Chapter IV

Results & Discussion

4.1 Semi Quantitative Results

Semi quantitative method provides a snapshot on all compounds detected qualitatively and quantitatively with reference to a known standard amount. The reference standard applied in this experiment, hexadecane-34 ($C_{16}D_{34}$, MW260) shows retention time at 20.39 min and its mass spectrum shows fragmented ions at m/z 50, 66, 82 and 98 (Figure 15). A difference of 16 m/z in the fragments is observed. This represents the addition of -CD_2- group to each fragment.

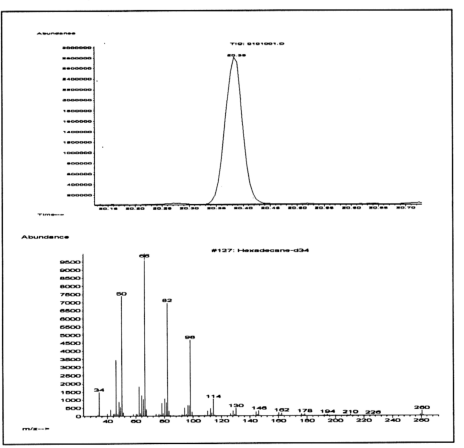


Figure 15. Mass Spectrum of hexadecane-d34

A representative GC chromatogram for each motor A, B, C and D are attached in Appendix 1. All peaks integrated with Chemstation integrator at threshold 20 were tabulated and their library- matched identities were examined by comparing their mass spectra with the standard mass spectra in the library.

The integrated peaks were quantified with reference to 1000 ng of deuterated hexadecane and the 'total outgas' and spiked standard recovery was calculated. Results for all samples are attached in Appendix 2. All compounds were classified into four groups: Acrylate/Methacrylate, Alcohol, Hydrocarbon (HC) and Others. The summation of the amounts of compounds for each group was termed as 'total acrylat/methacrylate', 'total alcohol', 'total HC' and 'total others'. The summation of all peaks amount was termed as 'total outgas'. In the following sections, the outgas results for individual motor was discussed, following by the comparison across all motors.

4.1.1 Motor A

There were a total of 16 peaks integrated. Overall, methacrylates has the most significant contribution, i.e. greater than >90%, of the 'total outgas'. This is illustrated in Figure 16.

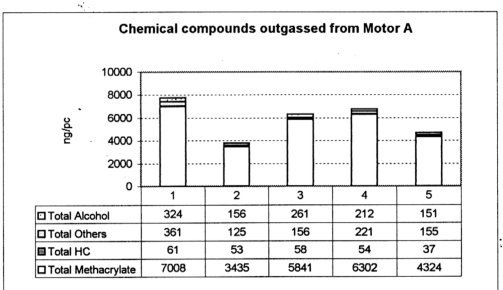


Figure 16. Type of chemical compounds outgassed from Motor A

3 types of methacrylates were detected in motor A, i.e. 2-hydroxyethyl methacrylate (HEMA), isobornyl methacrylate (IBM) and ethylene glycol dimethacrylate (EGDM). Among the three, HEMA has the highest outgassed amount, i.e. average (n=5) 67% of the 'total methacrylates'. The compound, with molecular formula of $C_6H_{10}O_3$ and MW130.1, was detected at the retention time 8.15 min. The mass spectrum of the compound shows major ion fragments at 41, 69 and 87 m/z, as shown in Figure 17.

