

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Structure of Lampang Diatomite

Preliminary study of Thai diatomite at Lampang basin was the structure of diatom remains by using the scanning electron microscope and its microphotograph was shown in Figure 1.7. It was found that the structure of the diatom remains of Lampang diatomite was the same as that of Gas Chrom Q, thus the trend of preparation of a solid support from Thai diatomite was possible and the chemical analysis of Lampang diatomite was studied.

4.2 Chemical Analysis of Lampang Diatomite

The results of the chemical analysis of Lampang Diatomite at the 26 feet and 42 feet depths of the Mae Tha deposit are shown in Table 4.1. It was seen that diatomite at the lower level was purer than that at the upper level since the silica contents at the 42 feet depth was higher than that at the 26 feet depth and the clay content (Al_2O_3) at the 42 feet depth was lower than at the 26 feet depth. Only two levels were not sufficient to conclude the trend of diatomite deposition. The chemical analysis of diatomite at various depths of the same shaft from the Department of Mineral Resources (21) as shown in the appendix 1 showed the fluctuation of SiO_2 and Al_2O_3 contents in diatomite at various depths. Therefore, the purity of diatomite might not depend on the depth at which diatomite reserved. The contents of alkali and alkali-earth oxides in diatomite at the two levels were very close except the content of Na_2O at the lower level was 0.69% higher than

Table 4.1 Chemical analysis of Thai diatomite at the Mae Tha deposit,
Lampang.

Composition	Percentages of Content	
	26 feet depth ^(a)	42 feet depth ^(b)
SiO ₂	70.58±0.15	71.09±0.40
Al ₂ O ₃	12.48±0.01	11.83±0.59
Fe ₂ O ₃	3.07±0.02	2.86±0.05
MgO	0.47±0.03	0.44±0.03
CaO	0.20±0.00	0.20±0.01
Na ₂ O	0.47±0.03	1.16±0.03
K ₂ O	1.54±0.04	1.55±0.04
Loss on ignition	7.03±0.11	6.35±0.34

Note (a) mean ± mean deviation of 3 samples

(b) mean ± mean deviation of 9 samples

that of the upper level. This might be because the diatom remains of the 26 feet depth and the 42 feet depth were in the different generation.

The content of Al_2O_3 12.48% and 11.83% indicated the presence of high content of Clay mineral. Assuming that all of alumina content was the composition of clay and clay was generally composed of 40% Al_2O_3 (40) thus the calculated amount of clay in the diatomite here was 31.20% and 29.58%, respectively. It was known that the clay particles were very small ($\leq 2 \mu\text{m}$), this reduced the surface area of diatomite because they covered the pores of diatomite structure. In addition, the surface of clay itself had an adsorptive property due to the presence of some cations. Considering the iron contents of 3.07% and 2.86%, they were quite high and could interfere the process of the flux calcination of diatomite, e.g., the excess content of iron caused the product colored. Fe_2O_3 acted as a fluxing agent, this made the difficulty of controlling the partial fusion of diatomite.

Comparing the chemical analysis results at the 42 feet depth from this study to those from the Department of Mineral Resources in Appendix 1, they were slightly different because of the different laboratories. Between the diatomite at the 26 feet depth and the 42 feet depth, the latter had higher content of silica; as a result, it was selected as a raw material for this study.

To remove the impurities from diatomite, several steps of water washing, settling, and acid treatment were performed.

4.3 Benefication of Lampang Diatomite

4.3.1 Mechanical Separation

The yield of the clean diatomite from mechanical separation as illustrated in Table 4.2 indicated insignificant difference between the use and nonuse of dispersant as well as no difference between the 3.3% slurry and 20.0% slurry. Therefore, Method 2 (without dispersant and 3.3% slurry) was selected for mechanical separation of diatomite.

To select the best method of benefication, the results of the chemical analysis of these clean diatomite were also considered. It was seen that the compositions of the clean diatomite with the treatments of dispersant and non-dispersant by either the filtration or decantation techniques were almost the same. The difference was from the techniques, filtration and decantation, not from the use and nonuse of dispersant. The higher percentage of SiO_2 and the lower percentage of Al_2O_3 were obtained from the decantation technique. This was because the filtration might retain all particles, both diatomite and clay, on the filter paper. Comparing the products from the decantation of Method 1 and Method 2, they were not so different. This corresponded to all of soluble salts which caused the clay particles flocculated (40) were removed after 3-time washing of the diatomite with distilled water and the clay particles could disperse themselves without the presence of dispersant.

Not only clay but also iron was removed from the diatomite by water washing and coarse-mineral settling. On account that coarse minerals were removed before the separation of clay from diatomite, the quantities of coarse minerals from all methods were equally 5.2%.

The chemical analysis of coarse minerals was also determined to indicate whether iron was valuable to be recovered. The result as,

Table 4.2 The yields of clean diatomite after mechanical separation

Type of Benefication	% Yield	
	By Filtration	By Decantation
Method 1 (With Dispersant)	77.8	59.7
Method 2 (Without Dispersant) 3.3% slurry	75.8	60.4
Method 3 (Without Dispersant) 20.0% slurry	-	60.6

Table 4.3 Chemical analysis of clean diatomite after mechanical separation.

Products	% Composition				
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO
DF	73.79	11.04	1.90	0.42	0.14
NDF	73.60	11.05	1.91	0.42	0.15
DD	76.17	9.57	1.67	0.34	0.12
NDD	75.92	9.60	1.67	0.34	0.11

Note DF was the product from using the dispersant and filtration.

(Method 1)

NDF was the product from using no dispersant and filtration.

(Method 2)

DD was the product from using the dispersant and decantation.

(Method 1)

NDD was the product from using no dispersant and decantation.

(Method 2)

shown in Table 4.4 showed that the quantity of iron in coarse minerals was just 6.88%. It was so small that the recovery of iron was not worthwhile.

Although some of iron (41% Fe_2O_3) was removed, the remained iron still caused the flux-calcined diatomite colored, pink instead of white. Therefore, the chemical treatment to remove the remained iron was necessary.

