. Helium was used as the carrier gas. Table 2.3 shows the instrument settings used for the GC-MS analysis.

Table 2.3 HP 6890-5973 GC-MS instrument set-up

Parameter	Setting
Injector temperature	300 °C
Injection mode	Splitless
Sample injection volume	3 µL
Column flow	1 mL/min
Column mode	Constant flow
Septum purge flow	1 mL/min
Initial column temperature	30 °C
Initial Time	1 min
Temperature ramp	15 °C/min
Final temperature	300 °C
Total run time	Approximately 40 min
MS interface temperature	300 °C
Solvent delay	4.5 min
Ion source	Electron ionisation
Electron energy	70 eV
Ion source temperature	230 °C
Mass analyser	Quadrupole
Quadrupole temperature	150 °C
Mass range	33-700 amu
Scan time	1.14 scan/s
Mass detector	Electron multiplier

2.3.3 Quantification

After GC-MS data acquisition, peaks obtained were integrated using Chemstation software. Hydrocarbon peaks were identified using NIST05 library. The amount of each hydrocarbon peak was calculated with reference to the peak area of hexadecane-d34 internal standard, as described in the following equation:

Amount of compound a

$$= \frac{x \ y \ (\text{Peak area of compound a/Peak area of internal standard})}{z}$$

... Equation 1

where x = Concentration of internal standard

y = Volume of internal standard

z = Number of sample used

If a hydrocarbon hump is present, the integration should include all hydrocarbon compounds that form the hump. Any peaks on top of the hump were integrated using valley-to-valley method. Only hydrocarbon peaks on top of the hump were included in the final results, while non-hydrocarbon peaks were excluded.

2.4 Determination of Acrylate and Methacrylate

2.4.1 Sample Preparation

Adsorbent tubes were used to collect samples for acrylate and methacrylate determination. These adsorbent tubes were stainless steel tube with graphitised carbon as sorbent and were obtained from Markes International (U.K.). This sampling technique is called dynamic headspace. The front ends of the tubes were installed at the flow exit of the stainless steel chambers and the tubes were placed inside an oven (Figure 2.1). Stainless steel chamber covers were opened for the sample placement. A method blank was prepared without putting the sample in the chamber. Each sample (including method blank) was spiked with 5 μL of 200 ppm anthracene-d10 standard for

recovery study. All chambers were closed tightly, followed by oven heating to 85 °C. Nitrogen flow was turned on once the oven reached 85 °C. Nitrogen flow rate was controlled at 65 ± 5 mL/min, which can be measured by a flow meter at the exit of the adsorbent tubes. The oven heating was continued up to 3 h. Through heating, volatile compounds were outgassed and adsorbed by the adsorbent tubes. The tubes were removed and 5 μ L of 200 ppm hexadecane-34 was injected as internal standard to the front end of the tubes.



Figure 2.1 Outgassing sample collection method

The same sample preparation procedure was repeated for other groups of samples, which resulted in sixteen replicates in total. To ensure the chambers are clean and there were no carried over contaminants, the chambers were cleaned using isopropyl alcohol, followed by nitrogen gas purging and oven baking at 150 °C for at least 5 h. All adsorbent tubes were then subjected to thermal desorption and GC-MS analysis.

Table 2.4 Sample for acrylate and methacrylate analysis

Component	Supplier	Number of Replicate
MBA	Supplier A	4
	Supplier B	4
Cover	Supplier C	4
	Supplier D	4

2.4.2 Instrumentation

Thermal desorption system used was UNITY series 1 thermal desorber, equipped with ULTRA series 2 autosampler and series 1 mass flow control (MFC) accessory from Markes International (U.K.). Each tube was heated with thermal desorber with nitrogen gas flowing through the tube to transfer the sample to a cold trap. Upon complete purging of the sample from the adsorbent tube to the cold trap, the cold trap was heated immediately. The heated sample was then swept into a GC-MS instrument that was attached to the thermal desorption system for separation and identification of compounds.

Table 2.5 Thermal desorption system set-up

Parameter	Setting
Mode	Standard 2 Stage Thermal Desorption
Split on in standby	Yes, 20 mL/min
Pre-purge time	1 min
Pre-purge flow rate	20 mL/min
Primary tube desorption	10 min at 320 °C
Split on during primary (tube) desorption	No
Trap flow rate	20 mL/min
Cold trap focussing temperature	-10 °C
Cold trap desorption temperature	320 °C
Cold trap heating rate	MAX
Trap hold time	10 min
Split on during secondary (trap) desorption	Yes, 28.8 mL/min
Flow path temperature	200 °C
GC cycle time	0 min
Minimum carrier gas pressure	5.0 psi

GC-MS system used was Agilent Technologies 6890N GC system coupled to 5975 mass selective detector. Standard spectra tuning was performed prior to sample run to ensure the system was in good condition with low air and water percentages. Poly(5%-diphenyl-95%-dimethylsiloxane) fused silica column (HP-5MS from Agilent Technologies) with 30 m length, 0.25 mm inner diameter and 0.25 μm film thickness was used for separation. Helium was used as the carrier gas. The quantification was based on Equation 1 as described in section 2.3.3.

Table 2.6 Agilent 6890N-5975 GC-MS instrument set-up

Parameter	Setting
Column flow	1 mL/min
Column mode	Constant pressure
Initial column temperature	40 °C
Initial Time	1 min
Temperature ramp	8 °C/min
Final temperature	260 °C
Total run time	Approximately 40 min
MS interface temperature	280 °C
Solvent delay	5 min
Ion source	Electron ionisation
Electron energy	70 eV
Ion source temperature	230 °C
Mass analyser	Quadrupole
Quadrupole temperature	150 °C
Mass range	33-700 amu
Scan time	2.22 scan/s
Mass detector	Electron multiplier

2.5 Determination of Silicone

2.5.1 Sample Preparation

Similar to the hydrocarbon extraction, extraction of silicone was performed using hexane as solvent. A total of 50 mL of hexane was used to rinse the sample directly using a glass dropper. The rinsing was covered the exposed sample surface and each surface was rinsed for at least two times. With the hexane rinse, silicone (if any) in the sample can be extracted (Ng, 2004). The extract was collected into an evaporating

dish, which was placed at an angle for collection of the residue in a localised area during solvent evaporation in a fume hood to dryness.

The residue was then re-extracted with 1 mL of hexane. Before transferring the extract to a 5 mL centrifuge tube, the solvent in the evaporating dish was swirled so that the residue was completely transferred. The extract in the centrifuge tube was evaporated to dryness by nitrogen gas purging, and was subjected to ATR FT-IR analysis. Then, 25 μ L of hexane was added in the dried centrifuge tube to re-dissolve the residue, and the solution was transferred completely onto a horizontal ATR cell composed of zinc selenium crystal. This step was repeated once more to ensure the residue in the tube was fully extracted.

A total of four samples with five replicates each were prepared as shown in Table 2.7. A method blank was prepared following the same procedure, but without any sample for extraction. For MBA samples, extraction at spindle motor area was excluded to prevent motor oil from being extracted.

Table 2.7 Sample for silicone analysis

Component	Supplier	Number of Replicate
MBA	Supplier A	5
	Supplier B	5
Cover	Supplier C	5
	Supplier D	5

2.5.2 Instrumentation

FT-IR spectra of the samples were collected using Nicolet iS50 FT-IR spectrometer from Thermo Scientific, equipped with Nex Smart Ark ATR bench and mercury cadmium telluride (MCT) detector. OMNIC Spectra software was used to

perform FT-IR spectra collection and treatment. Horizontal ATR cell composed of zinc selenium crystal was selected for sample placement. FT-IR spectra were scanned in region of $4000 - 650 \text{ cm}^{-1}$ by co-adding 64 scans and at resolution of 4 cm^{-1} . All spectra were rationed against a background of air spectrum each time before a new sample spectrum collection. All spectra collected were recorded as absorbance modes.

2.5.3 Quantification

In order to quantify the silicone that presents in the samples, calibration using dimethylpolysiloxane standard was carried out. The calibration plot was established using $0.01 \text{ }\mu\text{g/mL}$ dimethylpolysiloxane standard as shown in Table 2.8. $0.4 \text{ }\mu\text{g}$ of dimethylpolysiloxane check standard was prepared and analysed for dimethylpolysiloxane calibration curve verification. This check standard was prepared from a stock solution that was different from the calibration.

Table 2.8 Calibration range using $0.01 \text{ }\mu\text{g/mL}$ dimethylpolysiloxane standard

Volume of $0.01 \text{ }\mu\text{g/mL}$ dimethylpolysiloxane Standard (μL)	Amount (μg)
5	0.05
10	0.10
20	0.20
30	0.30
40	0.40
50	0.50
60	0.60
70	0.70
80	0.80
90	0.90
100	1.00

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Hydrocarbon Results

The extraction method accuracy was examined by the recoveries of 40 μL of 2 ppm anthracene-d10 standards which were spiked onto every sample before extraction. Figure 3.1 shows the chromatogram of the anthracene-d10 standard which was directly injected into the column with the peak area of 9385272 at the retention time of 13.537 min. Table 3.1 summarises the recovery of different samples.

