

## CHAPTER 4

### RESULTS AND DISCUSSION

The fact that waxes were separated from heavy distillate had high oil content and brown color, thus they were purified by deoiling and decolorizing process ( Fig. 4.1 ).



Figure 4.1 Unpurified wax before deoiling.

The crude paraffin waxes obtained from Fang heavy distillate could be deoiled by sweating or solvent deoiling process. The solvent deoiling process gave lower oil content in the wax than sweating process.

Therefore, we used solvent deoiling process in this study to obtain more refined waxes. There are two systems of solvent for solvent deoiling process, i.e. single and dual solvent. The single solvent was used because it was easier than the dual solvent in preparation. If single solvent could deoil the waxes in low oil content, it would not be necessary to use dual solvent. The ketone solvents were the most widely used for deoiling such as MEK, MIBK etc. It was not necessary to treat the deoiled waxes with sulfuric acid because of their low carbonizable matter content. ( The color of deoiled waxes were not dark. )

In this study, solvent deoiling method and the pressing method were used. This method made filtration faster and the solvent was removed at low temperature of admixtures (waxes and solvent). Methyl ethyl ketone ( MEK ) was used as a solvent and the amount of MEK was varied in solvent deoiling ( Table 4.1 ).

Table 4.1 Percentage yield of waxes after deoiling.

Wax : MEK ( g : ml )	Wt. of waxes after pressing ( g )	Wt. of waxes after drying ( g )	Filtrate ( ml )	MEK in wax before drying ( ml )	MEK loss ( ml )
1:1	108.62	95.66	55	12.96	32.04
1:3	107.28	95.50	245	11.78	43.22
1:5	108.46	94.44	450	14.02	35.98
1:7	106.32	93.74	645	12.58	42.42
1:9	111.92	92.10	840	19.84	40.16

From Table 4.1, weight of waxes after deoiling fluctuated because the press oil device was manual system. Therefore MEK could not be completely removed.

The increase in the wax to MEK ratio from 1:1 to 1:9 (g:ml) caused the decrease in wax recovery yield, probably due to the solubility of wax in larger quantity of MEK ( Fig. 4.2 ).

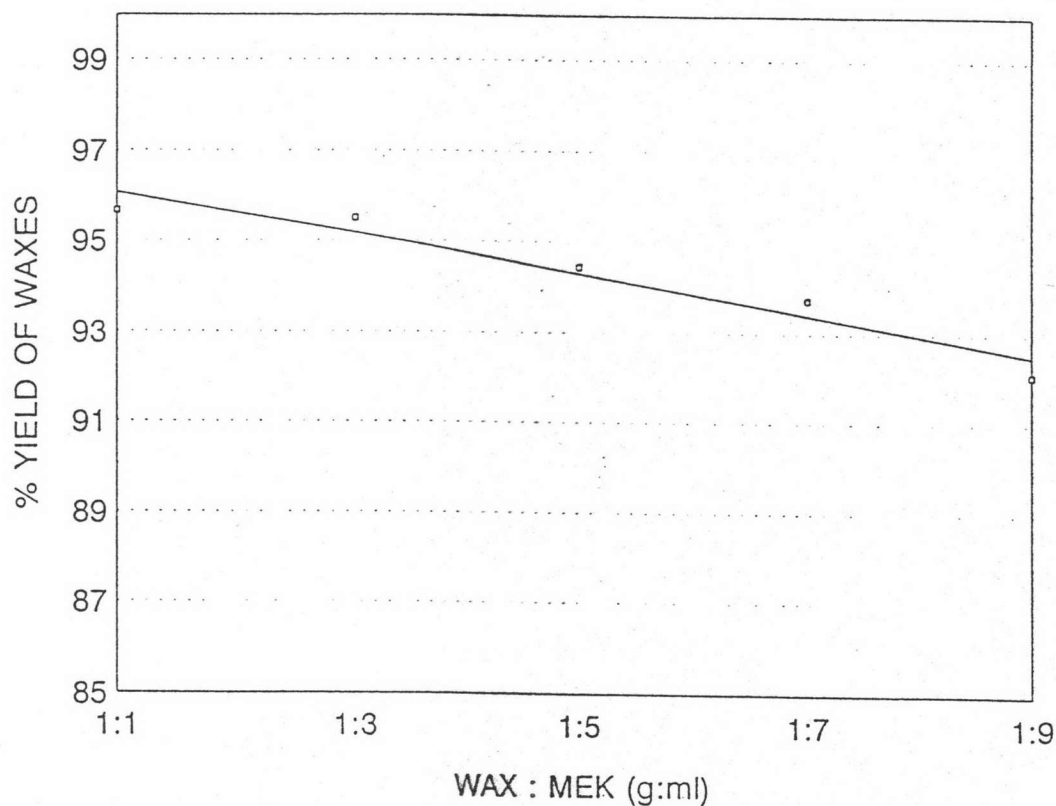


Figure 4.2 Percentage yield of waxes after deoiling.

Fig. 4.2 showed that with the higher ratio of wax to MEK ( g:ml ) the less yield of wax was obtained.

There were not results of oil content of Fang deoiled waxes because of some problems.

The waxes were decolorized by contacting with decolorizing agent i.e. fullers earth, activated carbon and clay after they were deoiled. The amount of decolorizing agents in decolorizing process were varied and the time of contacting of wax and decolorizing agents was 1 hour at 70 ° C. ( Table 4.2 ).

Table 4.2 Color of waxes ( ASTM D 1500 ) after decolorizing by decolorizing agents.

Wax no.	Decolorizing agent ( g )			Wt. of waxes after decolorizing ( g )	Color ASTM D1500
	Fullers earth	Activated carbon	Clay		
1	-	-	-	50.00	L 1.0
2	0.1	-	-	45.84	0.5
3	0.3	-	-	45.39	0.5
4	0.5	-	-	43.73	0.5
5	1	-	-	43.45	0.5
6	2	-	-	42.76	0.5
7	3	-	-	41.90	0.5
8	4	-	-	41.40	L 0.5
9	5	-	-	40.93	0
10	6	-	-	40.81	0
11	-	0.1	-	43.74	L 0.5
12	-	0.3	-	43.12	L 0.5
13	-	0.5	-	42.59	L 0.5

Table 4.2 Continued.

Wax no.	Decolorizing agent ( g )			Wt. of waxes after decolorizing ( g )	Color ASTM D1500
	Fullers earth	Activated carbon	Clay		
14	-	1	-	42.32	L 0.5
15	-	2	-	42.26	L 0.5
16	-	3	-	40.60	L 0.5
17	-	4	-	35.23	0
18	-	-	1	40.61	L 1.0
19	-	-	2	39.34	L 1.0
20	-	-	5	38.46	L 1.0
21	-	-	10	34.72	0.5
22	2	-	2	39.71	L 0.5
23	3	-	2	38.43	L 0.5
24	2	-	5	38.20	L 0.5
25	3	-	5	37.62	L 0.5
26	-	0.3	5	40.74	L 0.5
27	1	0.1	-	47.49	L 0.5
28	2	0.1	-	46.12	0
29	3	0.1	-	44.88	0
30	1	0.2	-	47.31	0
31	1	0.3	-	47.26	0
32	1	0.4	-	47.17	0
33	1	0.5	-	47.33	0

Table 4.2 Continued.

Wax no.	Decolorizing agent ( g )			Wt. of waxes after decolorizing ( g )	Color ASTM D1500
	Fullers earth	Activated carbon	Clay		
34	1	0.7	-	46.73	0
35	1	1	-	46.30	0
36	2	0.5	-	45.79	0
37	2	1	-	45.38	0
38	3	0.5	-	45.49	0
39	3	1	-	44.82	0
40	3	2	-	44.48	0
41	4	1	-	44.88	0
42	4	2	-	44.15	0
43	5	1	-	44.10	0
44	5	2	-	43.54	0
45	German wax is refined wax.				
46	Chinese wax is semirefined wax.				

The fullers earth used was from 0.1 to 6 grams per 50 grams of wax. Fullers earth six grams gave the best color of wax for this series ( Fig. 4.3 ).

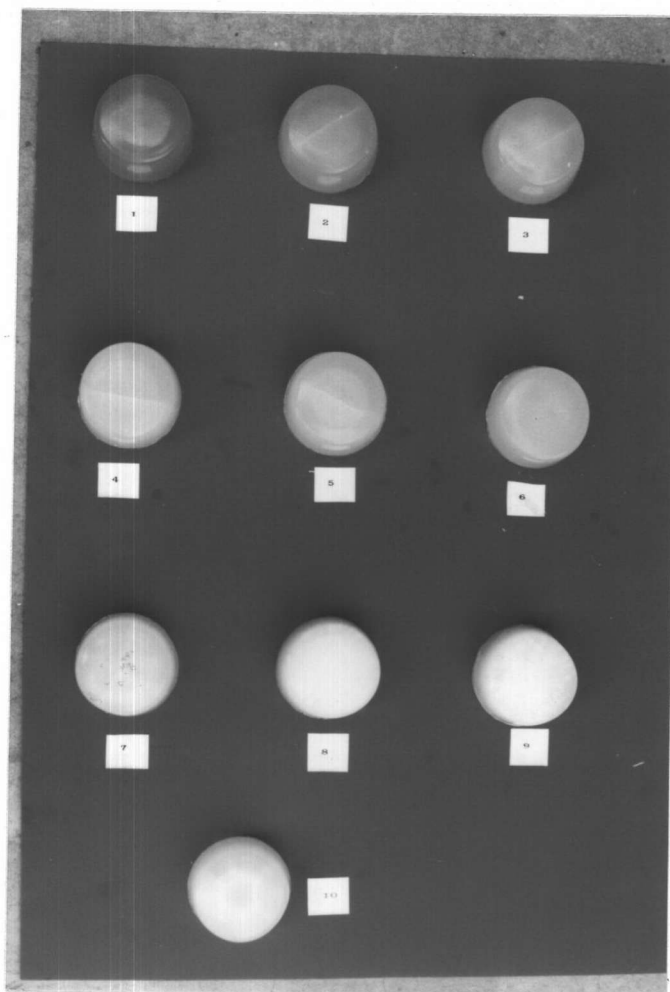


Figure 4.3 Color of waxes after decolorizing with fullers earth

From Fig. 4.3 , number of waxes in this figure was equivalent to number of waxes in Table 4.2 . The wax number 1 in Fig. 4.3 was an undecolorized wax. The waxes number 2, 3, 4, 5, 6, 7, 8, 9, and 10 were decolorized with 0.1, 0.3, 0.5, 1, 2, 3, 4, 5, and 6 grams of fullers earth, respectively.