4.3.2 Acid Treatment

The clean diatomite obtained from the mechanical separation was treated with HCl to remove the remained iron and chemical analyses of those products are shown in Table 4.5. The results showed that the degree of iron removal was proportional to the stage of HCl treatment, the amount of HCl, and period of warming. To consider which condition was suitable, the chemical analysis was not sufficient, the physical properties of the flux-calcined products were also required. The presence of iron in diatomite could affect to the hardness, color and surface area of the flux-calcined diatomite. If the content of iron was too high, the diatomite would be more fused than that required and might be colored of pink to brown. Color of the product was one index of the required product, which was white here. If the iron content was too low, the forming of sodium iron silicate was not as required, i.e., its hardness was not sufficient. After consideration of products from flux-calcination, the optimum condition of acid treatment was 1-time extraction with 1000 cm^3 15% HCl warming at $90^\circ\text{--}95^\circ\text{C}$ for 3 hours.

Table 4.4 Chemical analysis of coarse minerals from mechanical separation.

Composition	Percentages of Content
SiO_2	68.91
Al_2O_3	9.32
Fe_2O_3	6.88
MgO	0.41
CaO	0.14

Table 4.5 Chemical analyses of the HCl-treated diatomite.

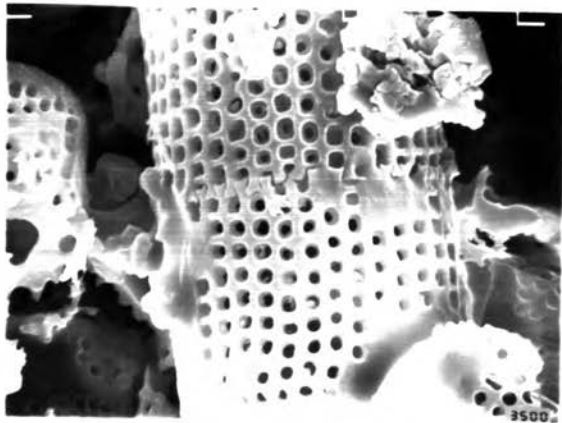
Conditions	Percentages of Content				
	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	MgO	CaO
I. 4-time, 1000 cm ³ 20% HCl warmed for 3 hours	0.51	82.08	5.72	0.12	nil.
II. 3-time, 1000 cm ³ 20% HCl warmed for 3 hours	0.57	82.08	6.35	0.18	nil.
III. 2-time, 1000 cm ³ 20% HCl warmed for 3 hours	0.63	80.35	7.20	0.22	nil.
IV. 1-time, 1000 cm ³ 20% HCl warmed for 3 hours	0.69	80.17	8.41	0.24	nil.
V. 1-time, 500 cm ³ 20% HCl warmed for 3 hours	0.72	81.32	7.73	0.23	nil.
VI. 1-time, 1000 cm ³ 10% HCl warmed for 3 hours	0.65	81.68	7.32	0.23	nil.
VII. 1-time, 500 cm ³ 10% HCl warmed for 3 hours	0.90	78.07	8.71	0.25	nil.
VIII. 1-time, 1000 cm ³ 10% HCl warmed for 2 hours	0.78	80.87	7.79	0.23	nil.

4.4 Preparation of the Solid Support

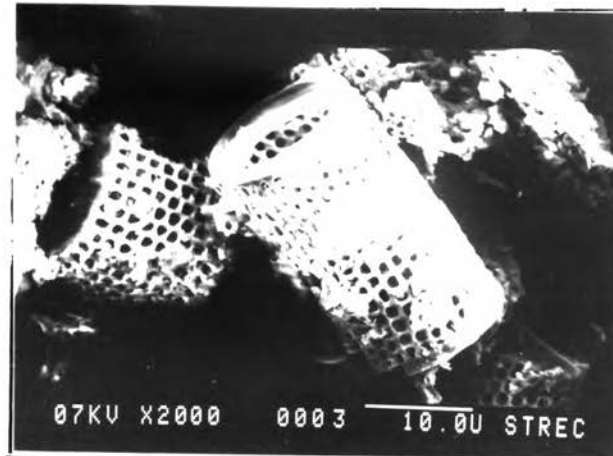
4.4.1 Flux Calcination

It was well known that the flux-calcined diatomite was white in color of alkali iron silicate, its structure was hardened and fine particles were fused. This was a mean to check whether the condition used in flux calcination was suitable. The observation and microphotographs of all flux-calcined diatomite which were calcined at various temperatures and periods were performed carefully and their results are tabulated in Tables 4.6 to 4.13. The microphotographs of required and unrequired products are shown in Figure 4.1.

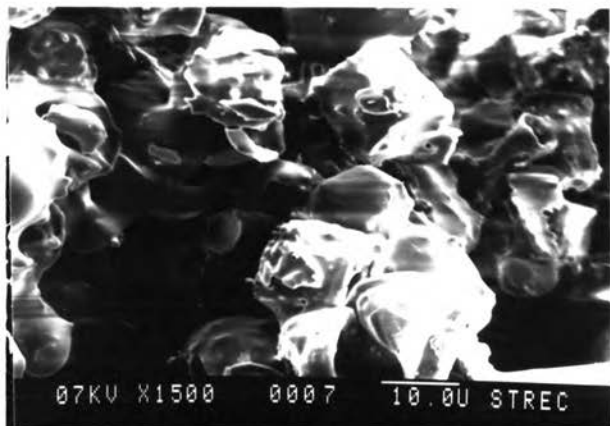
From Table 4.6, raw diatomite was used as a starting material and calcined under the condition of D.M. Ottenstein (23). The result indicated a severe failure because of the high temperature and long period of flux calcination as well as the presence of excess iron content in raw diatomite. Therefore, the clean diatomite from mechanical separation was used as the starting material and the temperature of calcination was reduced from 1200°C to 1100°C and 1000°C as shown in Table 4.7. The calcined products were fused more than that required and not white even at the temperature of 1000°C. Furthermore, the acid-treated diatomite were flux calcined at 1000°C for 1 to 6 hours. Their results are shown in Tables 4.7-4.13. From Table 4.7 and 4.8 it was seen that the optimum condition was calcining at 1000°C for 3 hours. Those results also indicated that the treatment of diatomite with 1-time, 1000 cm³ 10% HCl was sufficient, it was not necessary to use 20% HCl as in the literature (19). Other acid-treated diatomites were calcined under this optimum condition (8.55% flux, 1000°C, 3 hours) as shown in Table 4.9-4.12. It was successful when the diatomite was treated with 1-time, 500-1000 cm³ 10% HCl and warmed for 3 hours.