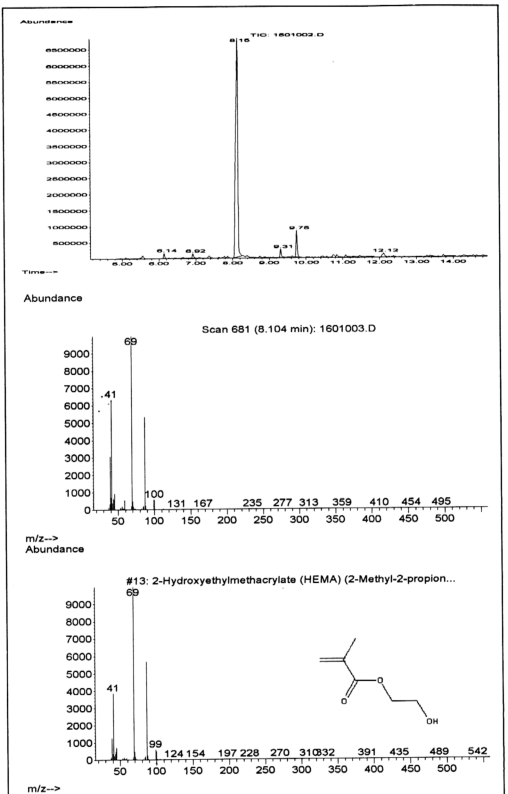


Figure 17. HEMA Peak and Its mass spectrum

Averagely, ~30% of the 'total methacrylate' was contributed by IBM which was detected at 18.28 min. From the GC chromatogram, it was observed that there were additional 2 peaks of IBM detected at trace level, i.e. at Rt 17.23 min and 18.95 min. The mass spectra of all three peaks show ion fragments at 41, 69, 95 and 136 m/z (Figure 18).

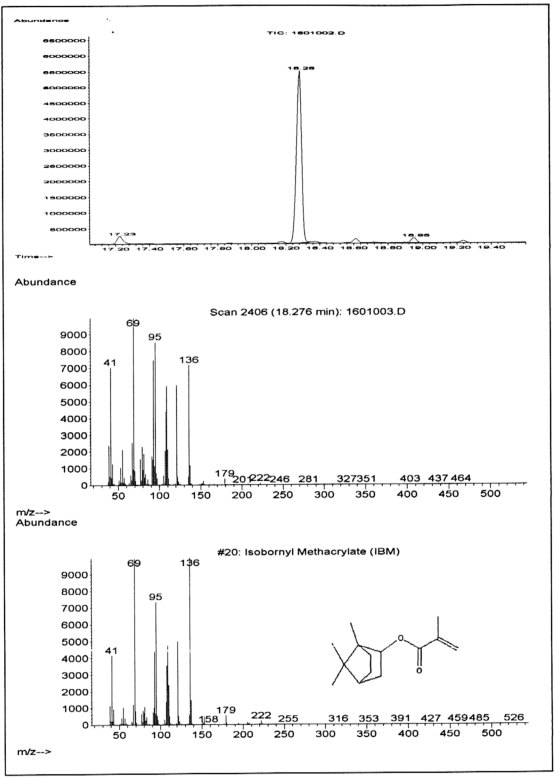


Figure 18. IBM peaks and the mass spectrum

EGDM ($C_{10}H_{14}O_4$ MW198.1) contributes <10 % of the 'Total methacrylates' detected in motor A. The compound showed Rt at 15.03 min. The mass spectrum for the compound is shown in Figure 19.

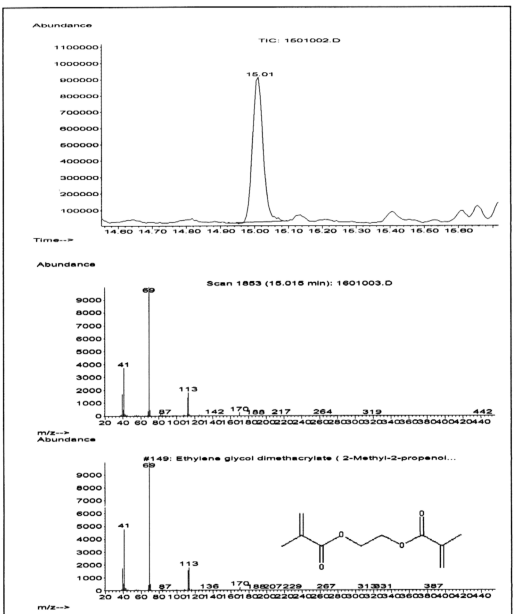
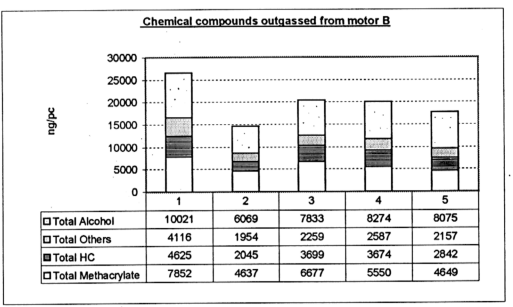