The activated carbon and clay used were similar to fullers earth but they differed from fullers earth in quantity for decolorizing i.e. 0.1 to 4 grams for activated carbon and 1 to 10 grams for clay. Four grams of activated carbon and ten grams of clay gave the best color of waxes for these series ( Fig. 4.4 and Fig. 4.5 ).

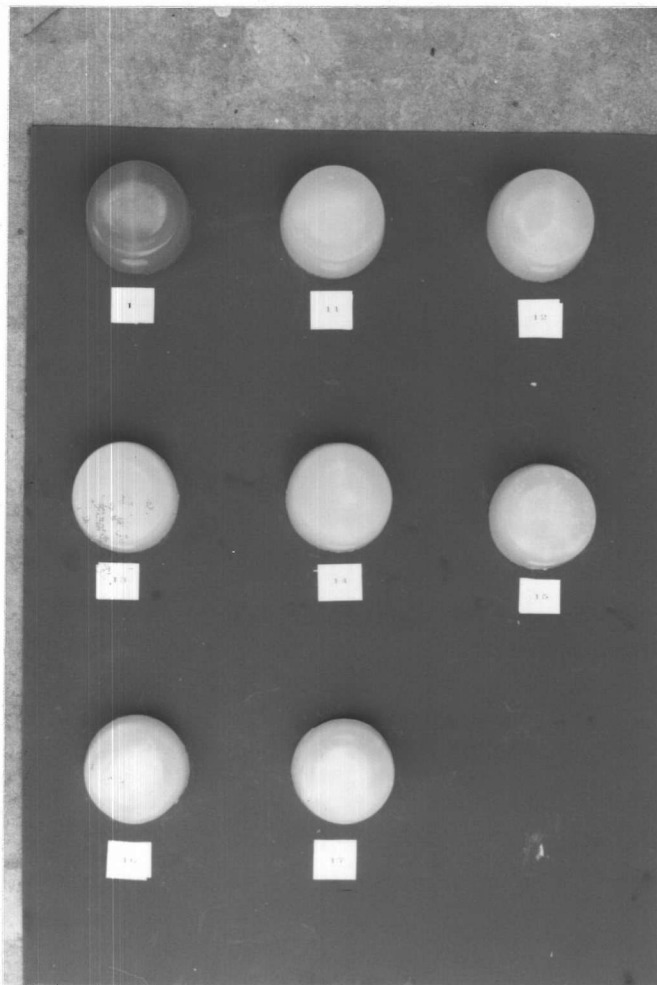


Fig. 4.4 Color of waxes after decolorizing with activated carbon

Fig. 4.4 showed the color of wax number 11, 12, 13, 14, 15, 16, and 17 after decolorizing with 0.1, 0.3, 0.5, 1, 2, 3, and 4 grams of activated carbon, respectively.



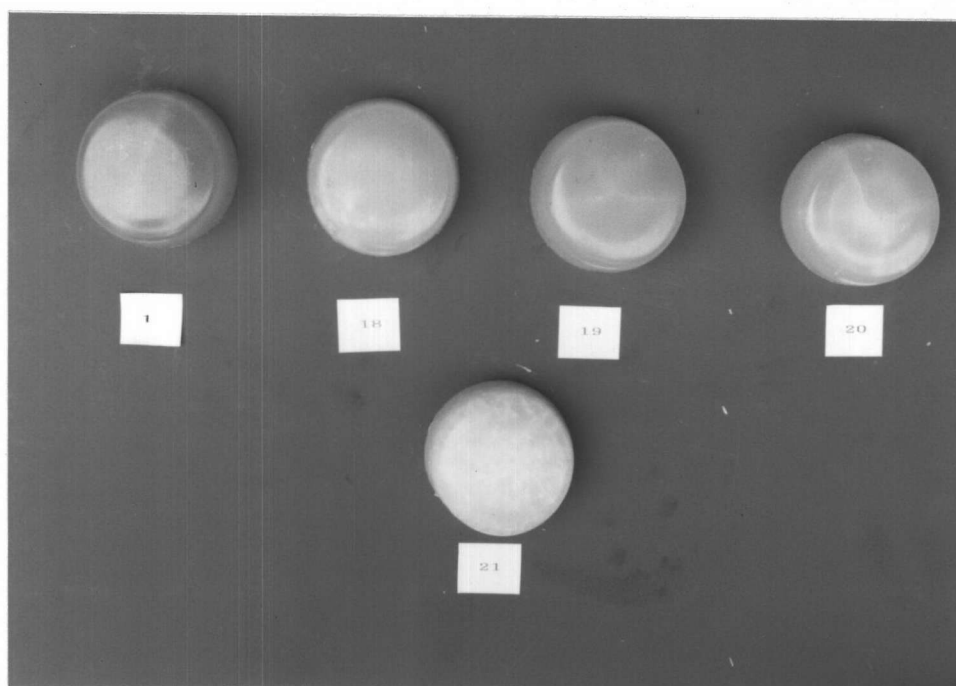


Figure 4.5 Color of waxes after decolorizing with clay

Fig. 4.5 showed the color of wax number 18, 19, 20, and 21 after decolorizing with 1, 2, 5, and 10 grams of clay, respectively.

Because of very low price of clay, it was used in this study. However from the experiment we found that it had quite inferior efficiency than the activated carbon and gave low percentage yield. Even if the clay was mixed with the activated carbon or fullers earth, the color of waxes were not better than the activated carbon or fullers earth alone. ( Fig. 4.6 ).

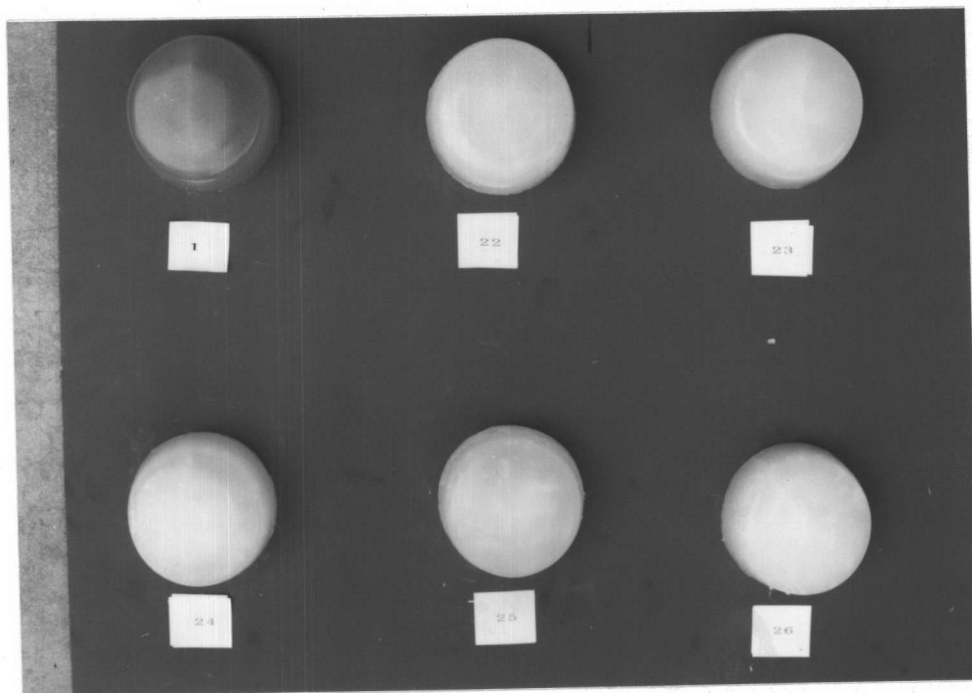


Fig. 4.6 Color of waxes after decolorizing with mixture of activated carbon and clay and mixture of fullers earth and clay

Fig. 4.6 showed the color of wax number 22, 23, 24, and 25 after decolorizing with 2 and 2 , 3 and 2 , 2 and 5 , and 3 and 5 grams of mixture of fullers earth and clay, respectively. The wax number 26 was decolorized with 0.3 and 5 grams of mixture of activated carbon and clay.

The activated carbon was more efficiency for decolorizing than fullers earth and clay. It gave the best decolorizing efficiency when compare to fullers earth and clay in the same amount. Although the fullers earth had lower efficiency than the activated carbon, it had some advantages that it was lower in price and gave higher per cent yield than the activated carbon, thus mixing activated carbon with fullers earth was a promising way to go. Mixture of the activated carbon and fullers earth decolorized waxes better than the method that used only one decolorizing agent. The best condition for decolorizing in this study was a mixture of the activated carbon ( 5 grams ) and fullers earth ( 2 grams ) per 50 grams of wax. ( Fig. 4.7 )

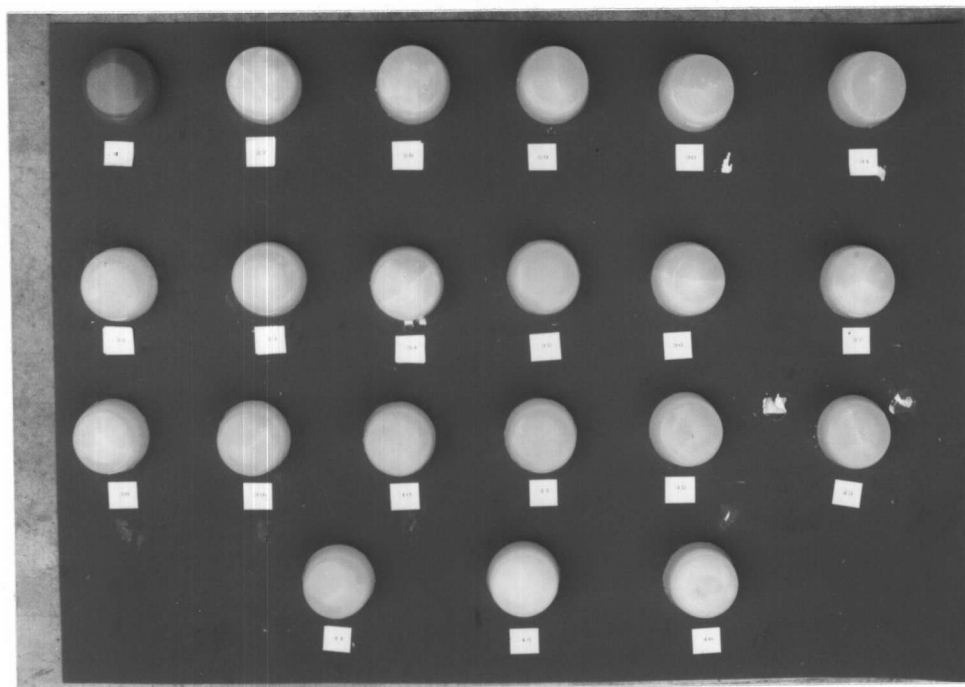


Fig. 4.7 Color of waxes after decolorizing with mixture of activated carbon and fullers earth

From Fig. 4.7, waxes number 27 to 44 were decolorized with mixture of activated carbon and fullers earth. Various ratios of activated carbon and fullers earth mixtures were shown in Table 4.2. The waxes number 45 and 46 were German and Chinese wax.