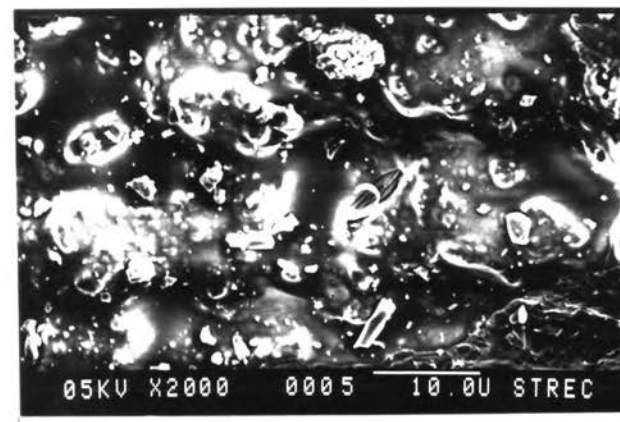
(a)



(b)



(c)



(d)

Figure 4.1 Microphotographs of required flux-calcined products 4, 5, 6, 10, 11 and 16 which were shown in (a) and those of unrequired products 1, 2, 3, 7, 8, 9, 12, 13, 14, 15, 17 and 18 which were shown in (b), (c) and (d)

Table 4.6 Surface study of the flux-calcined diatomite at various temperatures and periods of calcination using raw diatomite and the clean diatomite from mechanical separation.

Samples	Conditions of Calcination			Results
	% Flux	Temp. (°C)	Period (hrs.)	
1. Raw diatomite	8.55	1200	6	Observed: Very hard, chocolate glassy aggregate SEM: Totally fused
2. Clean diatomite	8.55	1100	3	Observed: Hard brown aggregate SEM: Totally fused
3. Clean diatomite	8.55	1000	4	Observed: Slightly hard, pink aggregate SEM: Totally fused and some fused into lumps of cylinders

Table 4.7 Surface study of the flux-calcined diatomite at 1000°C and various periods of calcination using the acid-treated diatomite, 1-time, 1000 cm³ 20% HCl, warmed for 3 hours.

Samples	Conditions of Calcination			Results
	% Flux	Temp. (°C)	Period (hrs.)	
4. 1-time 1000 cm ³ 20% HCl warmed for 3 hours	8.55	1000	3	Observed: Slightly hard, white aggregate SEM: Partially fused
5. 1-time 1000 cm ³ 20% HCl warmed for 3 hours.	8.55	1000	4	Observed: Slightly hard, white aggregate SEM: Partially fused
6. 1-time 1000 cm ³ 20% HCl warmed for 3 hours	8.55	1000	5	Observed: Slightly hard, white aggregate SEM: Partially fused
7. 1-time 1000 cm ³ 20% HCl	8.55	1000	6	Observed: Slightly hard, white aggregate SEM: Fused into lumps of cylinders and partially fused

Table 4.8 Surface study of the flux-calcined diatomite at 1000°C and various periods of calcination using the acid-treated diatomite, 1-time, 1000 cm³ 10% HCl, warmed for 3 hours.

Samples	Conditions of Calcination			Results
	% Flux	Temp. (°C)	Period (hrs.)	
8. 1-time 1000 cm ³ 10% HCl warmed for 3 hours	8.55	1000	1	Observed: Loose, white aggregate SEM: Non-fused
9. 1-time 1000 cm ³ 10% HCl warmed for 3 hours	8.55	1000	2	Observed: Loose, white aggregate SEM: Non-fused
10. 1-time 1000 cm ³ 10% HCl warmed for 3 hours	8.55	1000	3	Observed: Slightly hard, white aggregate SEM: Partially fused
11. 1-time 1000 cm ³ 10% HCl warmed for 3 hours	8.55	1000	4	Observed: Slightly hard, white aggregate SEM: Partially fused

Table 4.9 Surface study of the flux-calcined diatomite at various temperatures of calcination for 3 hours using the acid-treated diatomite, 4-time, 1000 cm³ 20% HCl, warmed for 3 hours.

Samples	Conditions of Calcination			Results
	% Flux	Temp. (°C)	Period (hrs.)	
12. 4-time 1000 cm ³ 20% HCl warmed for 3 hours	8.55	1000	3	Observed: Loose, white aggregate SEM: Non-fused
13. 4-time 1000 cm ³ 20% HCl warmed for 3 hours	8.55	1100	3	Observed: Very hard, white aggregate SEM: Totally fused

Table 4.10 Surface study of the flux-calcined diatomite at 1000°C for 3 hours using the acid-treated diatomite, 1-time, 10% HCl with various volumes of acid and periods of extraction.

Samples	Conditions of Calcination			Results
	% Flux	Temp. (°C)	Period (hrs.)	
10. 1-time 1000 cm ³ 10% HCl warmed for 3 hours	8.55	1000	3	Observed: Slightly hard, white aggregate SEM: Partially fused
14. 1-time 1000 cm ³ 10% HCl warmed for 2 hours	8.55	1000	3	Observed: Slightly hard, white aggregate SEM: Partially fused and some totally fused
15. 1-time 500 cm ³ 10% HCl warmed for 3 hours	8.55	1000	3	Observed: Slightly hard, white aggregate SEM: Partially fused and some totally fused

Table 4.11 Surface study of the flux-calcined diatomite at 1000°C for 3 hours using the acid-treated diatomite, 1-time, 500-1000 cm³ 20% HCl, warmed for 3 hours

Samples	Conditions of Calcination			Results
	% Flux	Temp. (°C)	Period (hrs.)	
4. 1-time 1000 cm ³ 20% HCl warmed for 3 hours	8.55	1000	3	Observed: Slightly hard, white aggregate SEM: Partially fused
16. 1-time 500 cm ³ 20% HCl warmed for 3 hours	8.55	1000	3	Observed: Slightly hard, white aggregate SEM: Partially fused

Table 4.12 Surface study of the flux-calcined diatomite at 1000°C for 3 hours using the acid-treated diatomite, 1-time, 1000 cm³ concentrated HCl and let to stand at the ambient temperature overnight.