Figure 19. EGDM Peak and Its mass spectrum

4.1.2 Motor B

The number of peaks integrated in motor B was more significant than that of supplier A where a total of 33 peaks were integrated. From Figure 20, it is observed that alcohol compounds were the main contributor to the 'total outgas', i.e. in the range of 38 to 46 %.



	1	2	3	4	5
Total Alcohol	10021	6069	7833	8274	8075
Total Others	4116	1954	2259	2587	2157
Total HC	4625	2045	3699	3674	2842
Total Methacrylate	7852	4637	6677	5550	4649

Figure 20. Types of chemical compounds outgassed from Motor B

There are 3 types of alcohol detected, i.e. at Rt 5.38 min (tetrahydrofurfuryl alcohol), 8.38 min (2-Ethyl hexanol) and 9.80 min (alpha-alpha-dimethylbenzene methanol). These alcohol compounds are likely to be the solvent used for the adhesive.

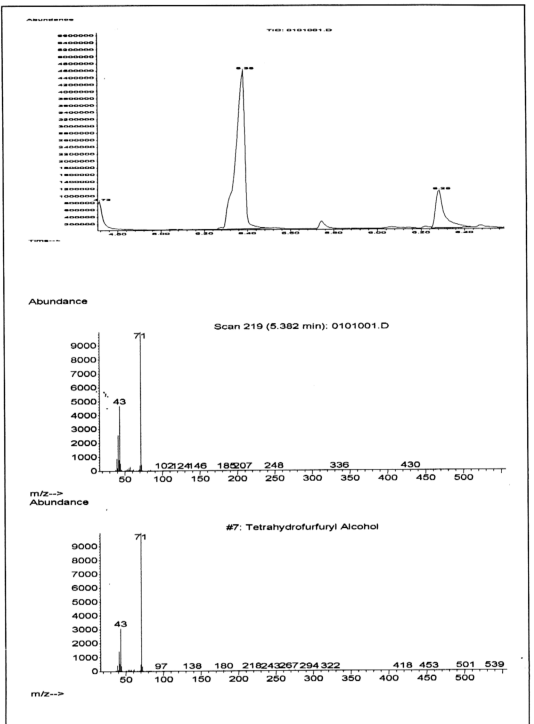


Figure 21. Tetrahydrofurfuryl Alcohol Peak and Its Mass Spectrum

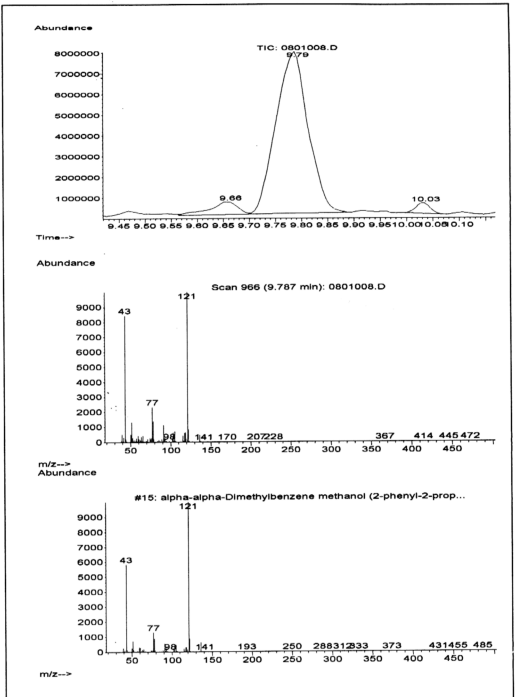


Figure 23. Alpha-alpha-dimethylbenzene Methanol Peak and Its Mass Spectrum