Because decolorizing agent could adsorb waxes therefore the higher the amount of decolorizing agent used, the lower the percentage yield of wax was obtained. ( Fig. 4.8 )

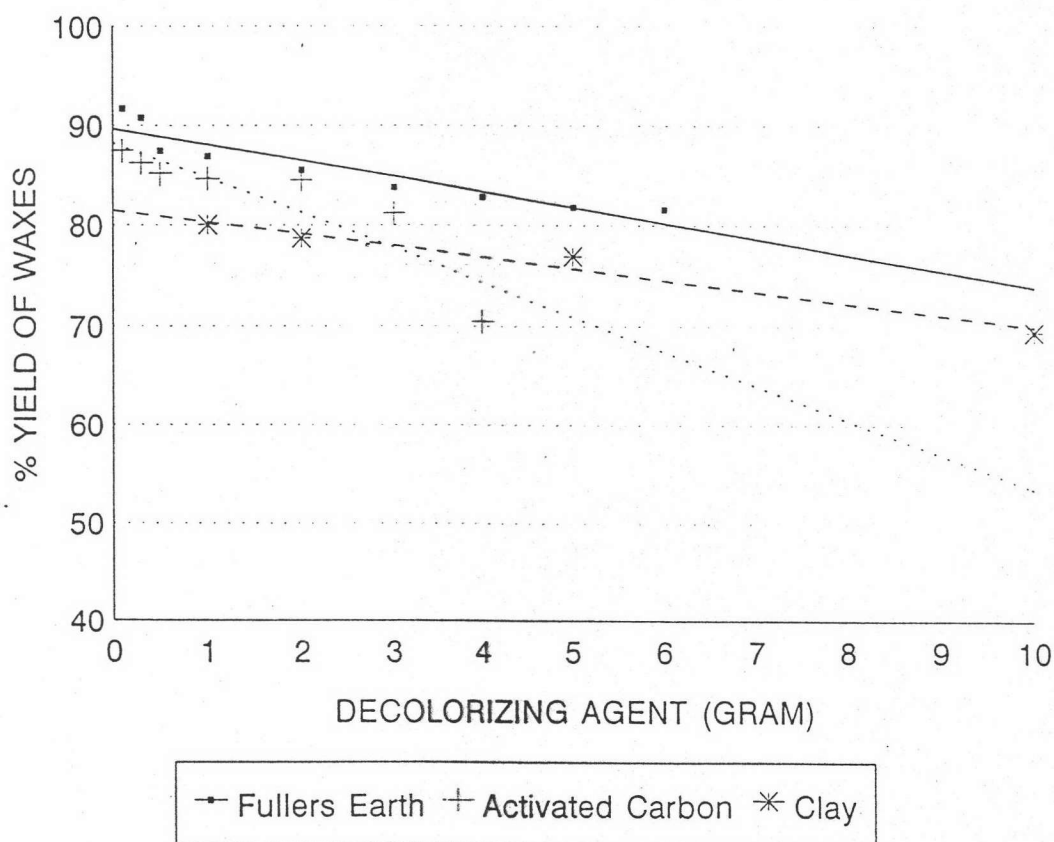


Figure 4.8 Percentage yield of wax after decolorizing.

Fig. 4.8 showed the trend of percentage yield of waxes after decolorizing with 0.1, 0.3, 0.5, 1, 2, 3, 4, 5, and 6 grams of fullers earth , with 0.1, 0.3, 0.5, 1, 2, 3, and 4 grams of activated carbon , and with 1, 2, 5, and 10 grams of clay.

The physical properties such as melting point, penetration, congealing point etc. of unrefined and refined waxes were tested and the data were summarized in Table 4.3.

Table 4.3 Physical properties of Fang unrefined and Fang refined wax .

Physical properties	Unrefined wax	Refined wax
Crystal type	Plate	Plate
Melting point ( ° C)		
-Cooling curve	59.50	60.00
-DSC	59.43	59.79
Congealing point ( ° C)	58	59
Penetration ASTM D1321( 1/10 mm)	12	9
Color ASTM D1500	L 1.0	0

From Table 4.3 after purification, the waxes changed in physical properties, i.e. melting point, congealing point, color, and hardness.

A melting point of Fang unrefined and Fang refined wax determined by ASTM D 87 method was closed to those determined by the DSC ( Fig. 4.9 to Fig. 4.12 ).

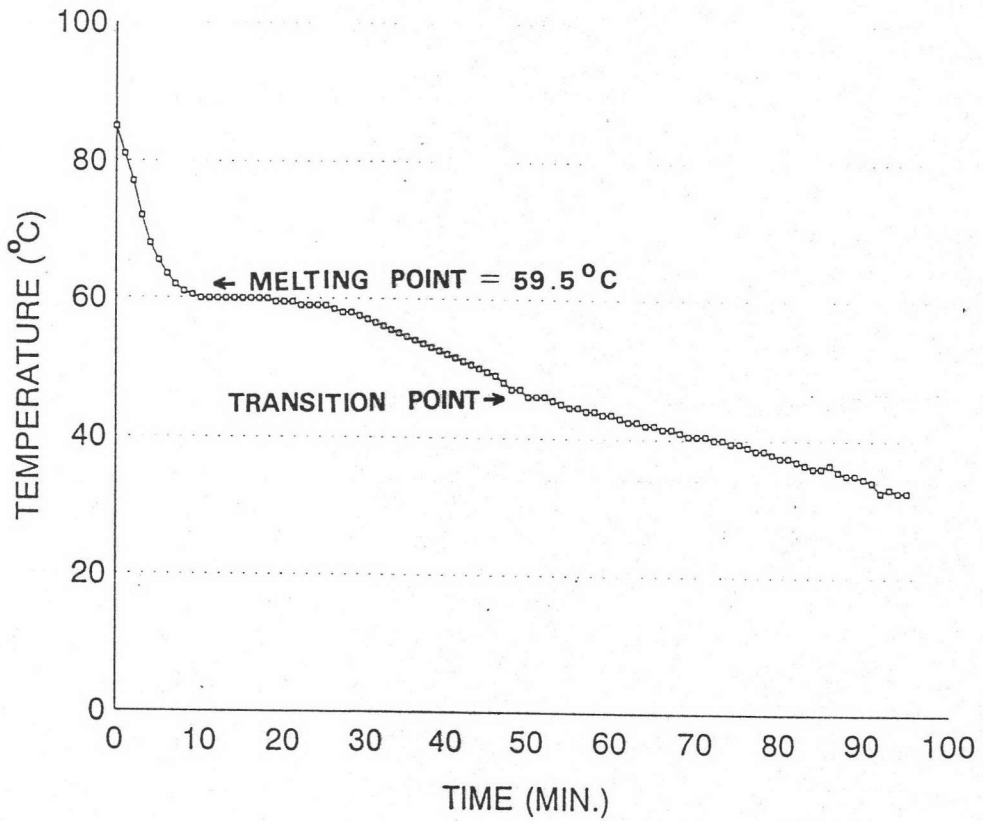


Figure 4.9 Cooling curve of Fang unrefined wax

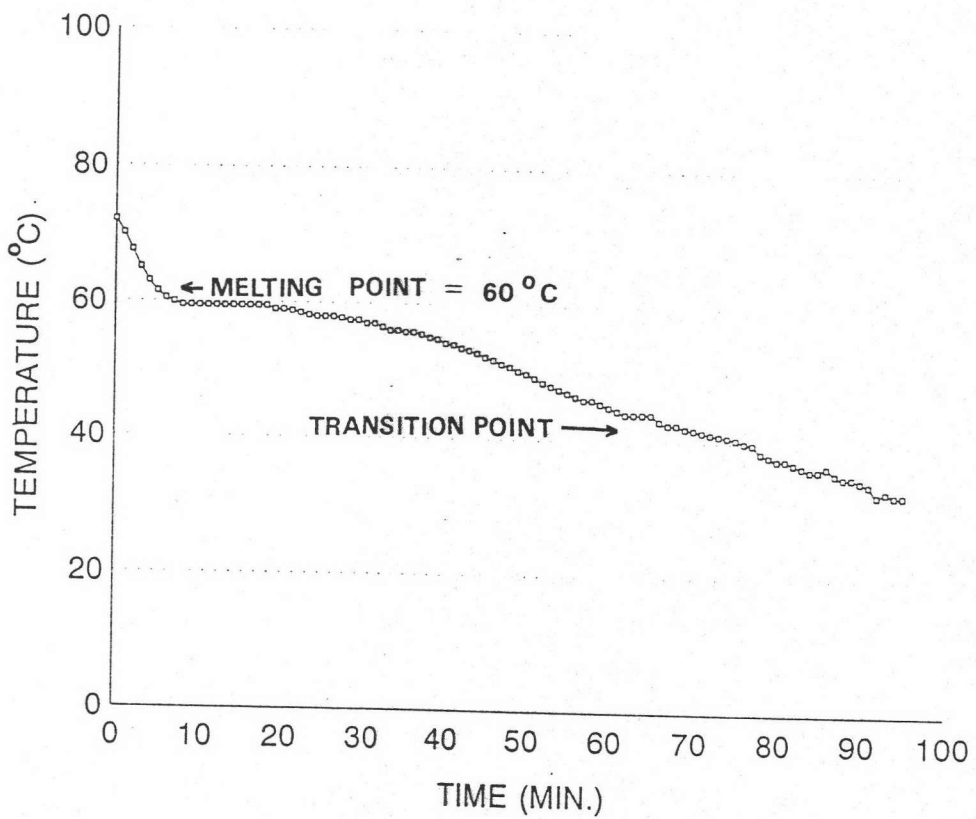


Figure 4.10 Cooling curve of Fang refined wax.