Samples	Conditions of Calcination			Results
	% Flux	Temp. (°C)	Period (hrs.)	
17. 1-time 1000 cm ³ conc. HCl T _{room} , overnight	8.55	1000	3	Observed: Slightly hard, brown aggregate SEM: Fused into lumps of cylinders and some totally fused

However, the treatment of diatomite with only 500 cm³ HCl did not provide the diatomite slurried homogeneously, i.e., HCl could not react to all particles of diatomite. Therefore, the optimum condition for acid treatment was 1-time, 1000 cm³ 10% HCl and warming at 90^o-95^oC for 3 hours. From Table 4.13, the use of 5.00% Na₂CO₃ for flux calcination was not sufficient since at high temperature Na₂CO₃ was converted to Na₂O and the latter acted as a flux. Thus using 5.0% flux in most of literature means that flux is in the form of Na₂O which is equivalent to 8.55% Na₂CO₃. From the above it can be concluded that the optimum conditions for acid treatment and flux calcination of Lampang diatomite were 1-time, 1000cm³ 10% HCl warming at 90^o-95^oC for 3 hours and 8.55% Na₂CO₃ at 1000^oC for 3 hours, respectively.

4.4.2 Deactivation of the Flux-Calcined Support

After the flux-calcined support was washed with concentrated HCl and then 2.0% KOH, it was silanized as mentioned in section 3.5.3.4. The silanized support was called as "the prepared support" in this study.

4.5 Surface Structure of the Solid Support

The surface structure of the prepared support was studied and compared to that of Gas Chrom Q. Their microphotographs as shown in Figure 4.2 illustrated that the pore size of the prepared support was wider than that of Gas Chrom Q, and most diatom remains in the prepared support were partially fused but those of Gas Chrom Q were fused at random, i.e., all patterns of fusion such as partial fusion, fusion into lumps of cylinders and complete fusion were found. Since the prepared support was prepared under acid treatment for removal of iron, the very fine particles obtained after this treatment might not be mixed homogeneously with the flux.

Table 4.13 Surface study of the flux-calcined diatomite with 5.00% flux at 1000°C for 3 hours using the acid-treated diatomite, 4-time, 1000 cm³ 20% HCl, warmed for 3 hours.

Samples	Conditions of Calcination			Results
	% Flux	Temp. (°C)	Period (hrs.)	
18. 4-time 1000 cm ³ 20% HCl warmed for 3 hours	8.55	1000	3	Observed: Slightly hard, creamy aggregate SEM: Partially fused