2 types of acrylates and 1 type of methacrylate, averagely ~30% of total outgas were detected in Motor B. The acrylates detected were 2-hydroxyethyl acrylate (HEA) at Rt 6.31 min and tetrahydrofurfuryl acrylate (THFA) at Rt 11.71 min. HEA has a molecular formula of $C_5H_8O_3$ and a MW 116. Its mass spectrum showed the parent ion is at 55 m/z, as shown in Figure 24.

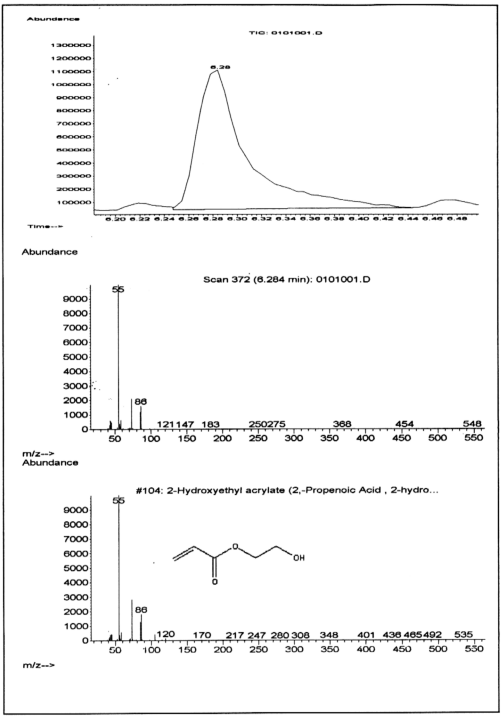


Figure 24. HEA Peak and Its Mass Spectrum

THFA has a molecular formula of $C_8H_{12}O_3$ and a MW 156.08. There are 3 main ion fragments, i.e. 43, 55, 71 m/z as shown in Figure 25.

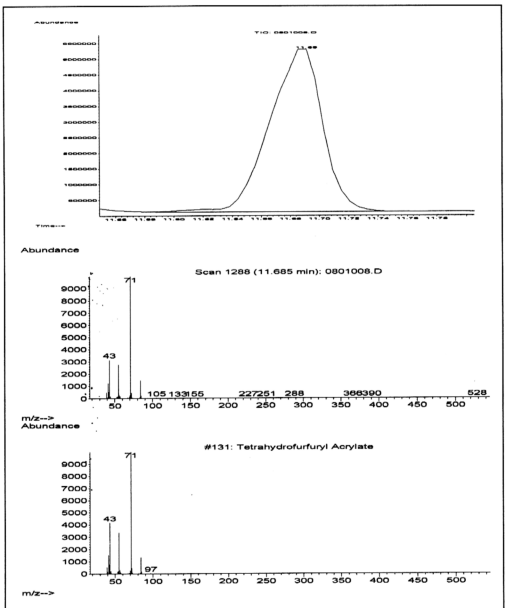


Figure 25. THFA Peak and Its Mass Spectrum

High variation of THFA amount was observed across 5 samples of Motor B, ranging from 43 to 71 % of the total. Comparing to THFA, HEA was detected at an insignificant level, i.e. <10%.

The methacrylate detected in Motor B, 2-hydroxypropyl methacrylate (HPM) ($C_7H_{12}O_3$ MW144.1) was the characteristic methacrylate in motor B. Its contribution to the total acrylates/ methacrylates showed in the range of 23 to 54%. The Rt of HPM showed at 8.75 min and 8.88 min (major peak). Both peaks showed ion fragments at 41, 69, 99 and 100 m/z in their mass spectra.