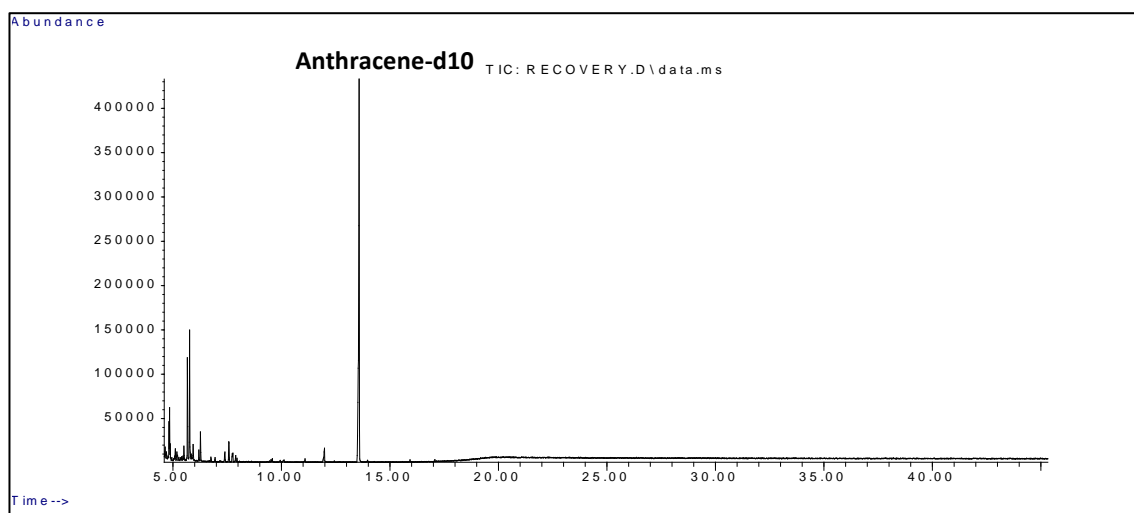


Figure 3.1 Gas chromatogram of 2 ppm anthracene-d10 standard

Table 3.1 Recovery of anthracene-d10 standard for hydrocarbon analysis

Component	Supplier	Recovery (%)	RSD (%)
		n=5	
MBA	Supplier A	147 \pm 34	22.9
	Supplier B	98 \pm 52	52.8
Cover	Supplier C	69 \pm 8	11.9
	Supplier D	115 \pm 4	4.0

In general, the recovery of the spiked standard for the samples was acceptable, confirming the method effectiveness in the hydrocarbon extraction. The recovery of 98% and 115% for MBA samples from Supplier B and cover samples from Supplier D, respectively, was satisfactory. The recovery for the other two groups of samples was slightly poor. Errors might have been introduced during the sample extraction steps, which lead to the loss of certain amount of sample. Higher recovery obtained could be due to inaccurate volume of hexane solvent that contains internal standard used to re-dissolve the extract residue at the final step. Care must be taken also when capping the GC vial. Evaporation of solvent may occur if the cap is loose, causing higher concentration of the standard and thus higher recovery.

After hexane solvent extraction, hydrocarbon level in MBA and cover samples was analysed using GC-MS. The amount of hydrocarbon was calculated with reference to the peak area of hexadecane-d34 internal standard in the chromatograms generated as per Equation 1, and the results are tabulated in Table 3.2.

Table 3.2 Total Concentration of hydrocarbon detected in MBA and cover samples

Component	Supplier	Total concentration of hydrocarbon (ng/sample) n=5	RSD (%)
MBA	Supplier A	$(3.4 \pm 0.7) \times 10^3$	20.8
	Supplier B	$(1.9 \pm 0.3) \times 10^3$	15.6
Cover	Supplier C	ND	-
	Supplier D	ND	-

Based on the results above, MBA from Supplier A contains the highest level of hydrocarbon, with the amount of $(3.4 \pm 0.7) \times 10^3$ ng/sample in average. This was followed by MBA from Supplier B with $(1.9 \pm 0.3) \times 10^3$ ng/sample of hydrocarbon.

The relative standard deviations between five replicates were found to be 20.8% and 15.6% for MBA Supplier A and Supplier B, respectively. This result shows the low sample to sample variation. On the other hand, hydrocarbons were not detected for cover samples from both suppliers.

Figure 3.2 shows the gas chromatogram and the distribution of hydrocarbon for one of the MBA samples. The presence of a hydrocarbon hump was observed from retention time of approximately 12 min up to 40 min. Thus, integration of the hydrocarbon hump is important and was included in the total hydrocarbon calculation.

By using the first MBA sample from Supplier A as example, a total of 54 peaks were integrated. Overall, hydrocarbon hump and peaks were the major compounds extracted for MBA samples. Apart from hydrocarbons, other peaks identified were fatty acid esters, phthalate, alcohol, and organophosphate. Note that few peaks prior to retention time of 10 min are actually hexane solvent contaminants which were also found in the method blank.

Gas chromatogram for one of the cover samples is shown in Figure 3.3. A total of 40 peaks were integrated from the chromatogram. There was no hydrocarbon detected from cover samples. Major compounds extracted from cover samples were Phthalic acid, monocyclohexyl ester along with other fatty acid esters.

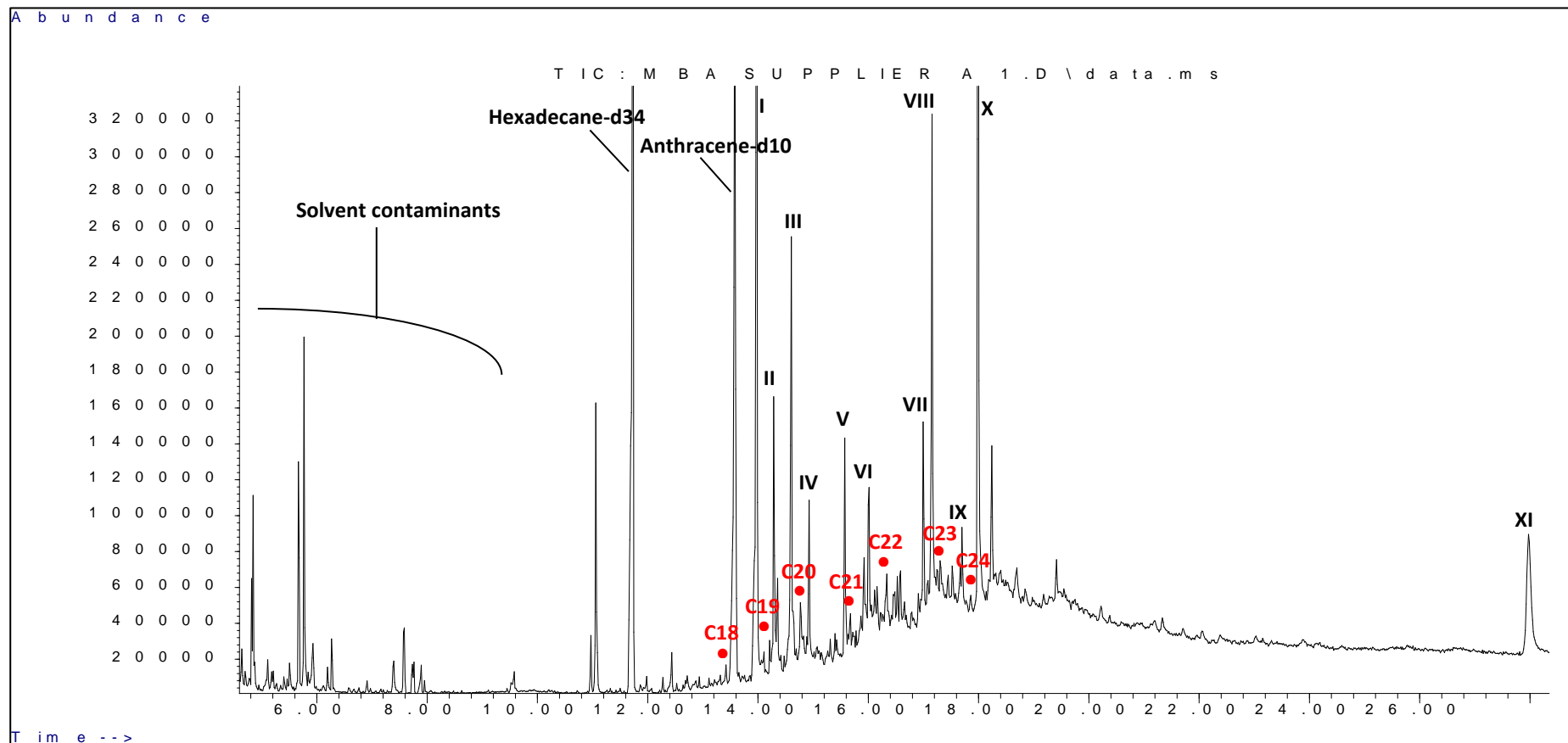


Figure 3.2 Gas chromatogram showing the distribution of hydrocarbon for MBA from Supplier A [1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester (I), Pentadecanoic acid, 14-methyl-, methyl ester (II), 1,2-Benzenedicarboxylic acid, butyl 2-methylpropyl ester (III), Isopropyl Palmitate (IV), Octadecanoic acid, methyl ester (V), Oxalic acid, isobutyl pentadecyl ester (VI), Benzyl butyl phthalate (VII), Hexanedioic acid, bis(2-ethylhexyl) ester (VIII), 1-Decanol, 2-hexyl- (IX), 1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester (X), Tris(2,4-di-t-butylphenyl)Phosphate (XI)]