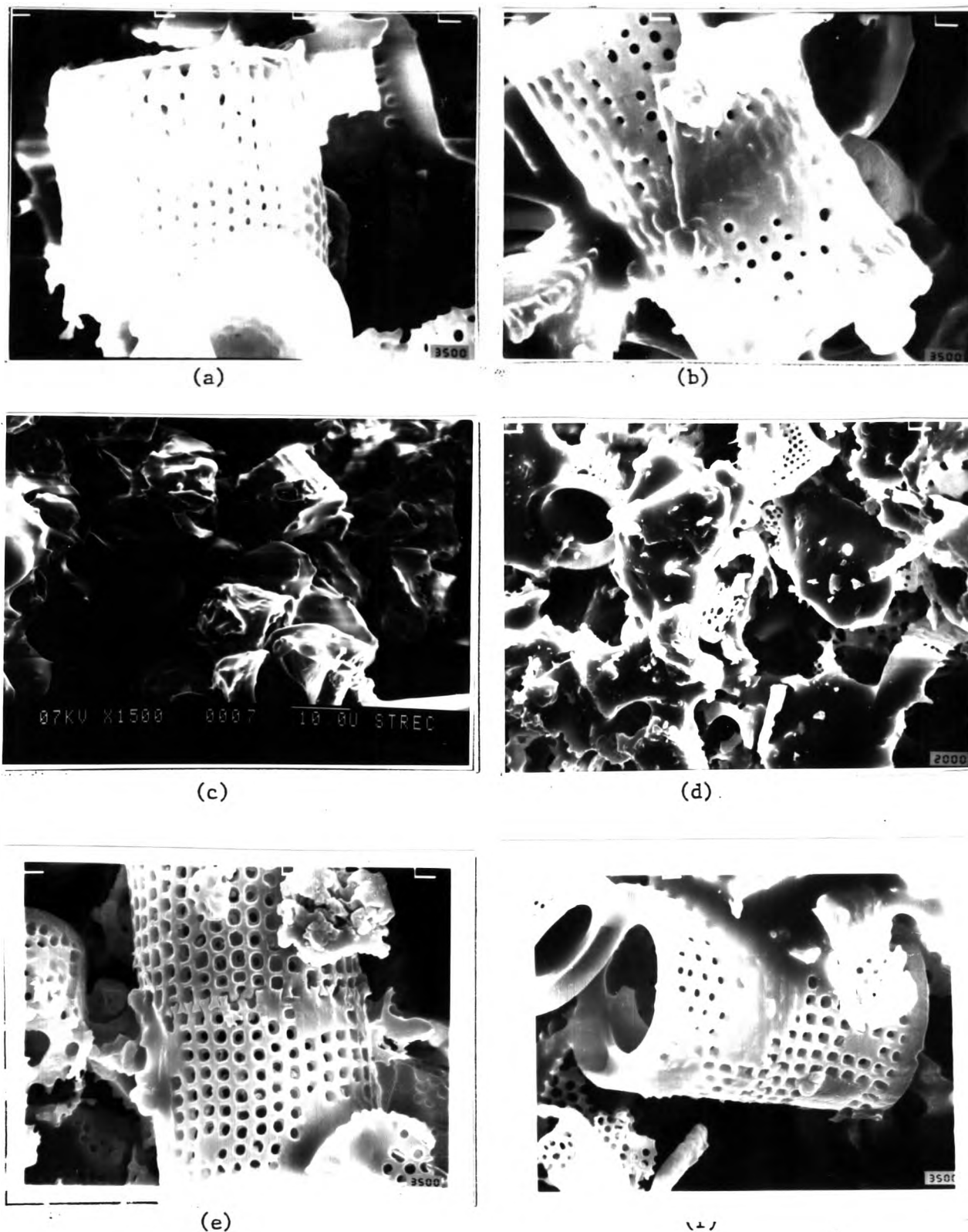


Figure 4.2 Microphotographs of Gas Chrom Q (a, b, c and d) and the prepared support (e and f) a, b, e and f were taken at x3500, c at x1500 and d at x2000

4.6 Chemical Analysis of the Supports

The results of chemical analysis of the prepared support and Gas Chrom Q are given in Table 4.14. The silica content of the prepared support was 6.82% lower than that of Gas Chrom Q and the alumina content of the prepared support was 0.27% higher than that of Gas Chrom Q. As usual, the less the silica content was, the more the alumina content was. Other impurities in the prepared support was clearly lower than those in Gas Chrom Q. However, when these results compared to those of raw diatomite, the purity of diatomite was improved (9.69% SiO₂ content was gained as well as 65.60% Al₂O₃ and 91.61% Fe₂O₃ were removed from the raw diatomite).

4.7 Physical Properties of the Supports

The physical properties such as free fall density, packed column density, hardness, specific gravity and porosity of Gas Chrom Q and the prepared support were studied and compared. The results as shown in Table 4.15 stated that their physical properties were not much different, e.g., the prepared support had 0.02% less free fall density, 0.02% less packed column density, 0.79% less hardness, 0.04% less specific gravity and 1.84% (wet method) and 0.95% (dry method) more porosity than Gas Chrom Q did. Therefore, it was very possible to use the prepared support as a solid support for gas chromatography.

4.8 Chromatographic Behavior of the Supports

4.8.1 Inertness of the Supports

As prescribed in the chapter 3, such compounds having the most equivalent boiling points but various polarity were heptane (98°C), 2-pentanone (102°C) and 2-butanol (99°C); 1.0 nm³ of each compound was injected onto the columns of the non-coated supports. The chromatograms

Table 4.14 Chemical analysis of Gas Chrom Q and the prepared support.

Composition	Percentages of Content	
	Gas Chrom Q	The Prepared Support
SiO ₂	84.80	77.98
Al ₂ O ₃	3.80	4.07
Fe ₂ O ₃	1.30	0.76
MgO	0.38	0.24
CaO	0.49	nil.
loss on ignition	0.20	0.22

Table 4.15 Physical properties of Gas Chrom Q and the prepared support.

Physical Properties	Gas Chrom Q	The Prepared Support
Free fall density (g/cm ³)	0.26	0.24
Packed column density (g/cm ³)	0.28	0.26
Hardness (percentage of particles passed through the 100-mesh sieve after packed in the column)	93.16%	92.37%
Specific gravity	1.78	1.74
Porosity (wet method)	84.97%	86.80%
Porosity (dry method)	84.39%	85.34%

are shown in Figure 4.3 (a) and 4.3 (b) and their retention times were recorded and listed in Table 4.16. For the column of Gas Chrom Q, the three compounds were almost eluted at the same retention time (0.01 minute difference). This indicated that Gas Chrom Q had no adsorptive effect. For the column of the prepared support, 2-pentanone and 2-butanol were eluted 0.02 minute before heptane whose retention time was very close to that obtained from the column of Gas Chrom Q. This might explain that the prepared support had more adsorptive effect than Gas Chrom Q did. Since the prepared support had more porosity than Gas Chrom Q did (see Table 4.15), the column of the bared prepared support provided the shorter retention times of the compounds than the column of Gas Chrom Q did. The more the porosity was, the less the hindrance was, i.e., the faster the molecule moved through the support. However, these differences of retention times were too small to explain any mechanism involved the chromatographic behaviour.

4.8.2 Tailing Factor

Tailing factors were determined on the columns of the supports coated with non-polar liquid phase, 5% OV-101. This is a mean to check inertness of the supports. The more the value of tailing factor is, the more inertness of the support is (1). Each of the compounds having different polarity such as dodecane (non-polar), ethyl ethanoate (intermediately polar) and methanol (polar) was injected onto the columns. Their chromatograms are shown in Figure 4.4 (a), 4.4 (b) and 4.4 (c), respectively and their tailing factors are tabulated in Table 4.17. Both columns, Gas Chrom Q and the prepared support, provided the degrees of tailing in the same manner: the degree of tailing increased as the polarity of the compound decreased. From the column of Gas Chrom Q, tailing factor of dodecane was 100% which indicated that the dodecane