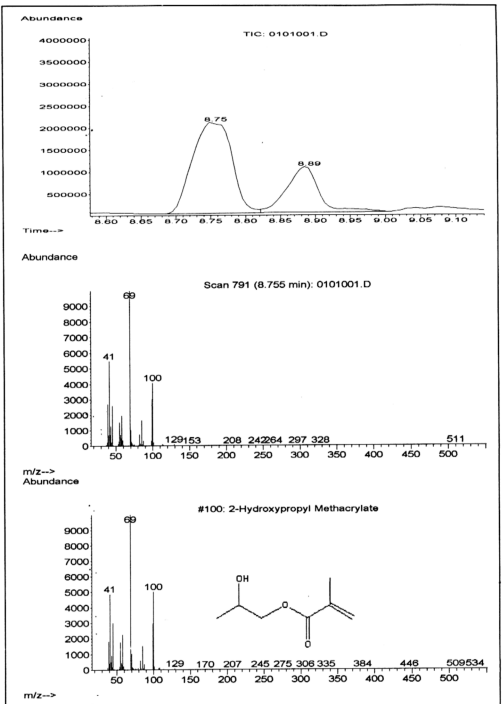
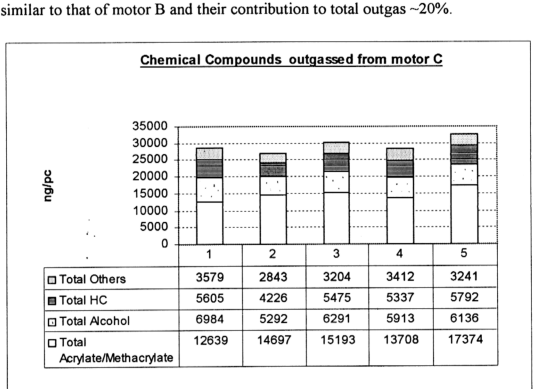


Figure 26. HPM Peak and Its Mass Spectrum

4.1.3 Motor C

35 peaks were integrated in the chromatogram of motor C. 3 types of methacrylates and 1 acrylate were detected, totaling a contribution of 44 to 54% of the 'total outgas' (Figure 27). The alcohol detected in motor C was similar to that of motor B and their contribution to total outgas ~20%.



	1	2	3	4	5
Total Others	3579	2843	3204	3412	3241
Total HC	5605	4226	5475	5337	5792
Total Alcohol	6984	5292	6291	5913	6136
Total Acrylate/Methacrylate	12639	14697	15193	13708	17374

Figure 27. Types of Chemical compounds outgassed from Motor C

HEMA was the main methacrylate detected, which contribution in the range of 54 to 59% of the 'total acrylate/methacrylates'. IBM contributed 21 to 28% and EGDM <10%. THFA was the only acrylate detected in motor C.

4.1.4 Motor D

From the GC chromatogram, it is observed that motor D outgassed the most compared to the others. As illustrated in Figure 28, 'Total acrylates/ methacrylates' contributed 43 to 48 % of the total outgas. 'Total alcohol' detected in motor D showed an insignificant level compared to that of the motor B and C. 'Total HC' of 16 to 22% showed a significant trend compared to the other motors as most of the peaks were aromatic hydrocarbon, i.e. benzene, 1,2-bis(1-methylethyl)-) at Rt 11.36 min and benzene, 1,4-bis(1-methylethyl)- at Rt 11.84 min. 2-Ethylhexanoic acid which was found in the adhesive primer was detected at Rt 11.08 min.

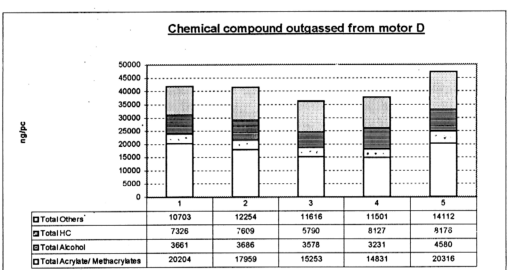


Figure 28. Chemical compounds outgassed from motor D

Contribution of HEMA to total acrylate/ methacrylates showed the highest, i.e. averagely ~ 60%, following by THFA (20-28%) and IBM (9-15%). HEA and EGDM were detected at an insignificant amount.