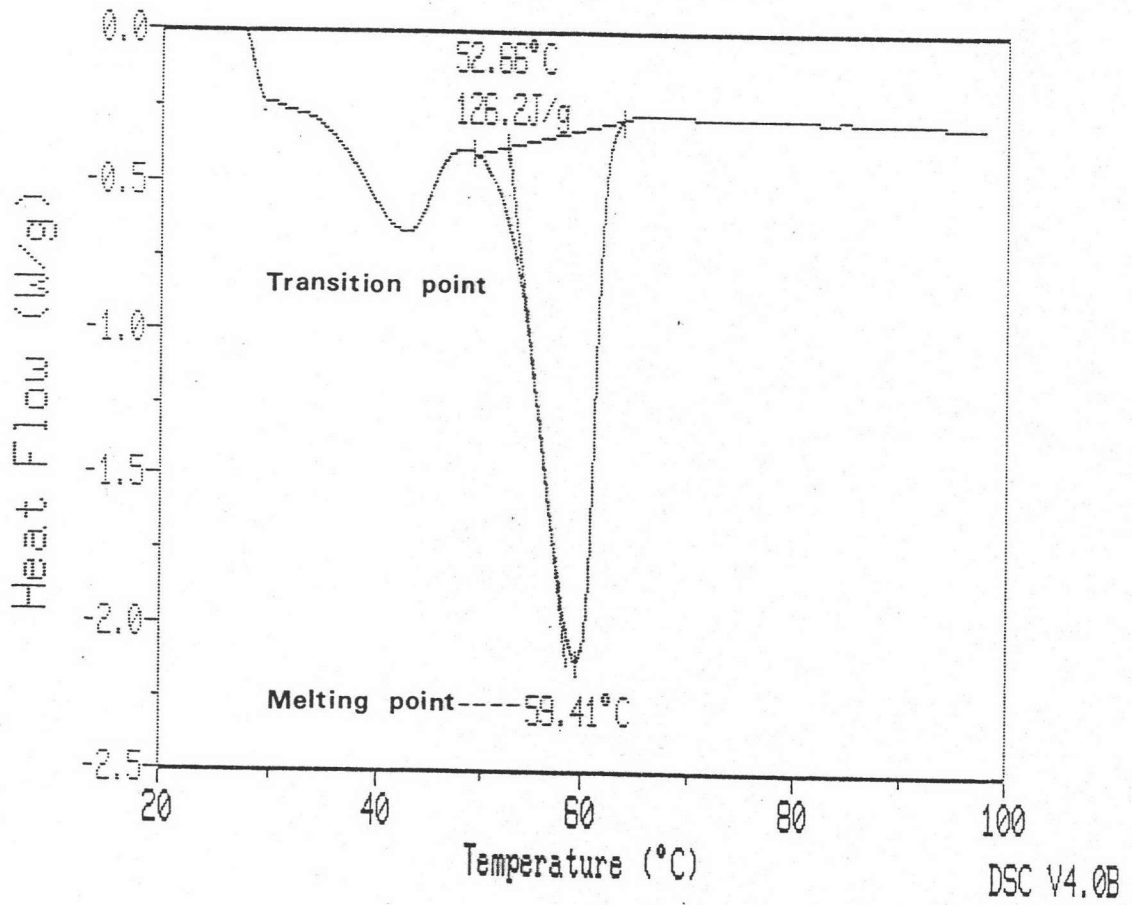


Figure 4.11 DSC of Fang unrefined wax.

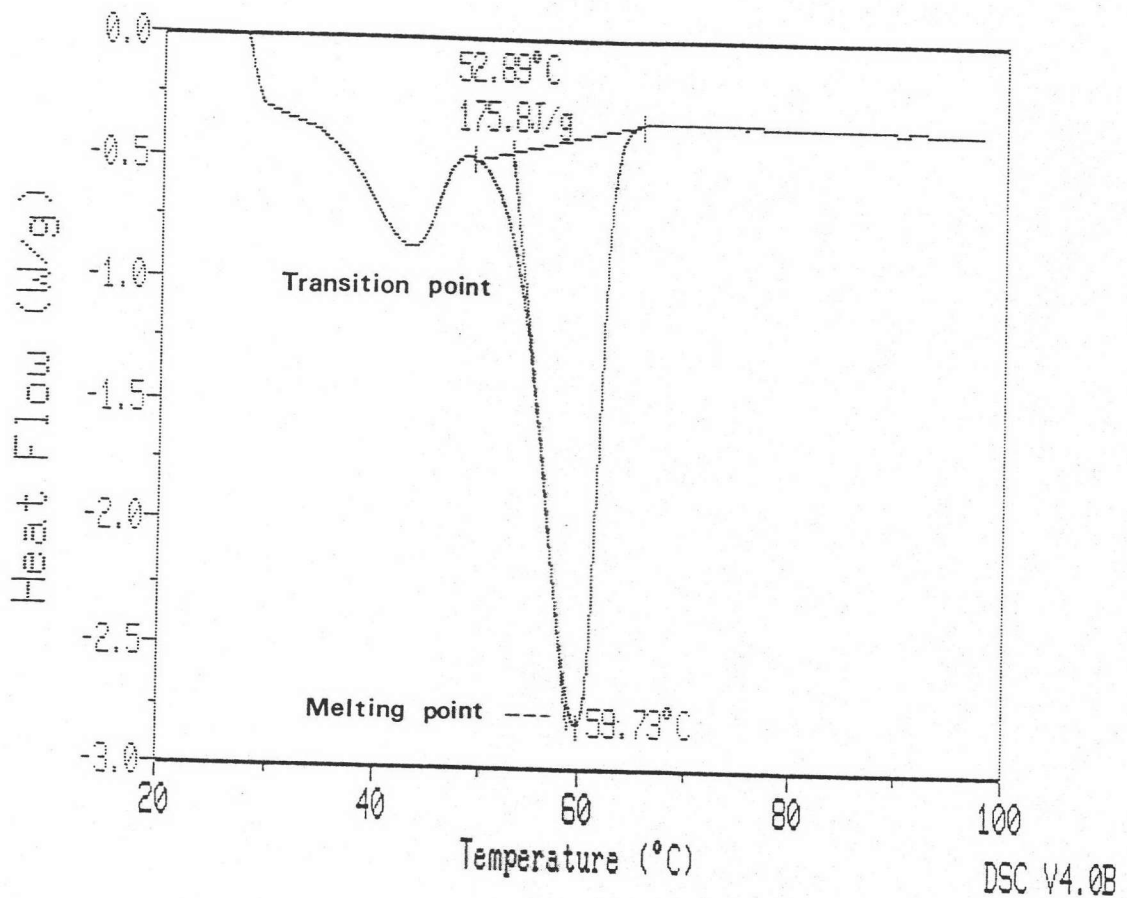


Figure 4.12 DSC of Fang refined wax.

From the pattern of cooling curve and DSC, they showed second order transition point. It was indicated that this wax was paraffin wax. Moreover, plate crystalline was also a character of paraffin wax.

Congealing point near melting point was a specific characteristic of only one component wax.

From penetration value, the refined wax was harder than unrefined wax because oil content in unrefined wax was higher than in refined wax.

The UV absorbance showed absorbance of benzene at 203 and 265 nm. ( Fig 4.13-4.15 )

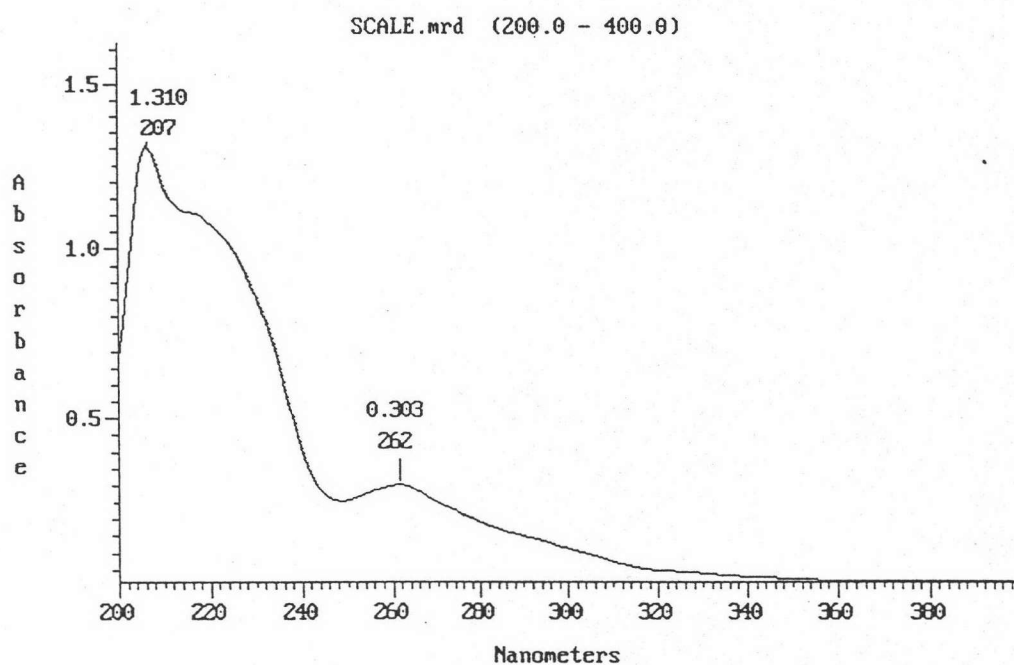


Figure 4.13 UV absorbance of Fang unrefined wax.

From Fig. 4.13, UV absorbance at 207 and 262 nm were 1.310 and 0.303 respectively.



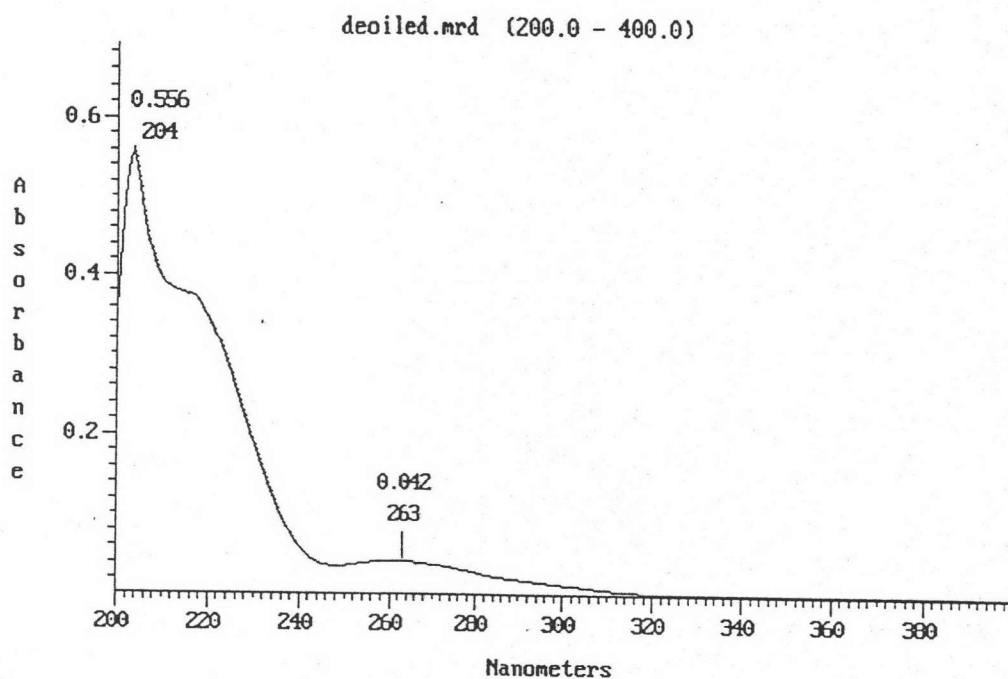


Figure 4.14 UV absorbance of Fang deoiled wax.