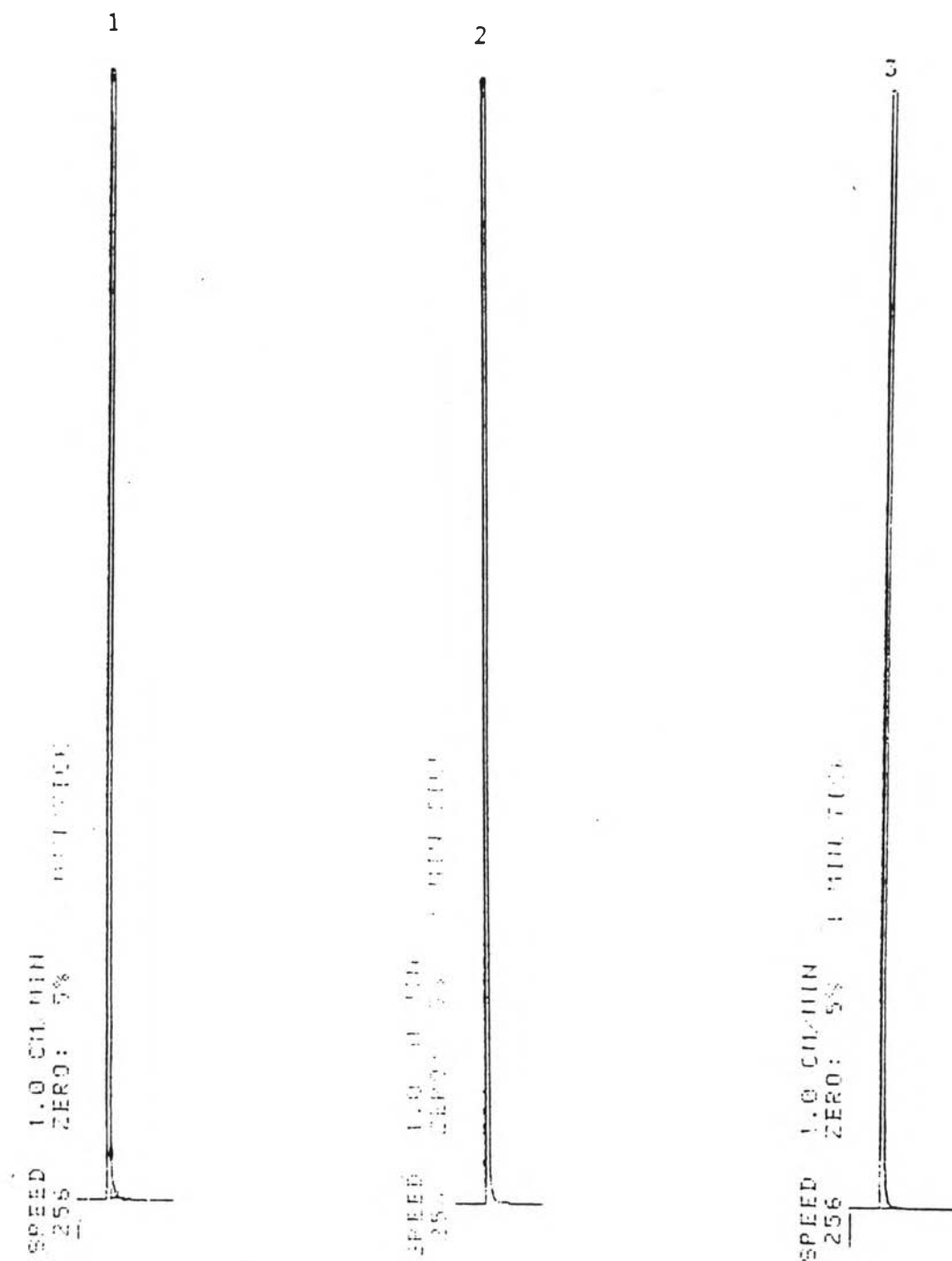


Figure 4.3 (a) Chromatograms of heptane (1), 2-pentanone (2) and 2-butanol (3) from the column of non-coated Gas Chrom Q. Conditions: column, 80°C; injector and FID, 130°C, N₂ carrier gas, 15 cm³/min; sample size, 1 nm³; detector range 8 x 10⁻⁹ AFS; chart speed, 1.0 cm/min.