4.1.5 Comparison across all motors

Overall, there were 2 types of acrylates (HEA and THF) and 4 types of methacrylates (HEMA, HPM, EGDM and IBM) detected in this experiment. All the acrylates and methacrylates detected in the motors were tabulated in Table 8. The type of acrylate and methacrylates detected in a motor provides information on the adhesives applied in the motor assembly.

It is obvious that motor A applied a different adhesive system than motor B as there is no similar acrylate and methacrylates detected in them. HPM appeared to be the outstanding methacrylate that was only detected in motor B. HEMA, IBM and EGDM are methacrylates originating from anaerobic adhesives which curing process were also by heat. Different amount of these methacryates detected in motor A, C and D are related to the curing process, amount of adhesive applied and also the mechanical design. Increase in baking time and baking temperature helped in reducing the outgas level of these compounds. THFA was detected in motor B, C and D. The acrylate originated from the cap adhesives that underwent UV curing process. Figure 28 summarizes all the methacrylates and acrylates detected across all motors.

Motor	(Rt 8.26 min) HEMA	(Rt 15.02 min) EGDM	(Rt18.28 min) IBM	(Rt 6.27 min) HEA	(Rt 8.75 min) HPM	(Rt 11.71 min) THFA
A	4610	311	2088	ND	ND	ND
	2149	243	1043	ND	ND	ND
	3552	491	1798	ND	ND	ND
	4429	367	1506	ND	ND	ND
	2529	365	1430	ND	ND	ND
B	ND	ND	ND	473	1792	5588
	ND	ND	ND	136	1464	3037
	ND	ND	ND	338	1976	4362
	ND	ND	ND	182	2396	2971
	ND	ND	ND	164	2012	2473
C	7238	926	2615	ND	ND	1860
	8244	781	4101	ND	ND	1570
	8860	806	3674	ND	ND	1854
	8135	747	2895	ND	ND	1932
	9398	1248	4731	ND	ND	1998
D	11650	116	1839	946	ND	5653
	10395	95	1655	815	ND	5000
	8689	162	1646	898	ND	3857
	7794	380	1780	652	ND	4226
	12192	231	2969	901	ND	4023

Table 8. Semi Quantitative Amount (ng) of Acrylates and Methacrylates detected in Spindle Motor A, B, C and D

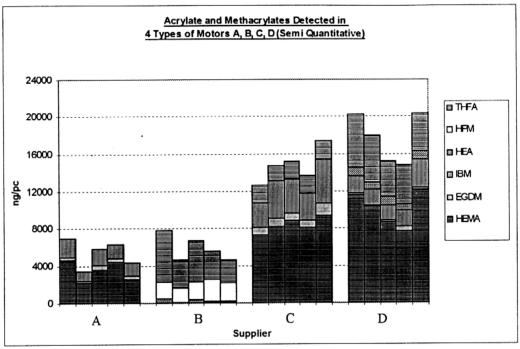


Figure 29. Acrylate and Methacrylate detected in Motor A, B, C and D

The semi-quantified total outgas for all motors provides a snapshot on the outgas level of the motors in 3 hours at 85 °C. As illustrated in Figure 29, motor D has the highest outgas amount ranging from 36 to 47 μg. This is followed by motor C, 27 to 32 μg, motor B, 14 to 26 μg and motor A, 4 to 8 μg. The average 'total outgas' of motor B, C and D were 3.4 times, 5 times and 7 times more than motor A.