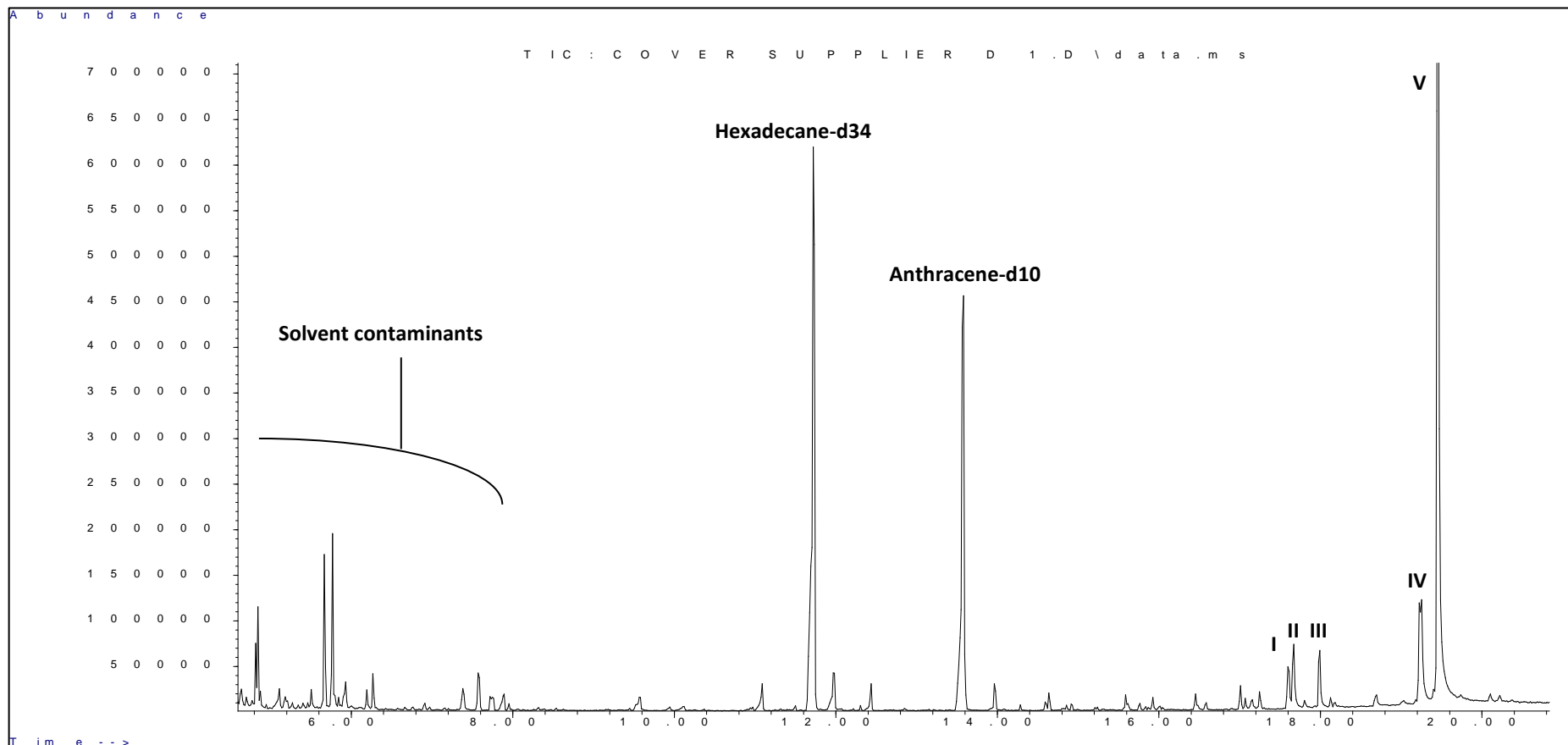


Figure 3.3 Gas chromatogram for cover from Supplier D [Morpholine, 4-phenyl- (I), 1-Propanol, 2-[2-(benzoyloxy)propoxy]-, benzoate (II), 1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester (III), 1,2-Benzenedicarboxylic acid, diisodecyl ester (VI), Phthalic acid, monocyclohexyl ester (V)]

3.2 Acrylate and Methacrylate Results

The accuracy of DHS outgassing procedure was examined by the recovery of anthracene-d10 standard which was spiked into every sampling container prior to sample baking. Figure 3.4 shows the chromatogram of the anthracene-d10 (peak area of 24186285 at the retention time of 22.367 min). Table 3.3 summarises the recovery of the spiked standard of different samples.

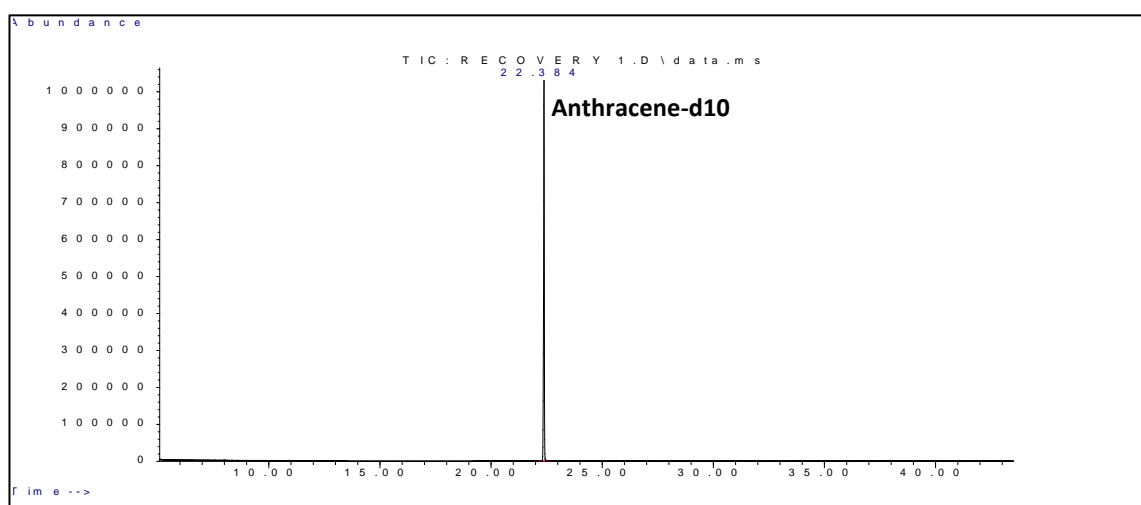


Figure 3.4 Gas chromatogram of 200 ppm anthracene-d10 standard

Table 3.3 Recovery of anthracene-d10 standard for acrylate and methacrylate analysis

Component	Supplier	Recovery (%)	RSD (%)
		n=4	
MBA	Supplier A	94 ± 5	3.9
	Supplier B	97 ± 7	7.2
Cover	Supplier C	151 ± 17	10.9
	Supplier D	146 ± 8	5.4

Overall, the recovery of anthracene-d10 for the samples was acceptable, confirming the method effectiveness in the acrylate and methacrylate extraction. The recovery of 94% and 97% for MBA samples from Supplier A and Supplier B, respectively, was satisfactory. The recovery for the cover samples was slightly poor, due to higher recovery obtained. Error could be introduced during standard injections into the sampling containers and sampling tubes. Slight difference in the volume injected may lead to variation in terms of recovery.

Acrylate and methacrylate compounds detected were quantified as per Equation 1. The calculated results are tabulated in Table 3.4.

Table 3.4 Total concentration of acrylate and methacrylate detected in MBA and cover samples

Component	Supplier	Total concentration of acrylate and methacrylate (ng/sample)	RSD (%)
		n=4	
MBA	Supplier A	$(4.4 \pm 2.3) \times 10^2$	52.3
	Supplier B	$(1.1 \pm 0.3) \times 10^2$	28.5
Cover	Supplier C	$(0.3 \pm 0.1) \times 10^2$	16.1
	Supplier D	ND	-

Based on the results above, MBA from Supplier A contains the highest concentration of acrylate and methacrylate. This was followed by MBA from Supplier B with $1.1 \pm 0.3 \times 10^2$ ng. The relative standard deviations between five replicates were found to be 52.8% and 16.4% for MBA Supplier A and Supplier B, respectively. This shows that the sample to sample variation was quite high, especially for MBA from Supplier A. On the other hand, relatively lower acrylate and methacrylate amount ($0.3 \pm$

0.1×10^2 ng/sample) was detected for the covers from Supplier C while the compounds were not detected for the covers from Supplier D.

Figure 3.5 shows the gas chromatogram for one of the MBA samples. A total of 13 peaks were integrated for the chromatogram. The presence of 2-hydroxyethyl methacrylate and isobornyl methacrylate were detected, at the retention time of 8.748 min and 17.317 min, respectively. In addition to the methacrylate compounds, hydrocarbon, alcohol, and antioxidant were also detected.

Gas chromatogram for one of the cover samples is shown in Figure 3.6. A total of 36 peaks were integrated. *n*-Hexyl acrylate was detected at the retention time of 15.149 min. Other than the acrylate compound, other detected compounds were hydrocarbon, alcohol, fatty acid ester, and antioxidant.