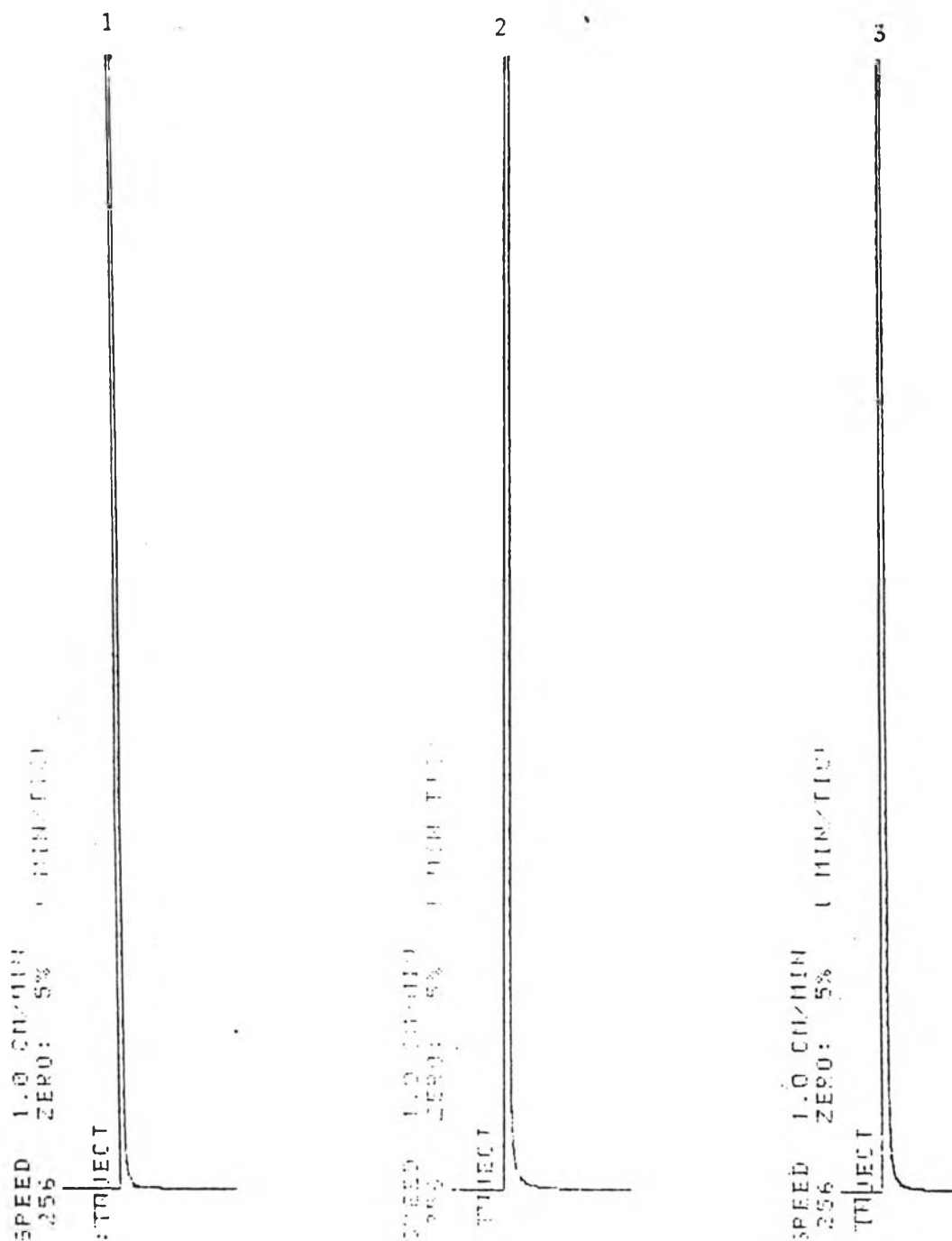


Figure 4.3 (b) Chromatograms of heptane (1), 2- pentanone (2) and 2- butanol (3) from the column of the non-coated prepared support at the operating condition as those in Figure 4.3 (a).

Table 4.16 Retention times of the compounds which had equivalent boiling points but different polarity on the columns of the non-coated supports.

Conditions: Column temperature, 80°C; injector and FID, 130°C, N₂ carrier gas, 15 cm³/min; sample size, 1 nm³

Compound	Boiling point	Retention time (min)	
		Gas Chrom Q	The prepared support
heptane	98°C	0.47	0.44
2-pentanone	102°C	0.48	0.44
2-butanol	99°C	0.48	0.46

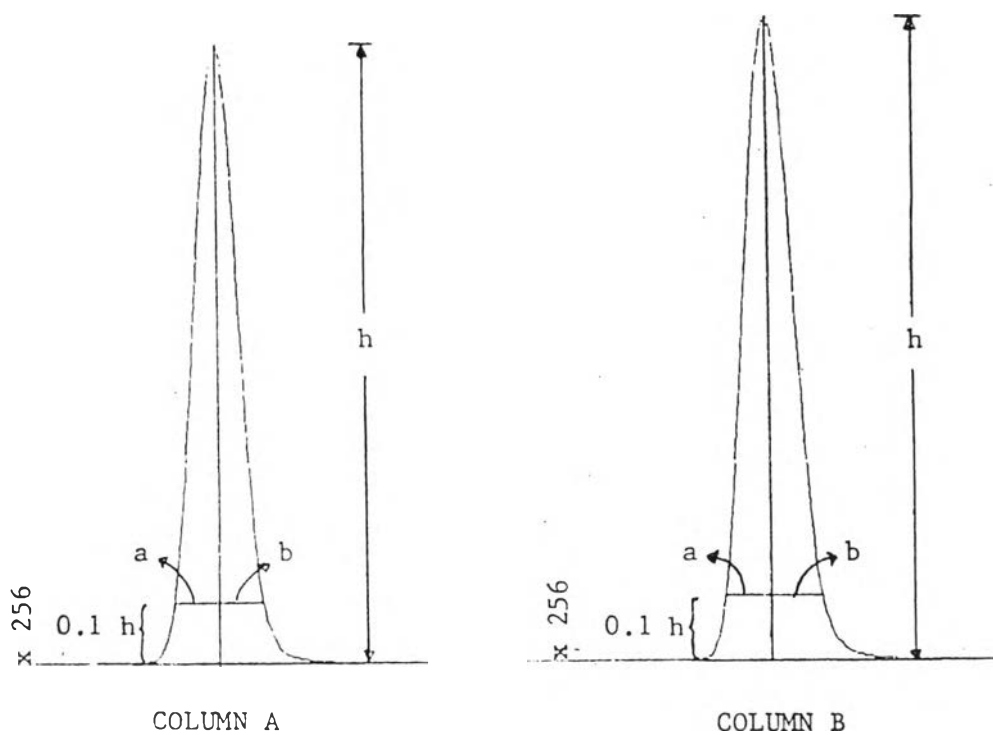


Figure 4.4 (a) Tailing of dodecane peaks. Columns: Column A, 5% OV-101 coated on Gas Chrom Q 80/100 mesh, 1.99 m x 2 mm I.D. and Column B, 5% OV-101 coated on the prepared support 80/100 mesh, 1.98 m x 2 mm I.D. Conditions: Columns, 180°C; injector, 200°C; FID, 230°C; N₂ carrier gas, 15 cm³/min; Sample size, 0.1 nm³; detector range, 8 x 10⁻⁹ AFS; chart speed, 10.0 cm/min. h = peak height and a, b = width of a half peak at 0.1 h.