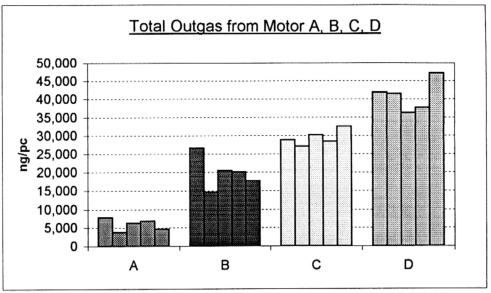


Figure 30. Total Outgas from Motor A, B, C and D

4.2 Quantitative Results for HEMA, THFA and IBM

From section 4.1, the common compounds outgassed from the motors were identified to be the HEMA, THFA and IBM. Calibration curve for these compounds were established and their respective overlaid GC chromatograms are attached in Appendix 3.

4.2.1 Calibration Curve for HEMA

Peak area obtained for the standard run are tabulated in Table 9. A linear regression curve with equation $y = 29.879x + 34.806$ and $R^2 = 0.9967$ was established where y = peak area and x = amount of HEMA in μg.

HEMA (ug)	Peak Area
10	314,183,197
20	637,598,696
30	944,686,722
40	1,265,040,106
50	1,494,431,914

Table 9. HEMA Standard Calibration

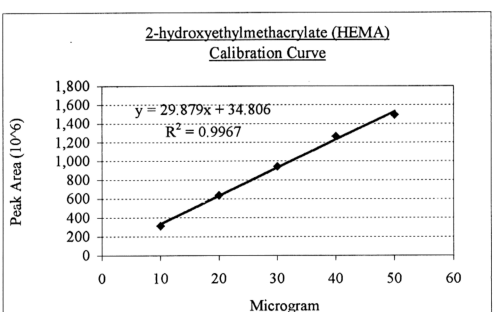


Figure 31. Calibration Curve of HEMA

4.2.2 Calibration Curve for THFA

Peak area of 5 level of THFA standards run are tabulated in Table 10. The calibration curve was established, with y = 35.722x - 4.3304 and R^2 = 0.9999 (Figure 30) where y = peak area and x = amount of THFA in µg.

THFA (ug)	Peak Area
2	66,660,288
5	171,910,226
10	355,470,756
15	535,054,634
20	706,775,460

Table 10. THFA Standard Calibration

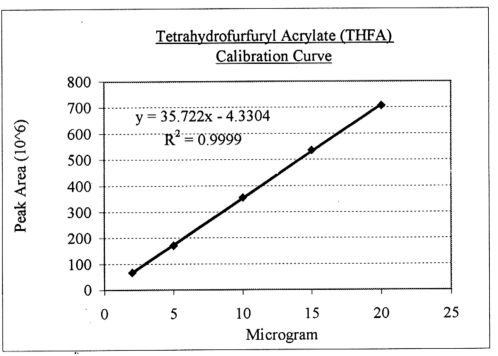


Figure 32. Calibration Curve for THFA

4.2.3 Calibration Curve for IBM

Peak area obtained from the GC chromatogram of 5 levels of standard and their corresponding solute amount are tabulated in Table 11. The linear regression established shows equation $y = 71.461x - 47.159$ with $R^2 = 0.984$ where y = peak area and x = amount of IBM in μg.

IBM (ug)	Peak Area
2.0	111,926,553
4.0	224,213,627
6.0	350,232,146
8.0	566,060,563
10.0	655,617,831

Table 11. IBM Standard Calibration

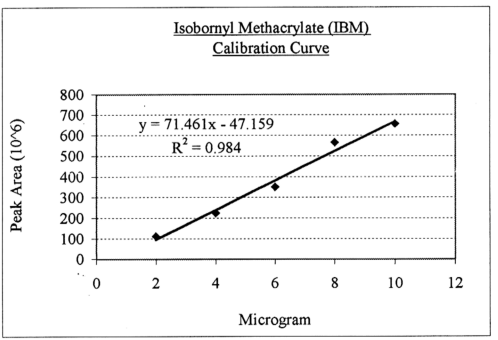


Figure 33. Calibration Curve for IBM

4.2.4 Check Standard

GC chromatograms for the check standard run are attached in Appendix 3.