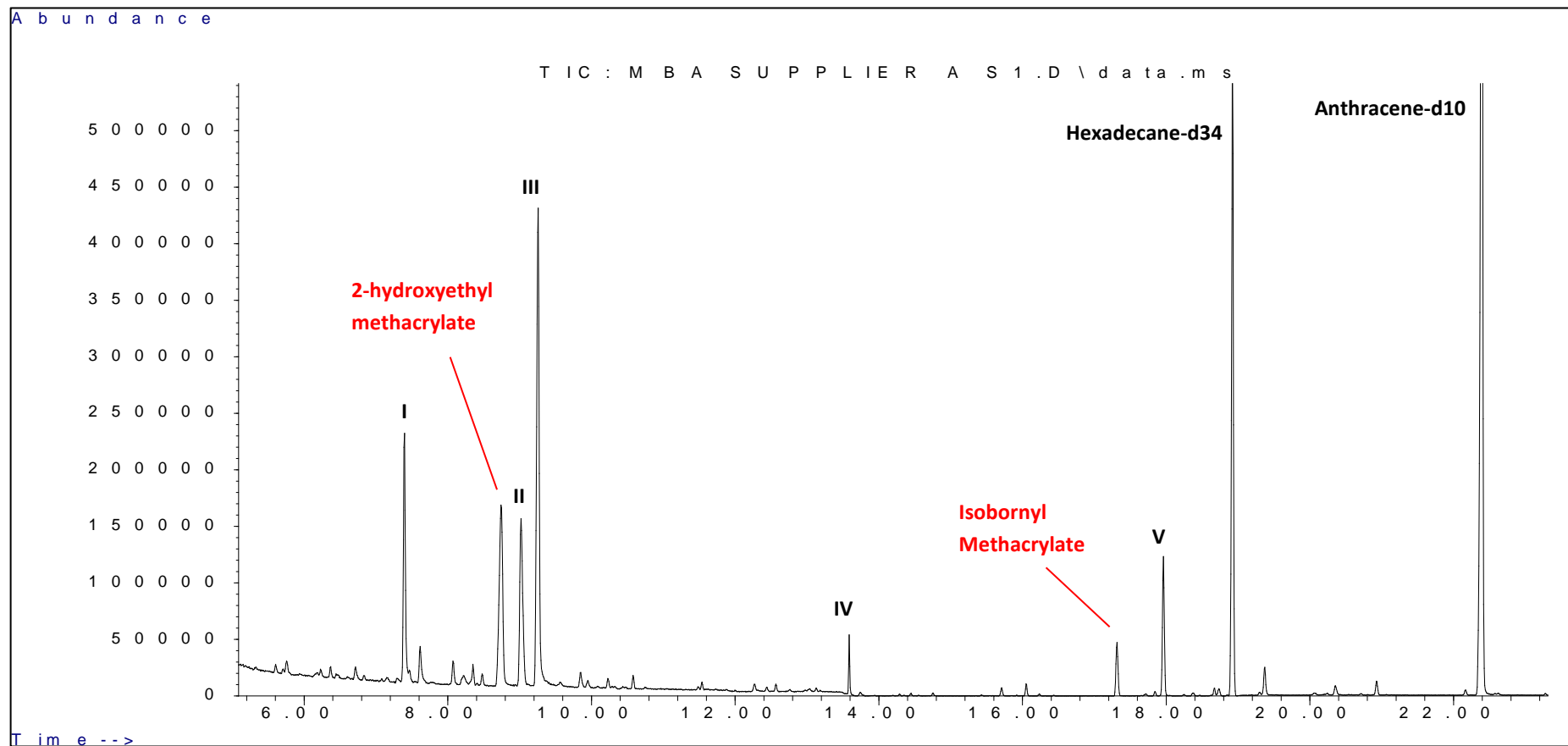


Figure 3.5 Gas chromatogram showing the detection of methacrylate for MBA from Supplier A [camphene (I), 2-Pyrrolidinone, 1-methyl- (II), 2-ethyl alcohol (III), hexane (IV), 2,4-di-t-butylphenol (V)]

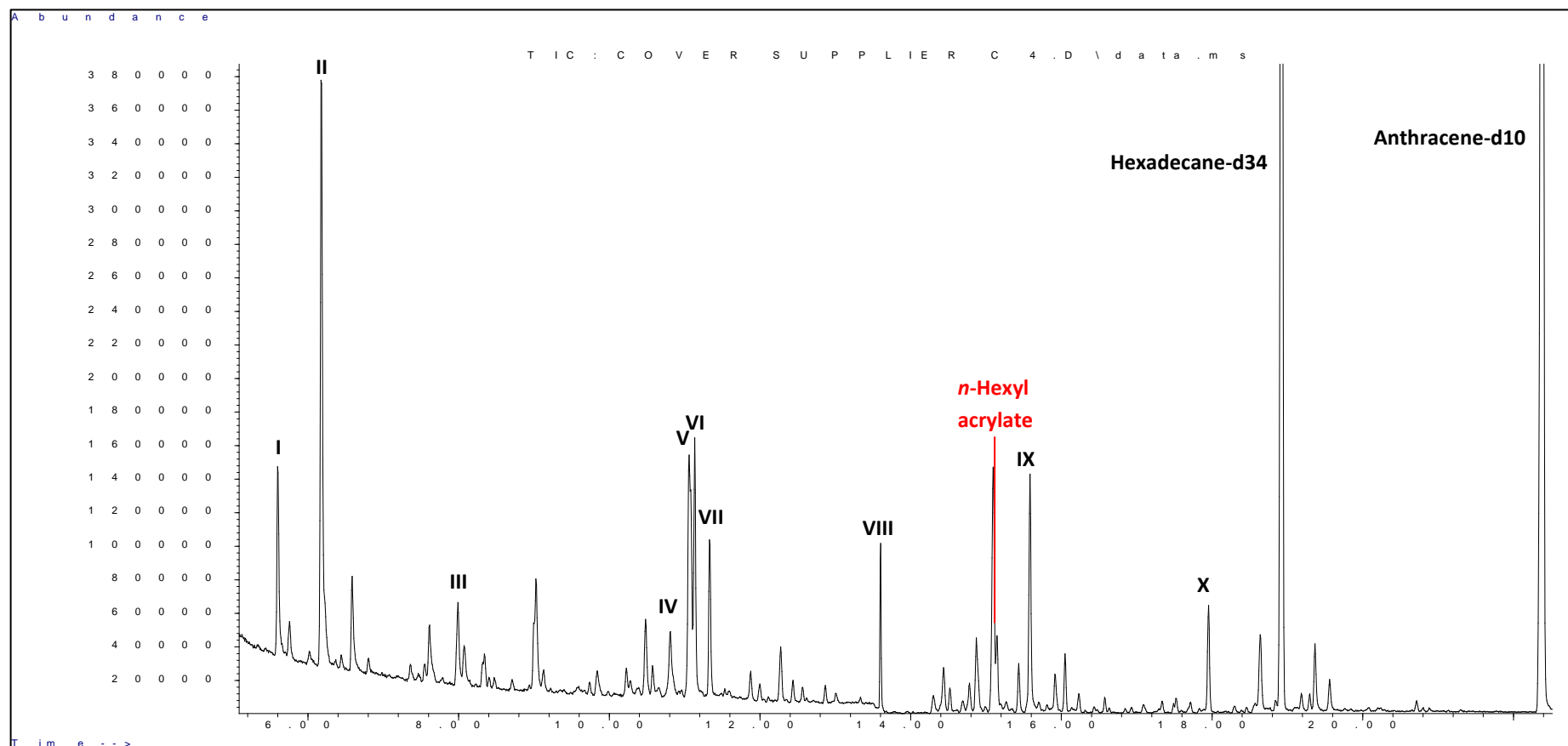


Figure 3.6 Gas chromatogram showing the detection of acrylate for cover from Supplier C [xylene (I), styrene (II), 2-Propenoic acid, 2-methyl-, butyl ester (III), 3-Heptene (IV), Cyclopentanone, 3-methyl- (V), Cyclopentane, ethyl- (VI), (S)-(+)-6-Methyl-1-octanol (VII), hexane (VIII), Cyclopropane, octyl- (IX), Phenol, 2,4-bis(1,1-dimethylethyl)- (X)]

3.3 Silicone

Silicone in hard disk drive components was determined using Nicolet iS50 FT-IR spectrometer. Calibration curve at the concentration of 0.05 to 1.00 μg was plotted by obtaining peak area of Si-C stretching at 800 cm^{-1} , which is one of the sharpest peaks observed (refer Appendix 5) for dimethylpolysiloxane standard via ATR FT-IR method. By referring to the curve, the amount of silicone detected from any components can be quantified. Other characteristic peaks of dimethylpolysiloxane are asymmetry deformation of Si-CH₃ at 1260 cm^{-1} and two broad bands of Si-O-Si vibration in the polymer chains at 1020 cm^{-1} and 1090 cm^{-1} . FT-IR spectrum generated from the sample, if silicone presents, may be slightly different from the spectrum of dimethylpolysiloxane standard, depending on whether the silicone compound is monomer or long chain polymer (Ng, 2004).

Table 3.5 is the data obtained from the calibration using dimethylpolysiloxane standard, and the calibration curve is shown in Figure 3.7. Coefficient of determination, R^2 value of 0.9858 was obtained for the standard at the concentration from 0.05 μg to 1.00 μg . This shows that a good linear correlation was achieved.