From Fig. 4.14, UV absorbance at 204 and 263 nm were 0.556 and 0.042 respectively.

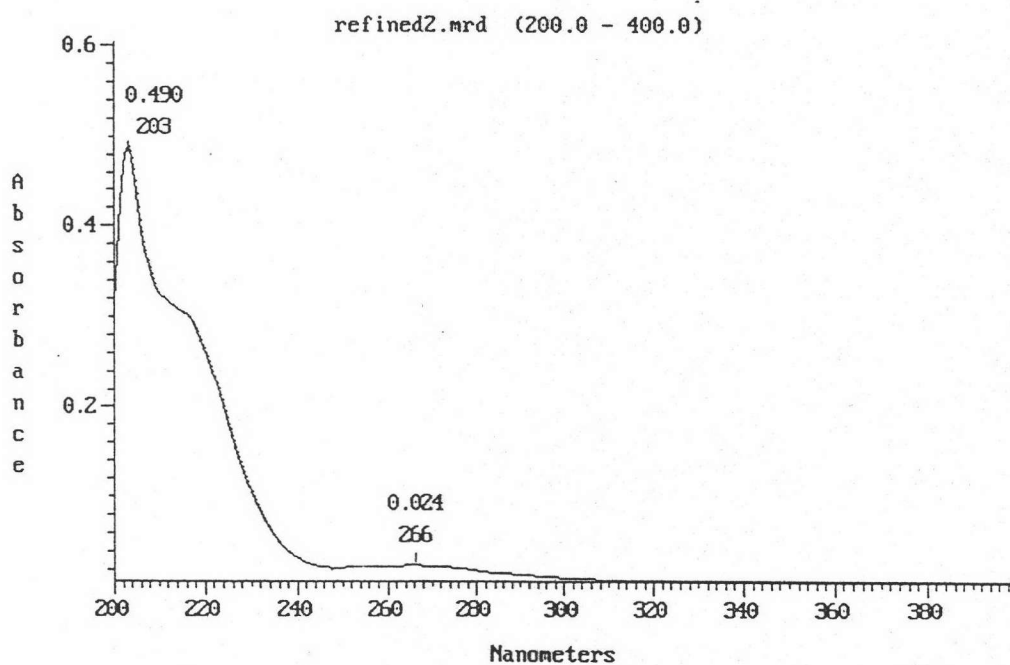


Figure 4.15 UV absorbance of Fang refined wax.

From Fig. 4.15, UV absorbance at 203 and 266 nm were 0.490 and 0.024 respectively.

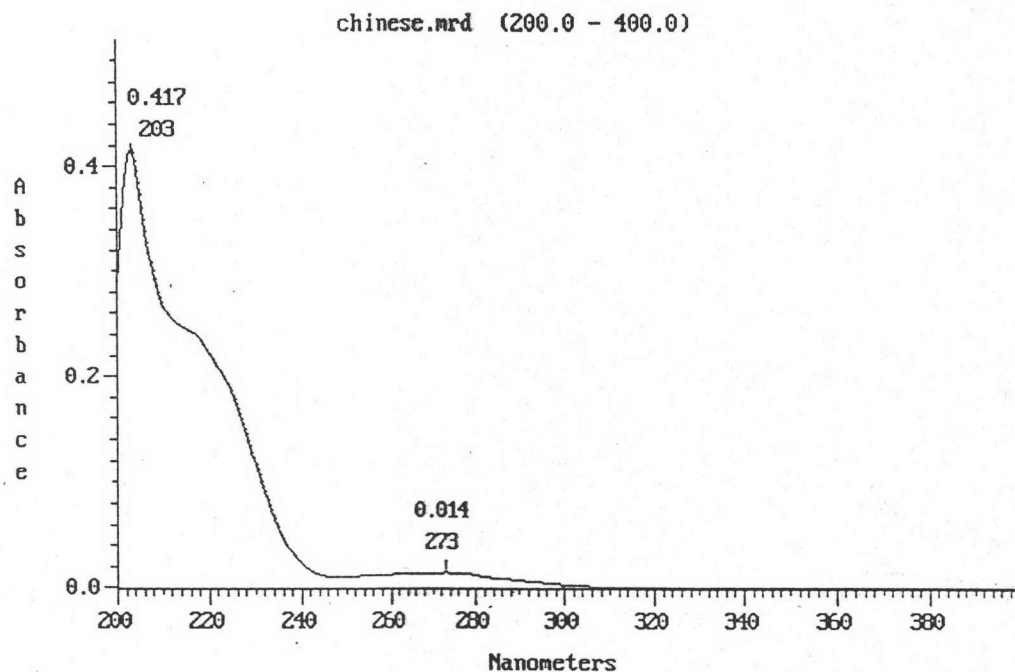


Figure 4.16 UV absorbance of Chinese wax ( semirefined wax ).

From Fig. 4.16, UV absorbance at 203 and 273 nm were 0.417 and 0.014 respectively.

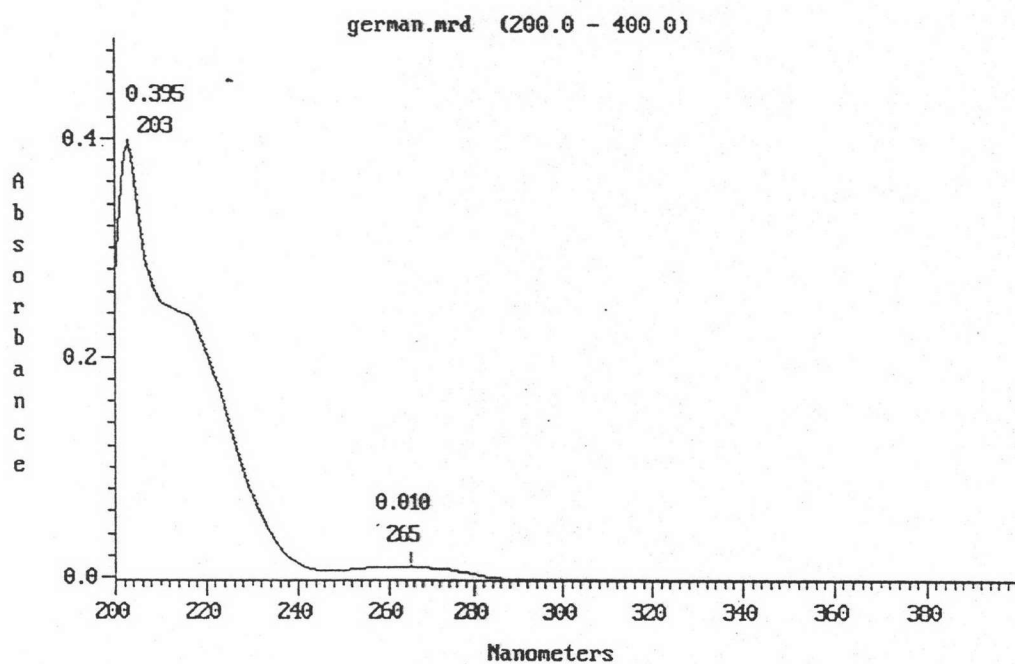


Figure 4.17 UV absorbance of German wax ( refined wax ).

From Fig. 4.17, UV absorbance at 203 and 265 nm were 0.395 and 0.010 respectively.

The remarkable data that is the higher purity wax was, the lower absorbance it showed ( Fig. 4.18 and Fig. 4.19 ).

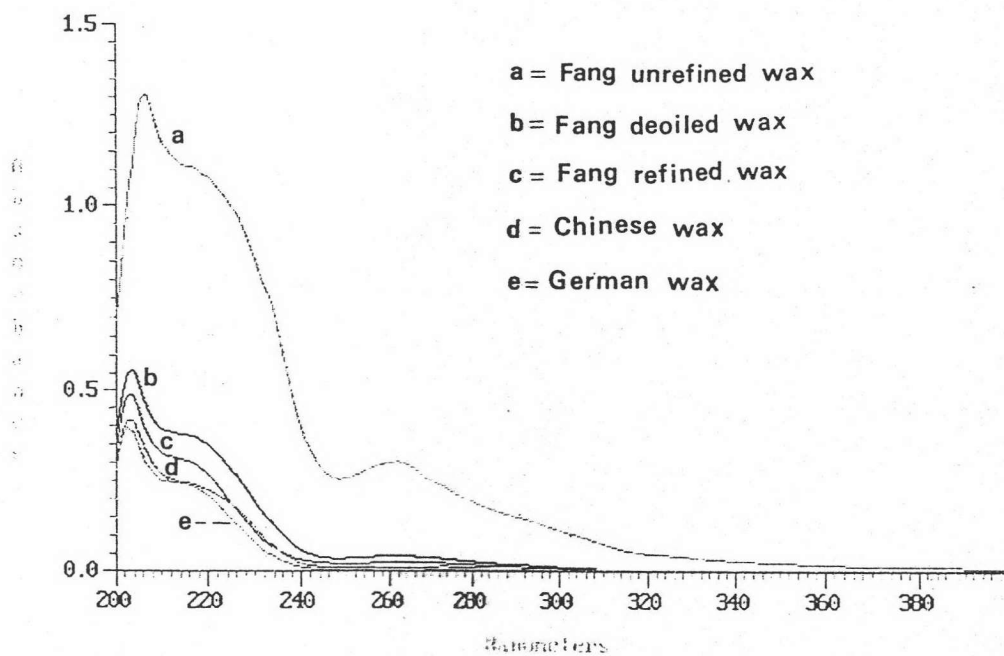


Figure 4.18 UV absorbance of Fang unrefined, Fang deoiled, Fang refined, Chinese and German waxes.