The amount of HEMA, THFA and IBM spiked into the tubes were calculated based on 2 methods:

i. Calibration Curve of respective compound

ii. Semi Quantitative – relative to deuterated hexadecane spiked into the adsorbent tubes

Table 12 shows the quantified amount for both methods and their relative error. The relative error was calculated based on the following:

Error = (Actual Reading - Quantified Reading)/ Actual Reading *100 %

Standard	Quantification Method	1		2		3	
		µg	Error (%)	µg	Error (%)	µg	Error (%)
25 µg HEMA	Quantitative	23.6	6	25.0	0	26.3	5
	Semi Quantitative	12.3	51	10.1	60	10.8	57
10 µg THFA	Quantitative	9.1	9	9.1	9	9.4	6
	Semi Quantitative	5.1	49	4.3	57	4.4	56
5 µg IBM	Quantitative	4.6	7	4.5	10	5.2	4
	Semi Quantitative	4.3	14	3.9	23	4.3	14

Table 12. Comparison of the 2 quantification methods

4.2.5 Quantification of HEMA, THFA and IBM

Peak area for HEMA, THFA and IBM were tabulated and quantified by using their respective calibration curves. Table 13 shows the comparison of both semi quantitative amount and the quantitative amount.

Motor	HEMA (Rt 8.26 min)		IBM (Rt18.28 min)		THFA (Rt 11.71 min)	
	Semi-Quantitative	Quanti-tative	Semi-Quantitative	Quanti-tative	Semi-Quantitative	Quanti-tative
A	4610	9469	2088	1647	ND	ND
	2149	4702	1043	882	ND	ND
	3552	7939	1798	1530	ND	ND
	4429	9793	1506	1268	ND	ND
	2529	5523	1430	1243	ND	ND
B	ND	ND	ND	ND	5588	9370
	ND	ND	ND	ND	3037	5647
	ND	ND	ND	ND	4362	8383
	ND	ND	ND	ND	2971	5578
	ND	ND	ND	ND	2473	4626
C	7238	17155	2615	2474	1860	3688
	8244	20889	4101	4514	1570	3420
	8860	17506	3674	3496	1854	3694
	8135	14382	2895	2741	1932	3837
	9398	20499	4731	4125	1998	3645
D	11650	24622	1839	1625	5653	9993
	10395	23974	1655	1596	5000	9645
	8689	26550	1646	1684	3857	7893
	7794	26068	1780	1857	4226	8822
	12192	30396	2969	3117	4023	8449

ND = Not Detected

Table 13. Quantified amount (ng) of 2-HEMA, THFA and IBM

4.3 Recovery

Anthracene d-10 (retention time 24.37 min) was used as the surrogate standard spiked into each chamber for recovery calculation. The mass spectrum of the standard shows at 188 m/z representing molecular ion ($C_{14}D_{10}$):

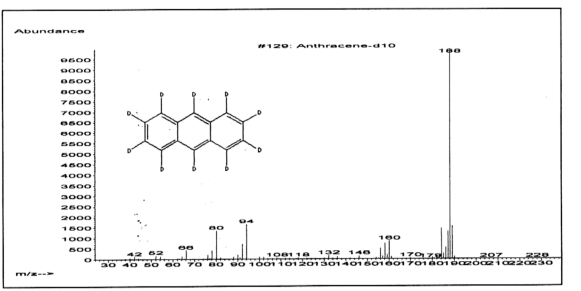


Figure 34. Mass Spectrum for Anthracene-d10

The recovery of standard Anthracene-d10 for all samples are tabulated in their respective data analysis results in Appendix 2. Recovery of Anthracene d-10 for all samples were >70%. However, sample 2 of motor A showed very low recovery, ie, less than 50%. This indicates that the sampling container had a minor leakage during the sampling process. The results for this sample was significantly lower than the other samples.