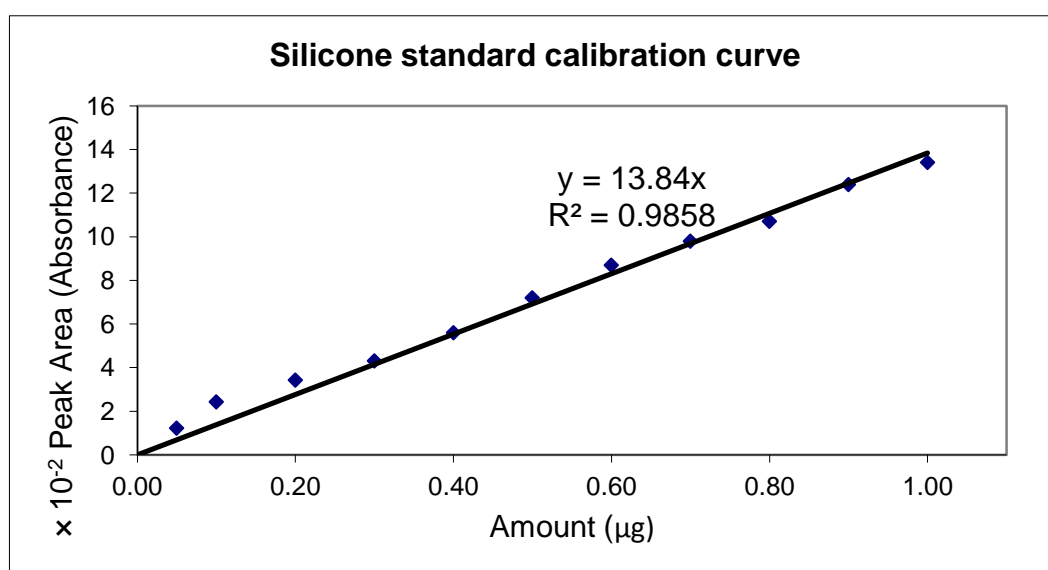


Figure 3.7 Calibration curve for dimethylpolysiloxane standard, ranging from 0.05 μg to 1.00 μg

Table 3.5 Calibration result using 0.01 µg/mL dimethylpolysiloxane standard

Amount (µg)	Peak Area (Absorbance)
0.05	1.23×10^{-2}
0.10	2.43×10^{-2}
0.20	3.42×10^{-2}
0.30	4.30×10^{-2}
0.40	5.60×10^{-2}
0.50	7.20×10^{-2}
0.60	8.70×10^{-2}
0.70	9.80×10^{-2}
0.80	10.7×10^{-2}
0.90	12.4×10^{-2}
1.00	13.4×10^{-2}

To ensure accuracy of the calibration curve, check standard was used for verification. 0.4 µg of dimethylpolysiloxane standard was analysed for three times. Figure 3.8 shows the overlay of 0.4 µg of dimethylpolysiloxane check standard against 0.4 µg of dimethylpolysiloxane calibration standard. The accuracy of the calibration plot is proven to be good since only 1% of difference between the areas of the standards.

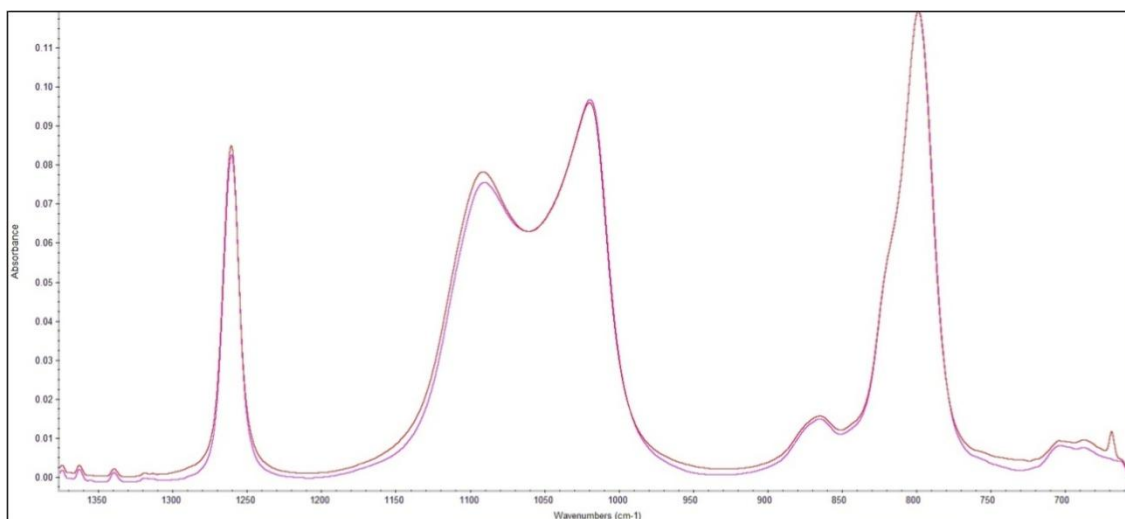


Figure 3.8 FT-IR spectra overlay for 0.4 µg of dimethylpolysiloxane check standard against calibration standard

Silicone was detected from all MBA samples, regardless of the supplier, using solvent extraction and ATR FT-IR analysis. However, the peak generated is too small (in the peak area range of $0.09-0.20 \times 10^{-2}$) to be quantified, thus the actual amount of silicone present cannot be determined accurately. FTIR spectrum of one of the MBA samples is shown in Figure 3.9. Other functional groups that were also detected via ATR FTIR method is aliphatic hydrocarbons and esters.

On the other hand, silicone was not detected from all cover samples using ATR FT-IR analysis. FT-IR spectra generated were quite clean in general. For instance, as shown in Figure 3.10, only atmospheric interferences like noise, water and carbon dioxide were detected.