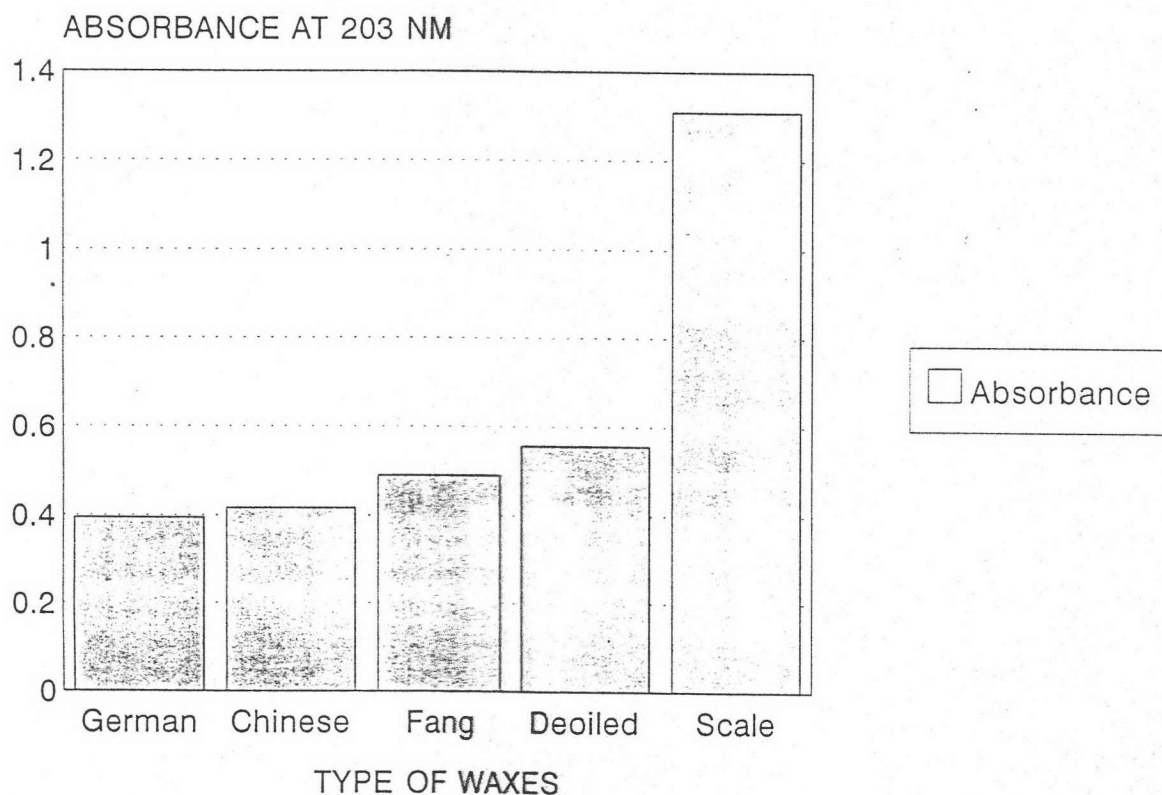


Figure 4.19 Value of UV absorbance at 203 nm.

From Fig. 4.19, German was German wax. Chinese was Chinese wax. Fang was Fang refined wax that decolorized with a mixture of the activated carbon 5 grams and fullers earth 2 grams. Deoiled was Fang deoiled wax and Scale was Fang unrefined wax.

The GC and GC-MS were performed in a column packed with OV-1. The composition of Fang refined wax was determined from chromatogram and mass spectrum.

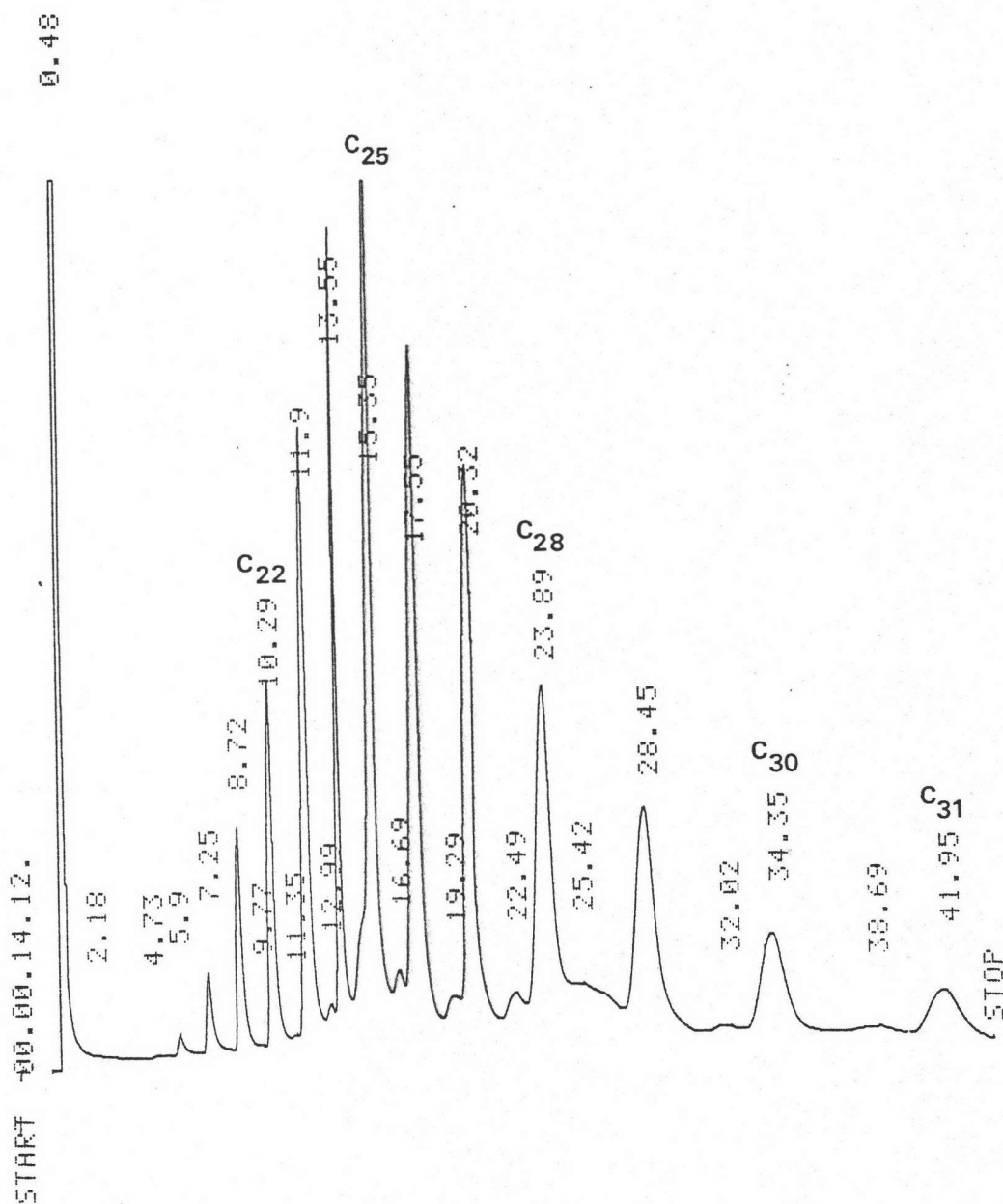


Figure 4.20 Chromatogram of Fang refined wax

From Fig. 4.20, we found that Fang refined wax was composed of C<sub>20</sub> to C<sub>31</sub> n-alkane and the main composition was C<sub>25</sub> n-alkane.

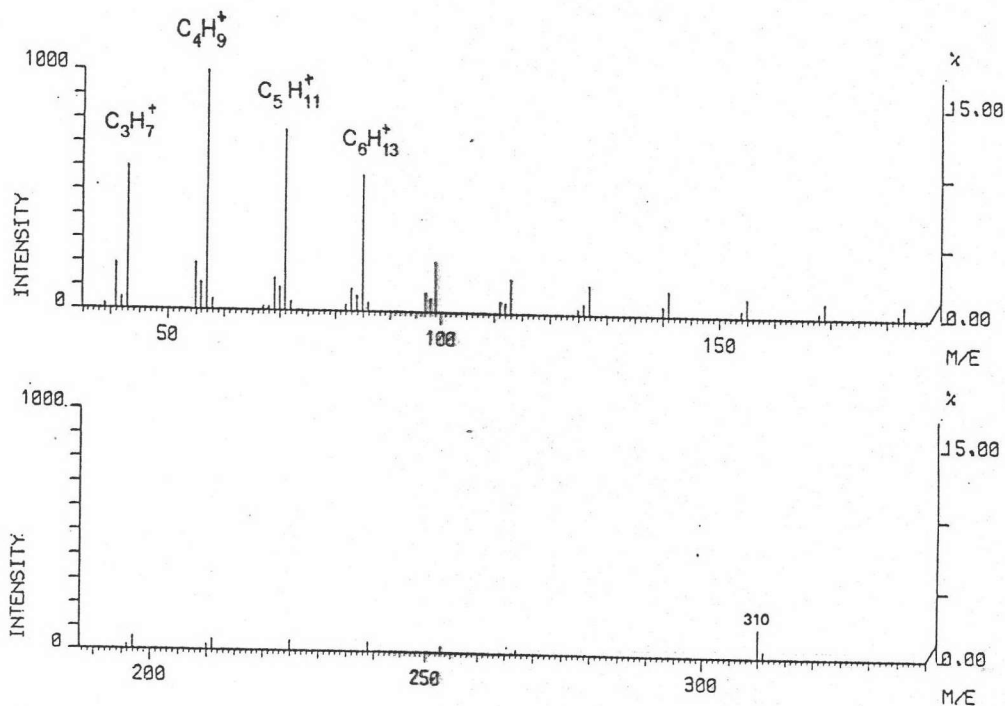


Figure 4.21 The first mass spectrum of Fang refined wax.

Fig. 4.21 was mass spectrum of  $C_{22}$  n-alkane because molecular ion peak was 310

and this mass spectrum was the same fragmentation pattern as n-alkane mass spectrum.

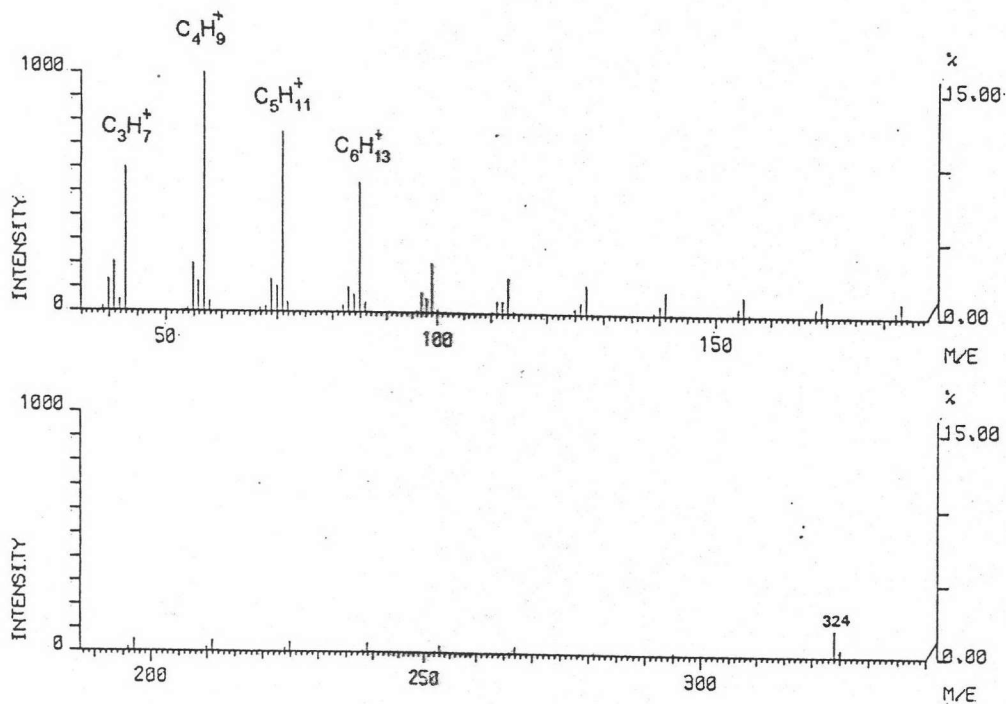


Figure 4.22 The second mass spectrum of Fang refined wax.