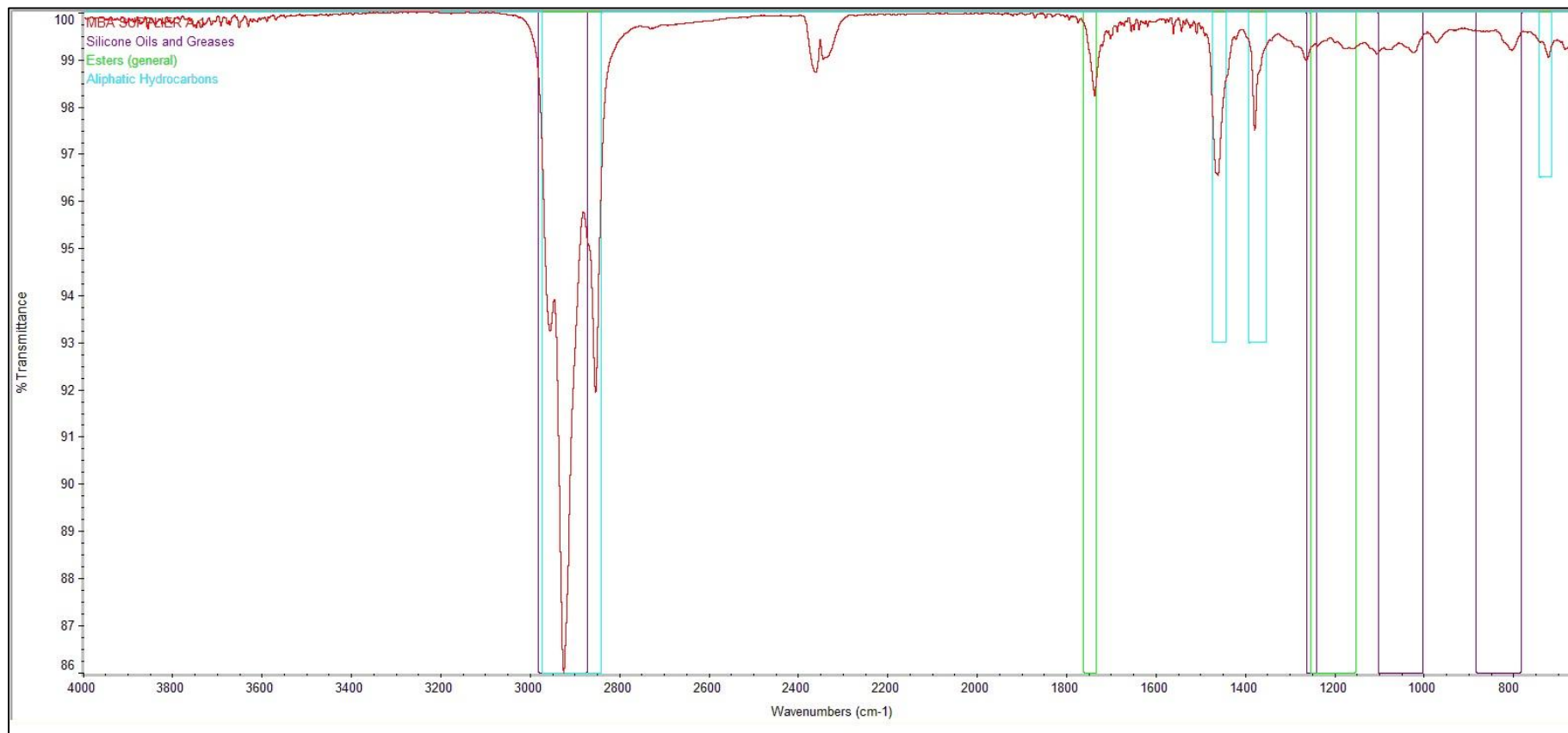


Figure 3.9 FT-IR spectrum and its spectral interpretation of a MBA sample

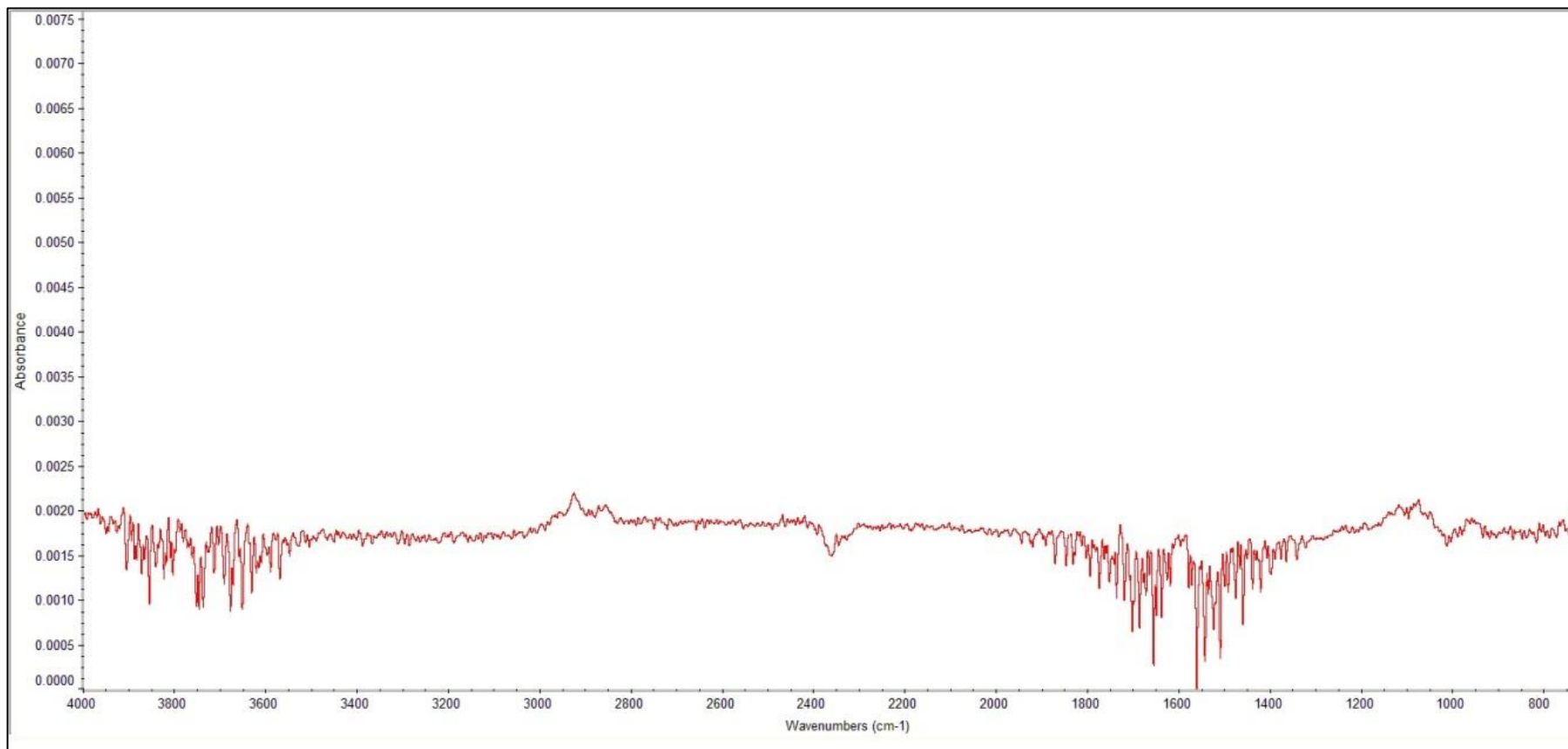


Figure 3.10 FT-IR spectrum of a cover sample

CHAPTER 4

CONCLUSION

The presence of different types of organic contaminants in hard disk drive components were determined using three different methods. Hydrocarbon in MBA samples was successfully detected and quantified using hexane extraction followed by GC-MS analysis. The recovery obtained from this method was satisfactory.

By using DHS outgassing procedure and analysis via thermal desorption unit coupled with GC-MS, 2-hydroxyethyl methacrylate, isobornyl methacrylate, and *n*-hexyl acrylate outgassed from the hard disk drive components can be identified and quantified. For MBA samples, two types of methacrylate, 2-hydroxyethyl methacrylate and isobornyl methacrylate were detected, while *n*-hexyl acrylate was found in cover samples. The recovery obtained was good.

Determination of silicone using hexane extraction followed by the detection with ATR FT-IR method was carried out as well. A linear calibration curve of dimethylpolysiloxane standard at different concentrations was obtained. Silicone that presents in MBA samples could not be quantified using the calibration curve due to relatively lower amount of silicone detected. Silicone was not detected in cover samples.

Although the presence of organic contaminants in hard disk drive components is not favourable, but it is unavoidable. Through setting up contamination limits and improving process of contamination control at the component production stage, these contaminants could be minimised or even removed totally. Monitoring of the level of

contamination is essential to prevent severe contamination that would lead to drive failure.

For future studies, determination of the organic contaminants for other hard disk drive components can be done. Comparison between similar compounds that could be extracted via hexane extraction and DHS outgassing methods, hydrocarbons for example, is recommended since both methods are able to detect the compounds. Lower calibration curve range is suggested for silicone detection at lower limit. Moreover, the employment of other instruments with lower detection limits is highly desirable.

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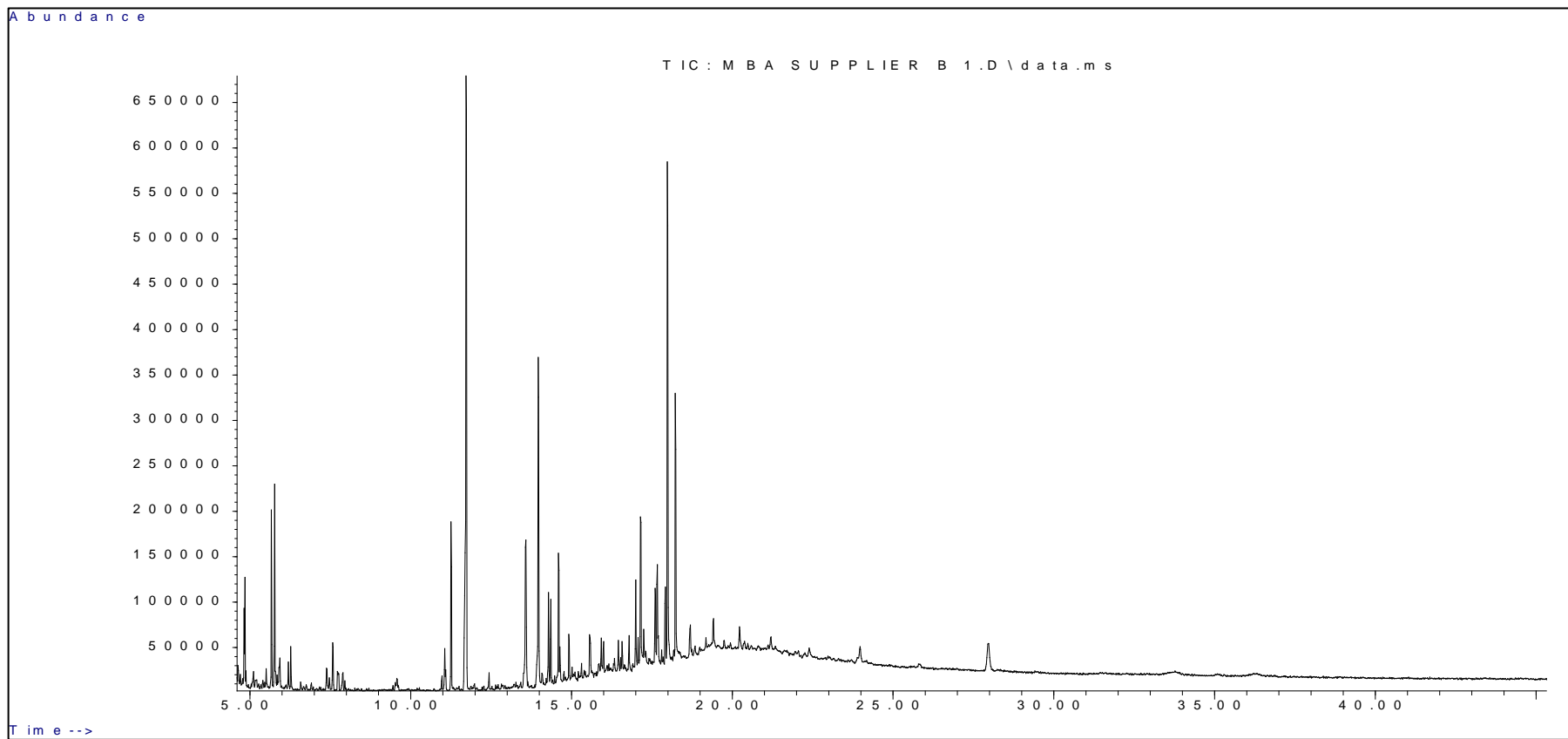
APPENDICES