Fig. 4.22 was mass spectrum of  $C_{23}$  n-alkane because molecular ion peak was 324

and this mass spectrum was the same fragmentation pattern as n-alkane mass spectrum.

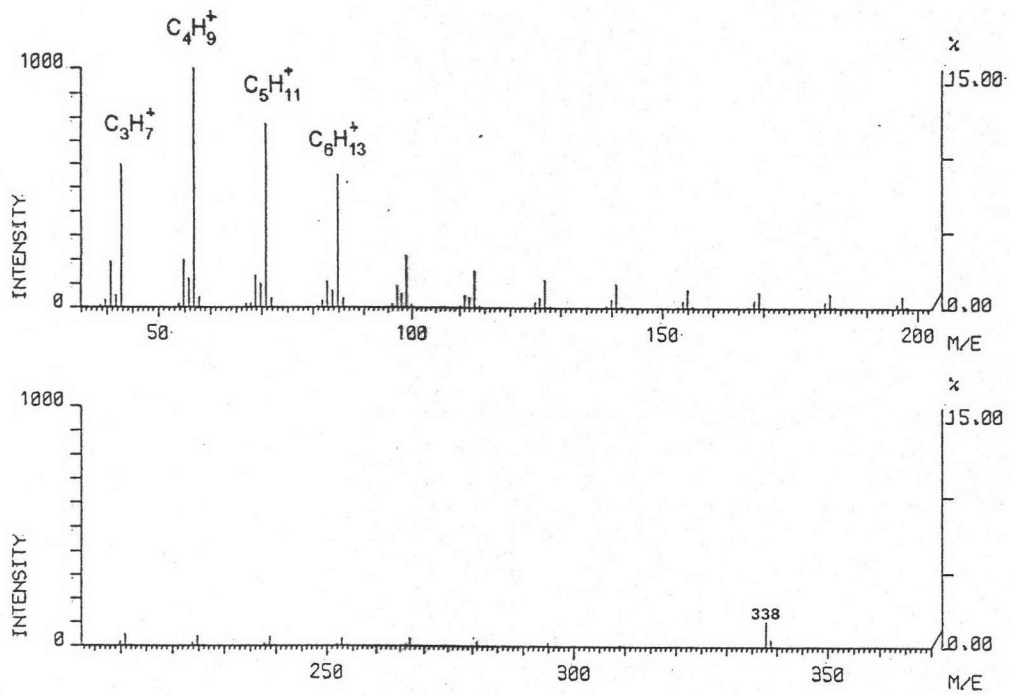


Figure 4.23 The third mass spectrum of Fang refined wax.

Fig. 4.23 was mass spectrum of  $C_{24}$  n-alkane because molecular ion peak was 338

and this mass spectrum was the same fragmentation pattern as n-alkane mass spectrum.

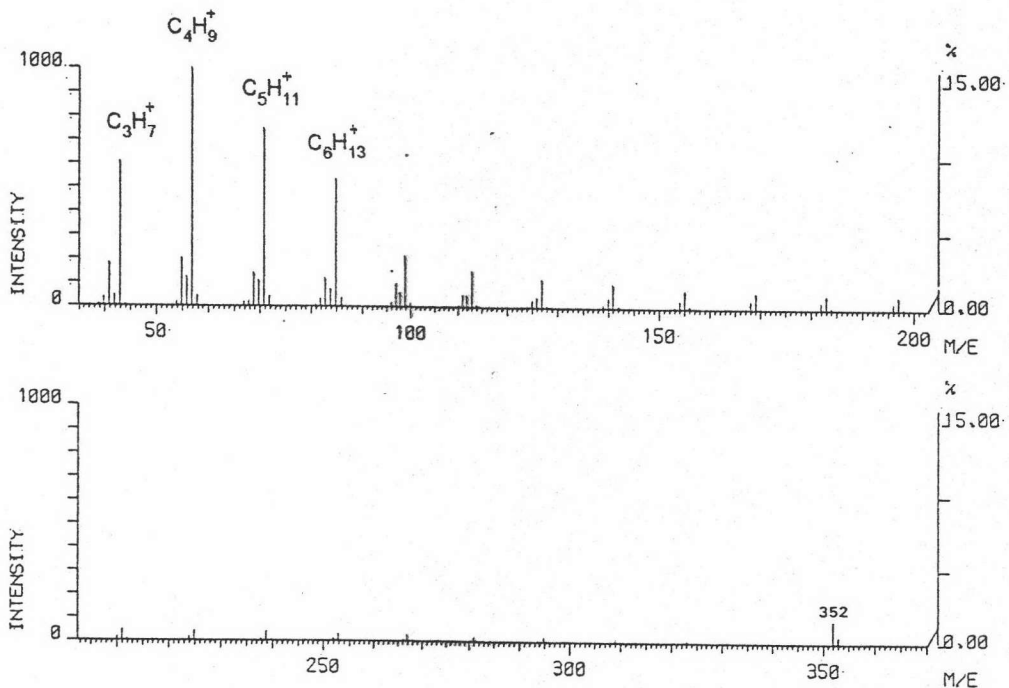


Figure 4.24 The fourth mass spectrum of Fang refined wax.

Fig. 4.24 was mass spectrum of  $C_{25}$  n-alkane because molecular ion peak was 352

and this mass spectrum was the same fragmentation pattern as n-alkane mass spectrum.

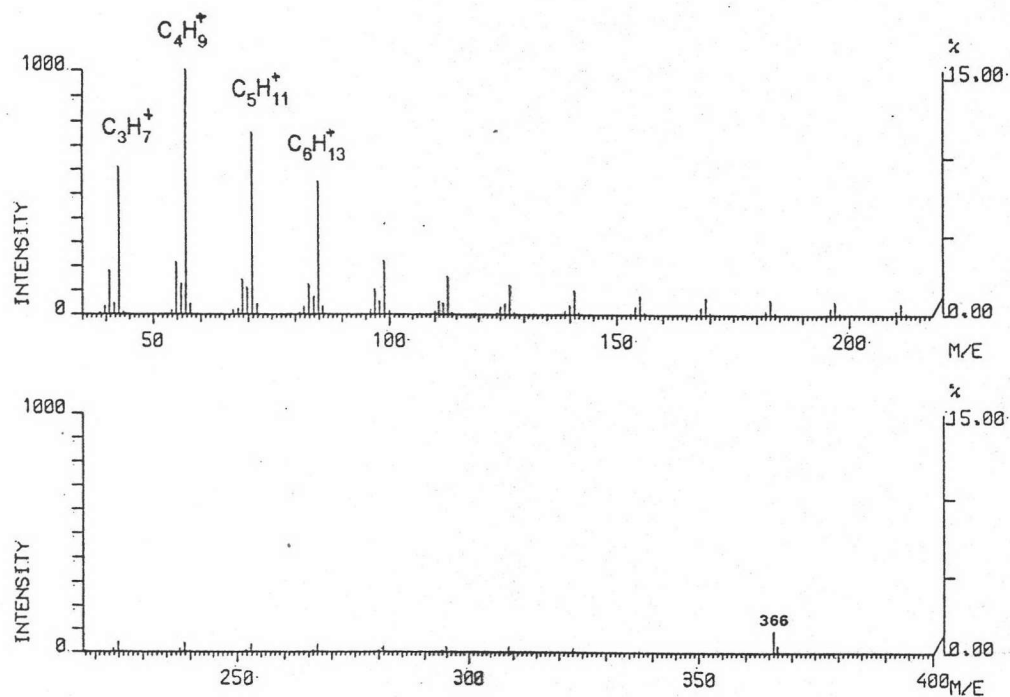


Figure 4.25 The fifth mass spectrum of Fang refined wax.

Fig. 4.25 was mass spectrum of  $C_{26}$  n-alkane because molecular ion peak was 366

and this mass spectrum was the same fragmentation pattern as n-alkane mass spectrum.

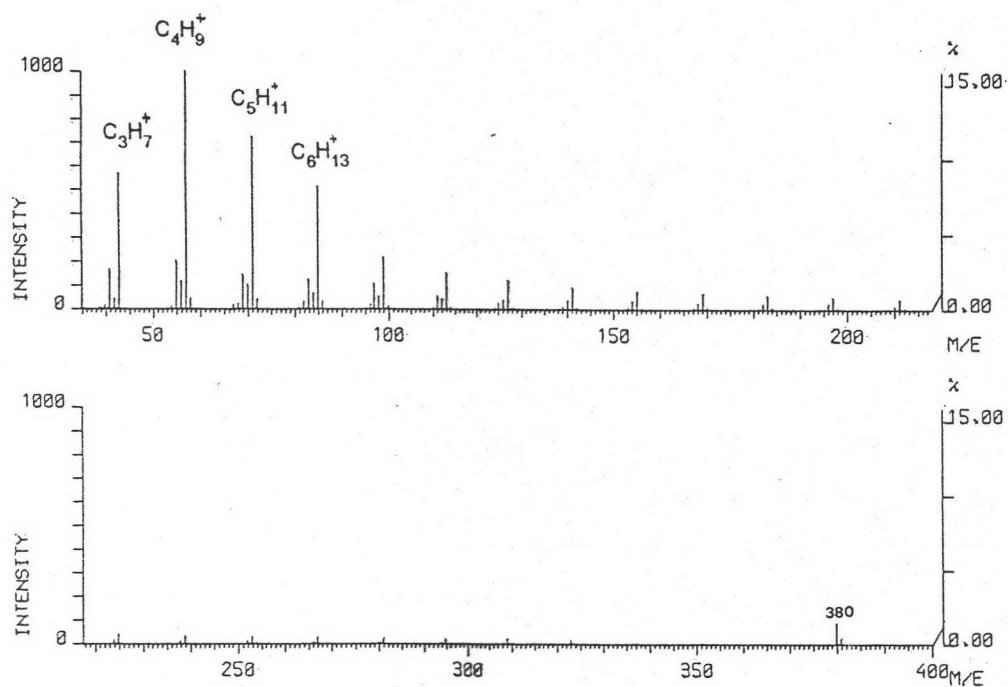


Figure 4.26 The sixth mass spectrum of Fang refined wax.