Appendix 1: Total concentration of hydrocarbon detected in each MBA and cover sample

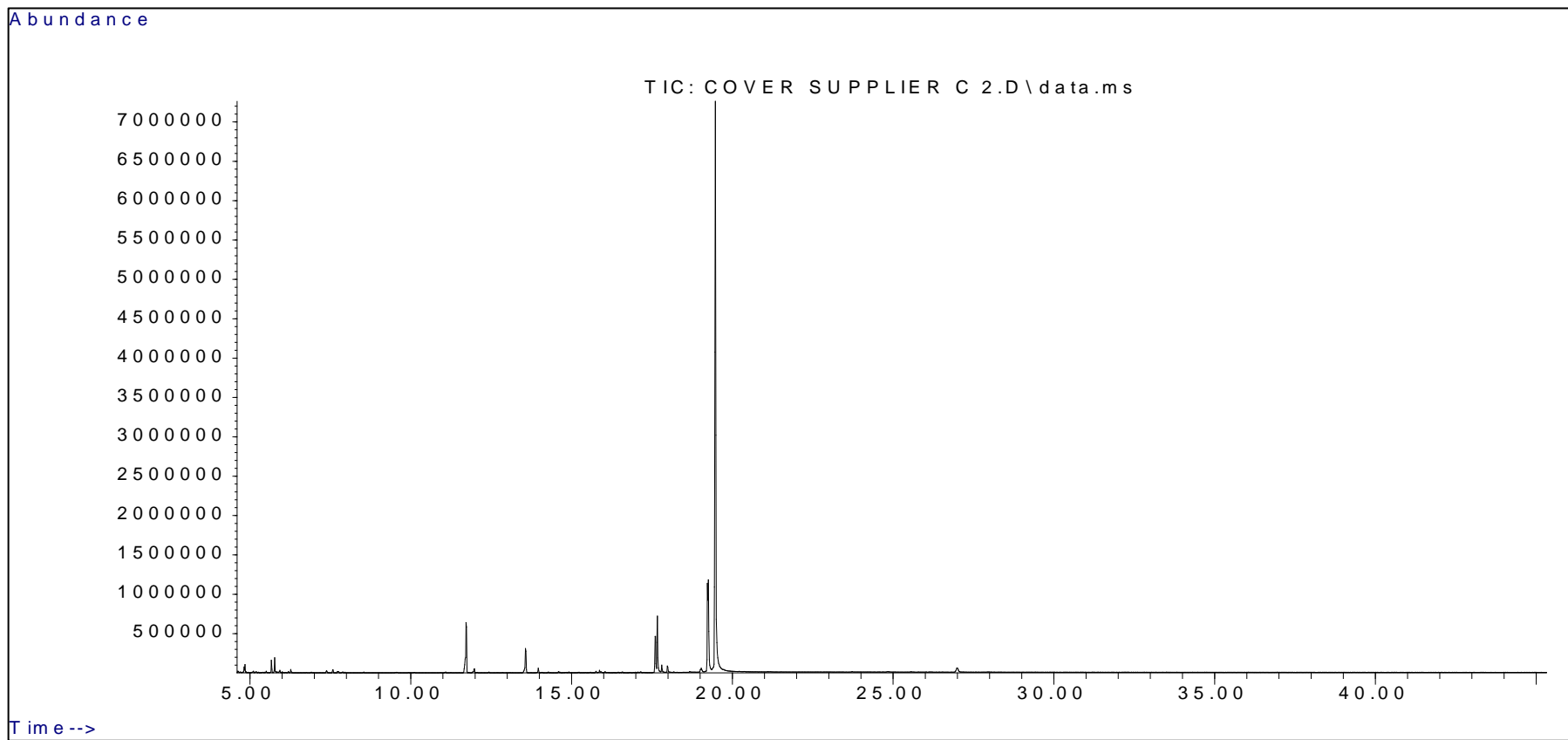
Component	Supplier	Total concentration of hydrocarbon (ng/sample)	Total concentration of hydrocarbon average (ng/sample)	RSD (%)
MBA	Supplier A	2.4×10^3	$(3.4 \pm 0.7) \times 10^3$	20.8
		3.4×10^3		
		3.7×10^3		
		4.3×10^3		
		3.1×10^3		
	Supplier B	1.6×10^3	$(1.9 \pm 0.3) \times 10^3$	15.6
		2.1×10^3		
		2.4×10^3		
		1.9×10^3		
		1.7×10^3		
Cover	Supplier C	ND	ND	-
		ND		
		ND		
		ND		
		ND		
	Supplier D	ND	ND	-
		ND		
		ND		
		ND		
		ND		

Appendix 2: Individual anthracene-d10 standard recovery for hydrocarbon analysis

Component	Supplier	Area of anthracene-d10	Recovery (%)	Recovery average (%)	RSD (%)			
MBA	Supplier A	9925319	106	147 ± 34	22.9			
		15528675	165					
		10999751	117					
		17261883	184					
	Supplier B	15268690	163	98 ± 52	52.8			
		4296584	46					
		5902343	63					
		7162124	76					
		15394267	164					
		13346276	142					
		5304124	57					
		7038109	75					
		Supplier C	6823093			73	69 ± 8	11.9
		Cover	Supplier D			7159256	76	115 ± 4
6155715	66							
10971577	117							
11340568	121							
10287636	110							
10376797	111							
		10822171	115					



Appendix 3: Gas chromatogram for MBA from Supplier B (Hydrocarbon determination)



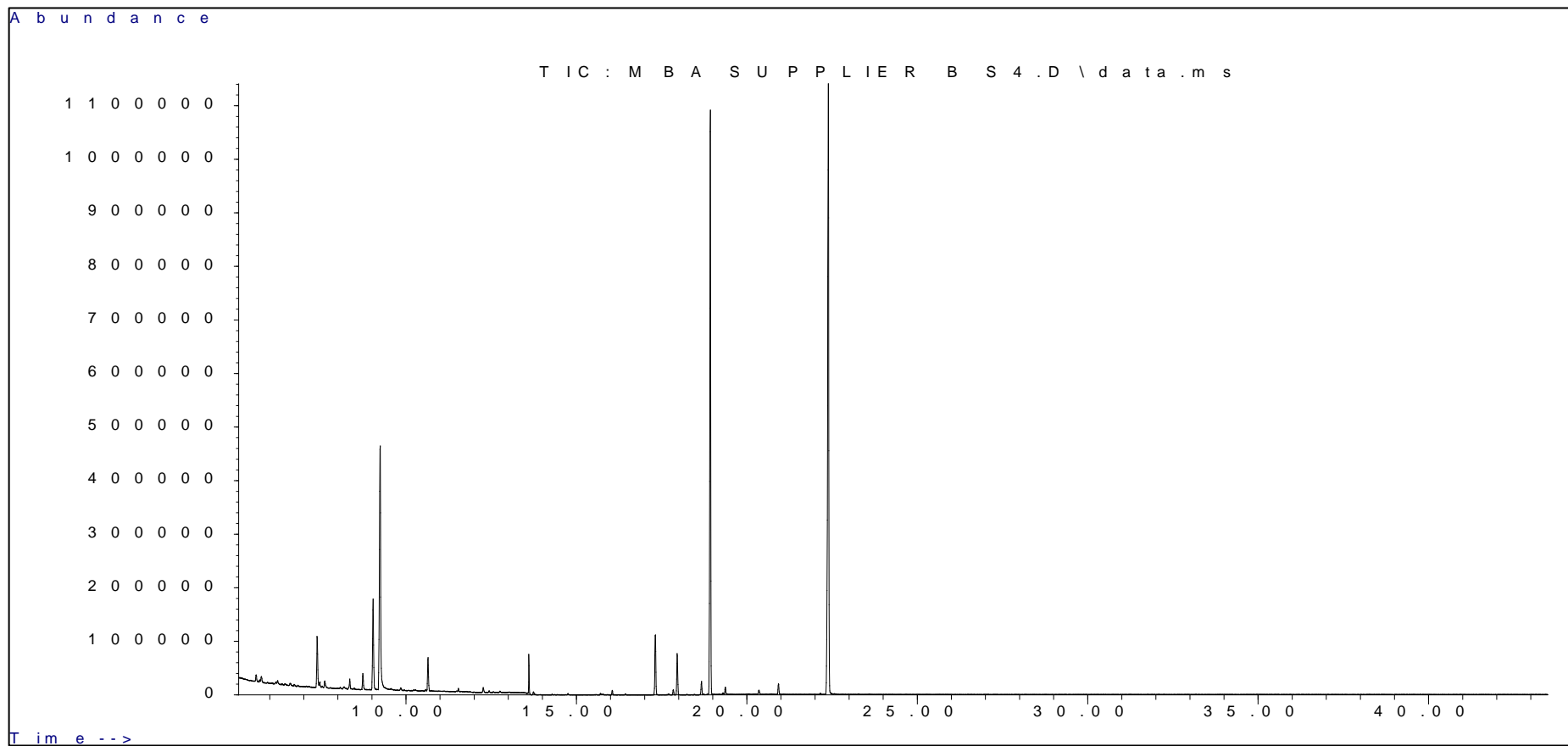
Appendix 4: Gas chromatogram for cover from Supplier C (Hydrocarbon determination)

Appendix 5: Total concentration of acrylate and methacrylate detected in each MBA and cover sample

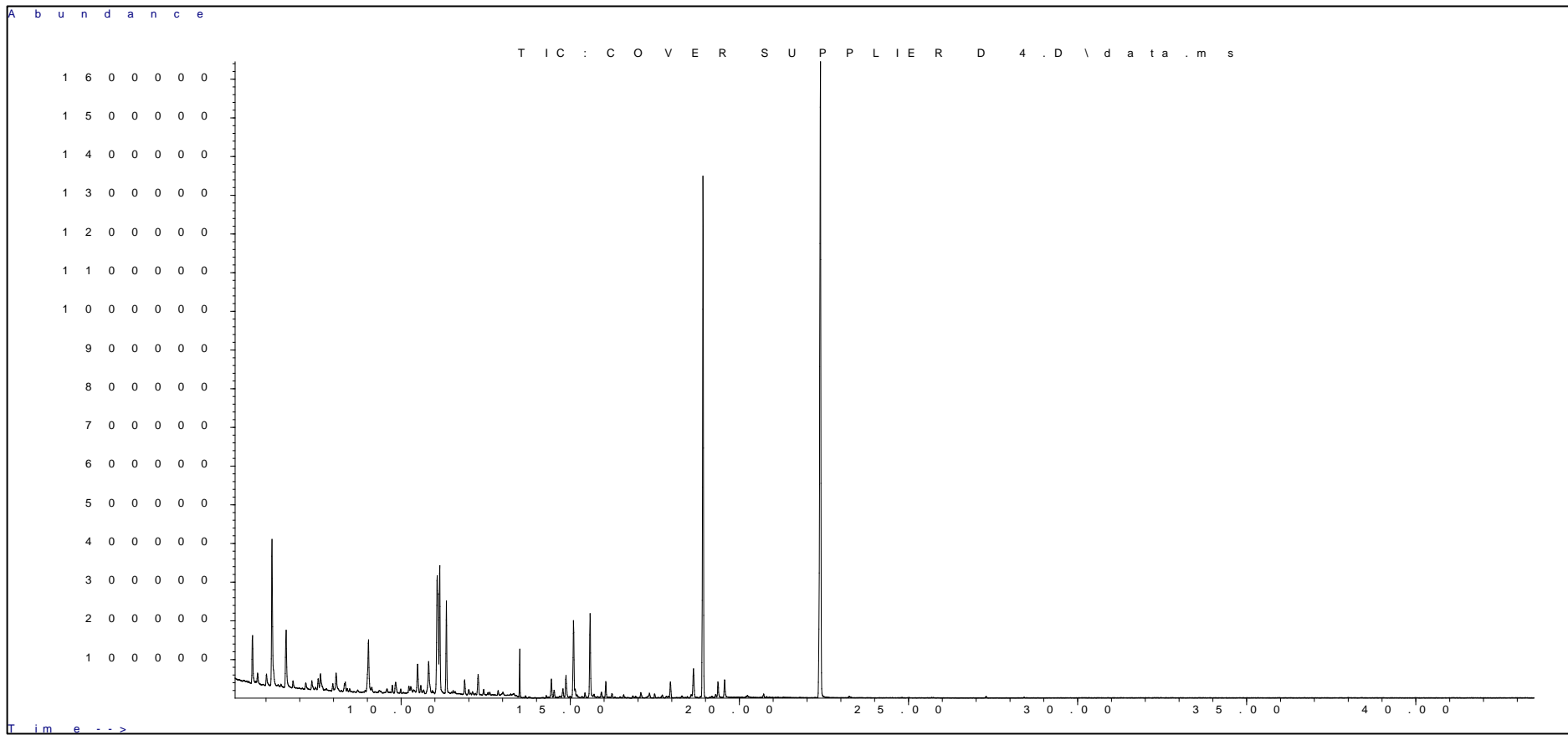
Component	Supplier	Total concentration of acrylate and methacrylate (ng/sample)	Total concentration of acrylate and methacrylate average (ng/sample)	RSD (%)
MBA	Supplier A	6.4×10^2	$(4.4 \pm 2.3) \times 10^2$	52.3
		6.4×10^2		
		2.5×10^2		
	Supplier B	2.3×10^2	$(1.1 \pm 0.3) \times 10^2$	28.5
		0.7×10^2		
		1.3×10^2		
Cover	Supplier C	1.1×10^2	$(0.3 \pm 0.1) \times 10^2$	16.1
		1.4×10^2		
		0.4×10^2		
	Supplier D	0.3×10^2	ND	-
		ND		
		ND		
		ND		

Appendix 6: Individual anthracene-d10 standard recovery for acrylate and methacrylate analysis

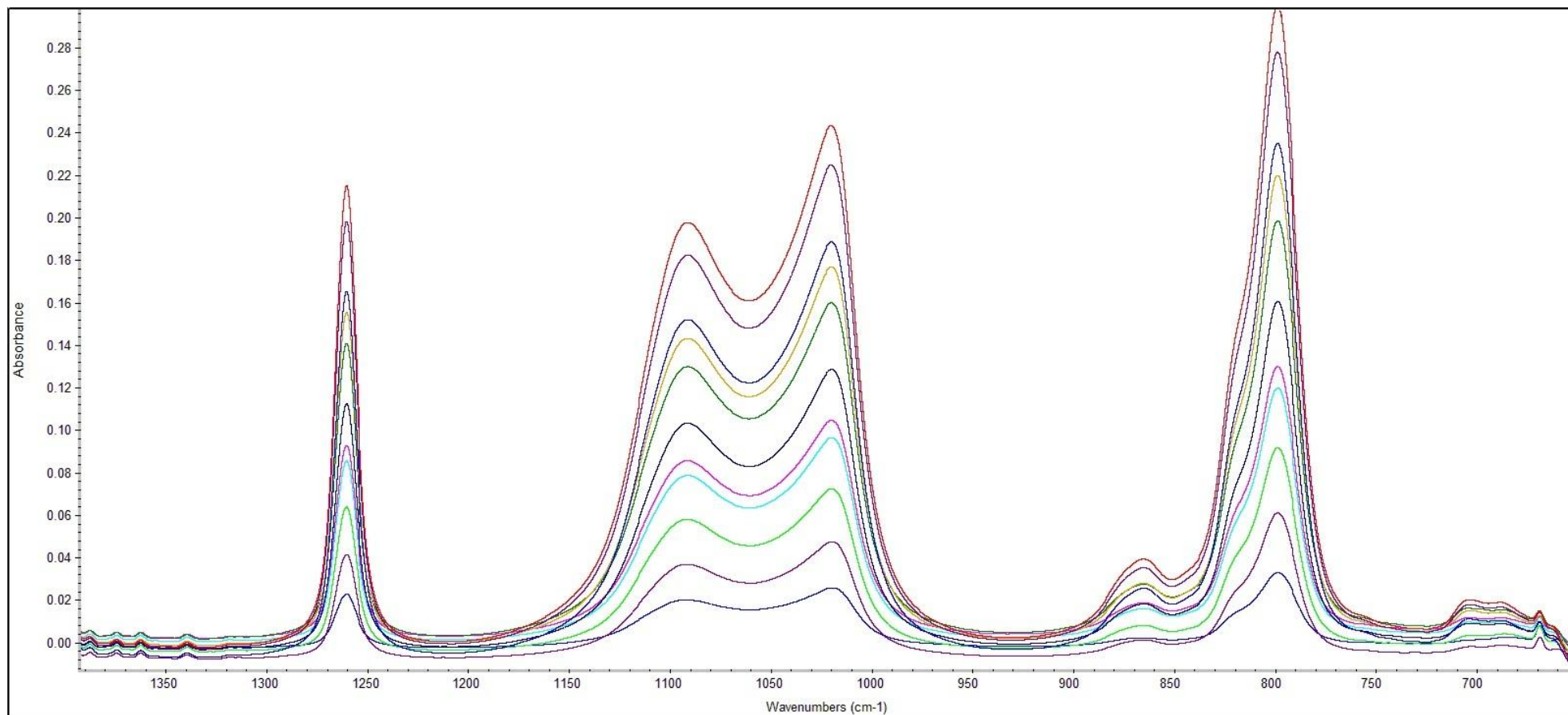
Component	Supplier	Area of anthracene-d10	Recovery (%)	Recovery average (%)	RSD (%)		
MBA	Supplier A	21435388	86	94 ± 5	3.9		
		23290547	96				
		23343131	97				
	Supplier B	22591932	93	97 ± 7	7.2		
		23187656	96				
		22660460	94				
		22006373	91				
		25863968	107				
		33583158	139				
		33005671	136				
Supplier C	38421276	159	151 ± 17	10.9			
	41297148	171					
	33688987	139					
	Supplier D	34142083			141	146 ± 8	5.4
		35549298			147		
		37932429			157		



Appendix 7: Gas chromatogram for MBA from Supplier B (Acrylates and methacrylates determination)



Appendix 8: Gas chromatogram for cover from Supplier D (Acrylates and methacrylates determination)



Appendix 9: ATR FT-IR spectrum for dimethylpolysiloxane standard at different concentration, ranging from 0.05 µg to 1.00 µg