Fig. 4.26 was mass spectrum of  $C_{27}$  n-alkane because molecular ion peak was 380

and this mass spectrum was the same fragmentation pattern as n-alkane mass spectrum.

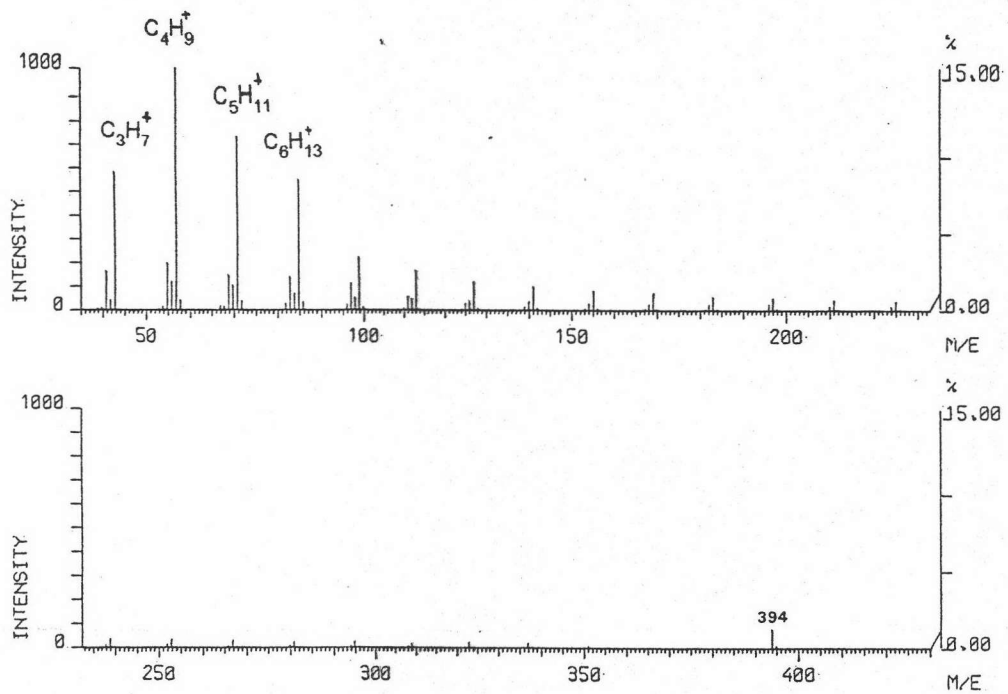


Figure 4.27 The seventh mass spectrum of Fang refined wax.

Fig. 4.27 was mass spectrum of  $C_{28}$  n-alkane because molecular ion peak was 394

and this mass spectrum was the same fragmentation pattern as n-alkane mass spectrum.

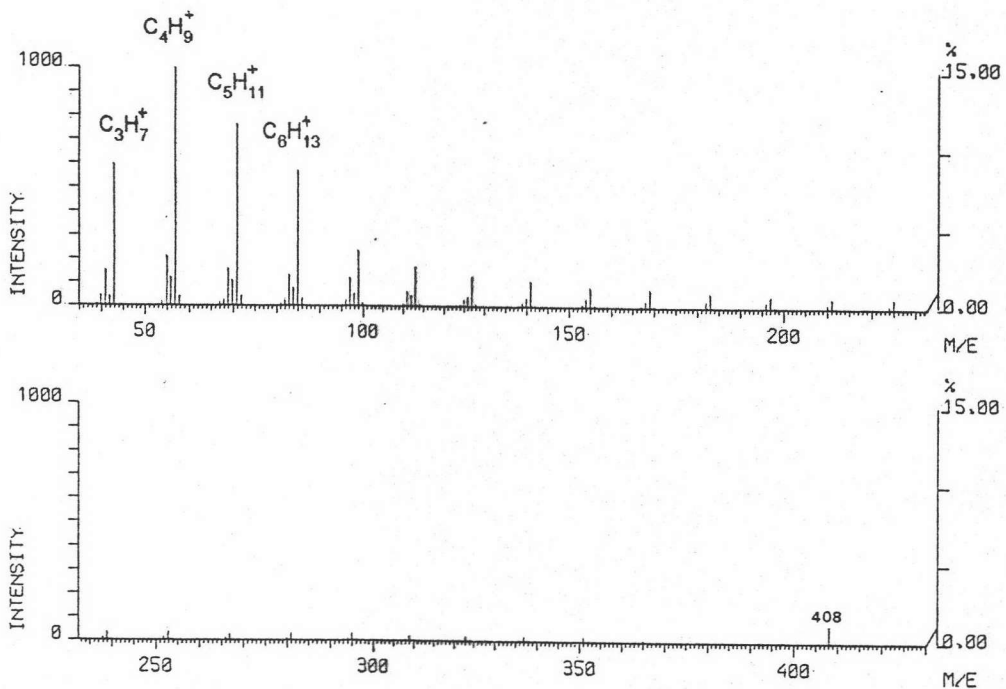


Figure 4.28 The eighth mass spectrum of Fang refined wax.

Fig. 4.28 was mass spectrum of  $C_{29}$  n-alkane because molecular ion peak was 408

and this mass spectrum was the same fragmentation pattern as n-alkane mass spectrum.



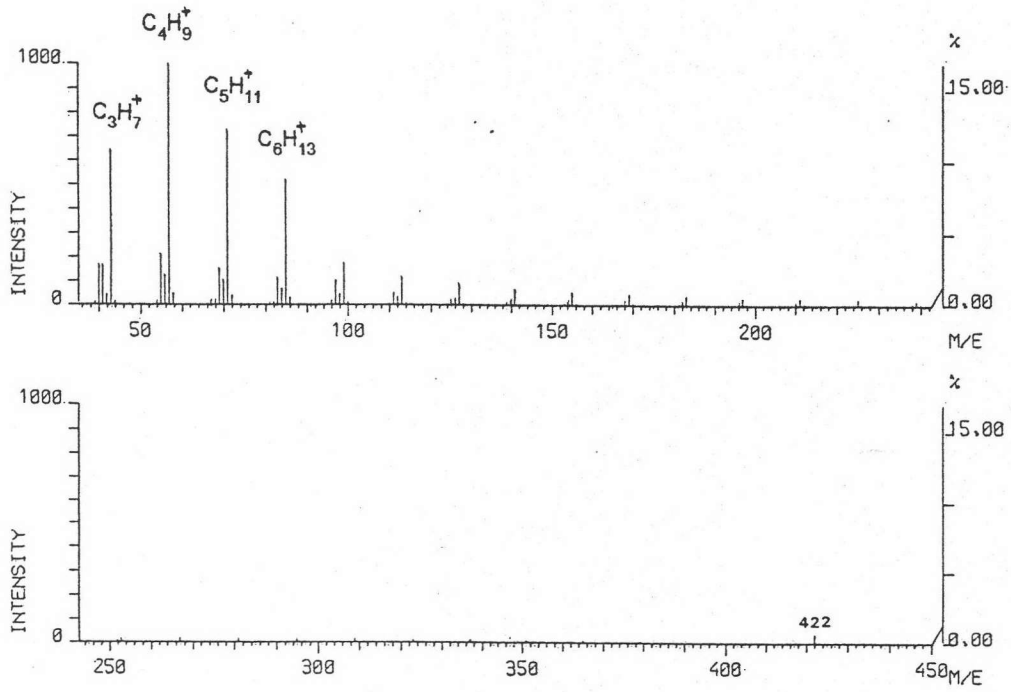


Figure 4.29 The ninth mass spectrum of Fang refined wax.

Fig. 4.29 was mass spectrum of C<sub>30</sub> n-alkane because molecular ion peak was 422

and this mass spectrum was the same fragmentation pattern as n-alkane mass spectrum.

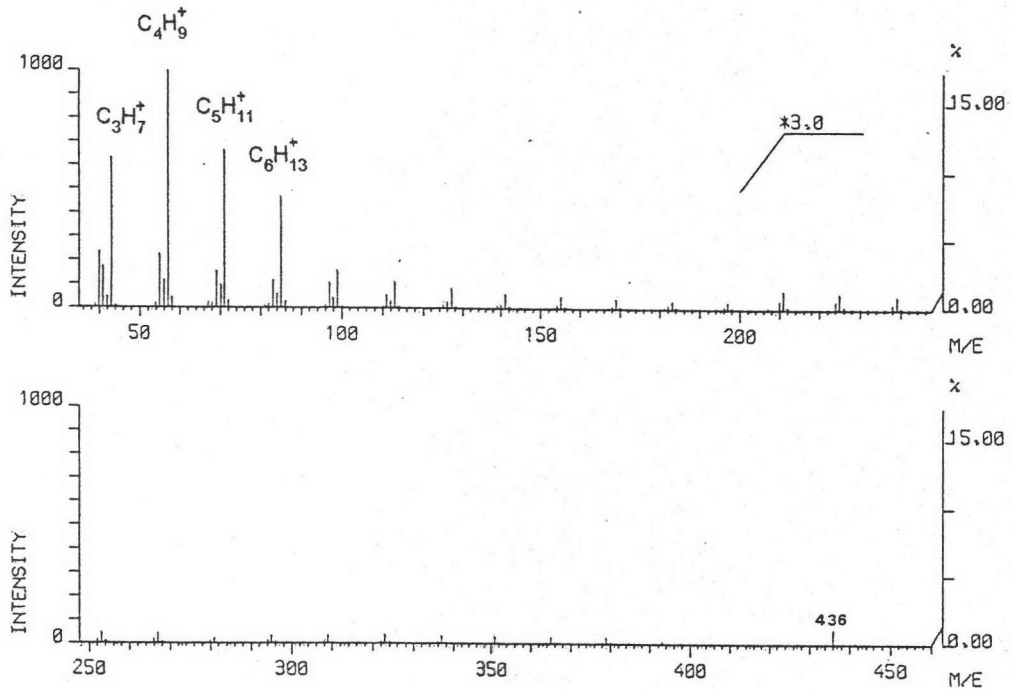


Figure 4.30 The tenth mass spectrum of Fang refined wax.

Fig. 4.30 was mass spectrum of C<sub>31</sub> n-alkane because molecular ion peak was 436

and this mass spectrum was the same fragmentation pattern as n-alkane mass spectrum.