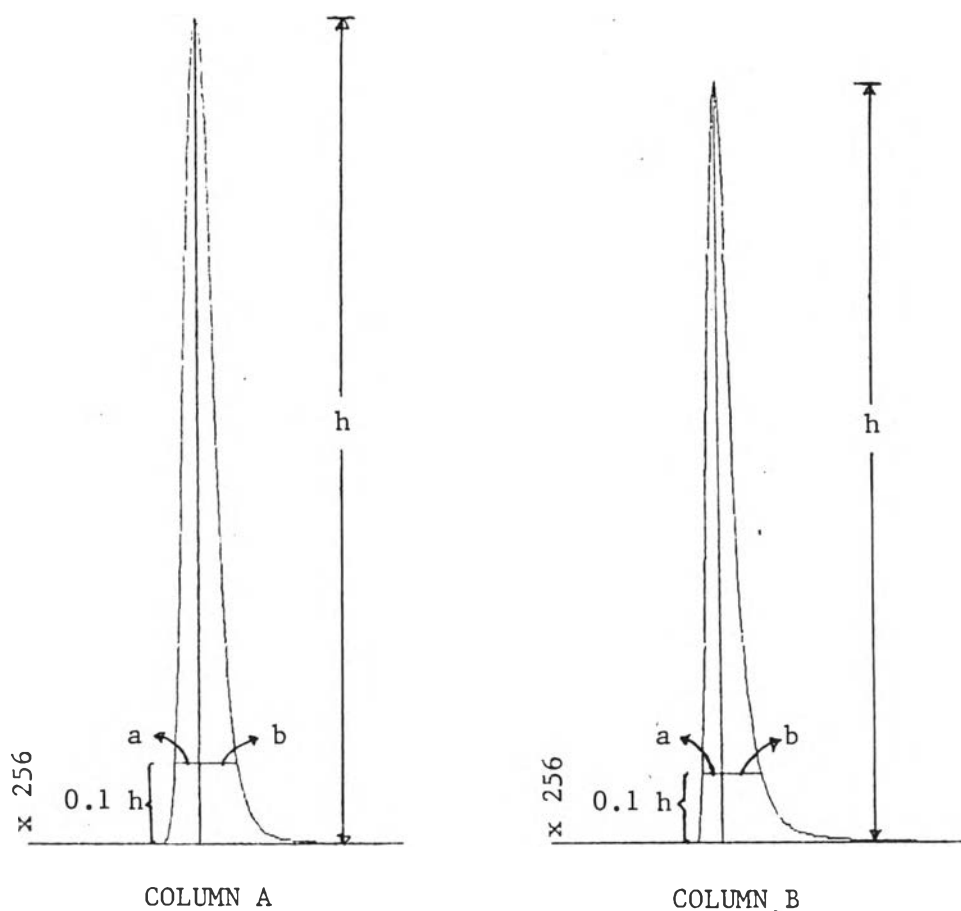


Figure 4.4 (b) Tailing of ethyl ethanoate peaks. Columns are the same as in figure 4.6 (b) Conditions: Columns, 80°C ; injector and FID, 150°C ; N_2 carrier gas, $20\text{ cm}^3/\text{min}$; sample size, 0.1 nm^3 ; detector range 8×10^{-9} AFS; chart speed $10.0\text{ cm}/\text{min}$. h = peak height and a , b = width of a half peak at $0.1 h$.

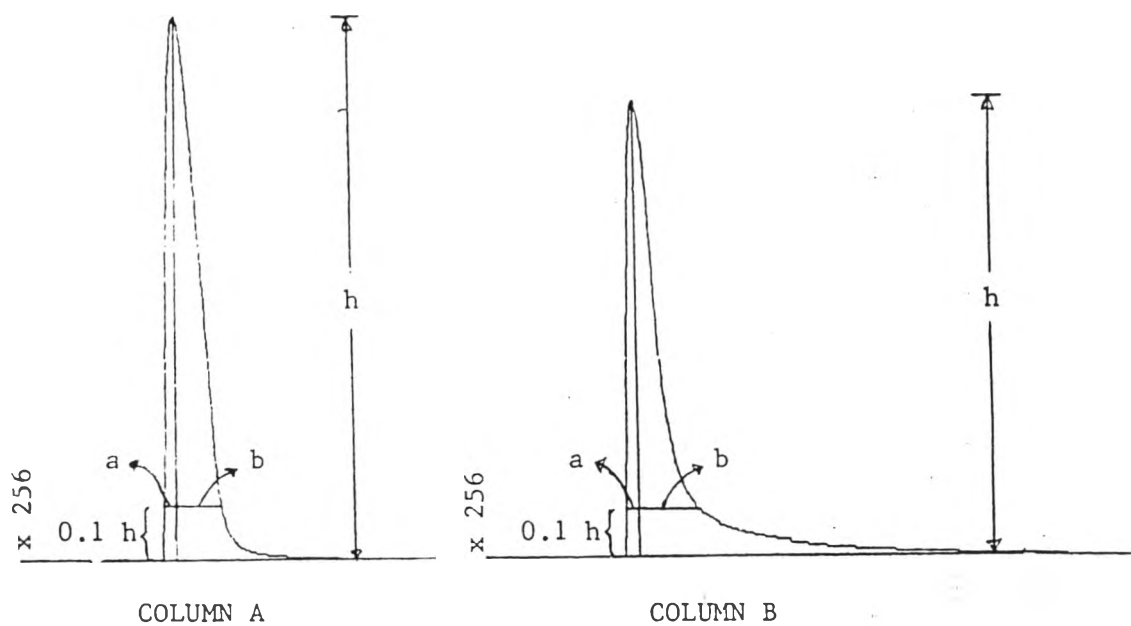


Figure 4.4 (c) Tailing of methanol peaks. Columns: Column A, 5% OV-101 coated on Gas Chrom Q 80/100 mesh, 1.99 m x 2 mm I.D. and column B, 5% OV-101 coated on the prepared support 80/100 mesh, 1.98 m x 2 mm I.D. Conditions: columns, 89°C; injector and FID, 150°C; N₂ carrier gas, 20 cm³/min; sample size, 0.1 nm³; detector range, 8 x 10⁻⁹ AFS; chart speed, 10.0 cm/min. h = peak height and a, b = width of a half peak at 0.1 h.

Table 4.17 Tailing factors of the compounds having different polarity on the columns of 5% OV 101.

Compounds	Tailing factor	
	Gas Chrom Q	The prepared support
Dodecane	100%	87%
Ethyl ehtanoate	64%	50%
Methanol	25%	19%

peak was symmetrical, i.e., dodecane was not adsorbed by Gas Chrom Q. The tailing factor of 64% for ethyl ethanoate and 25% for methanol indicated that the intermediately polar and polar compounds were adsorbed by Gas Chrom Q. Tailing factor of each compound on the column of the prepared support was less than those on the column of Gas Chrom Q, this expressed that the prepared support was less inert than Gas Chrom Q. It was notified that tailing of polar-compound peaks on non-polar column occurred even using Gas Chrom Q as the solid support.

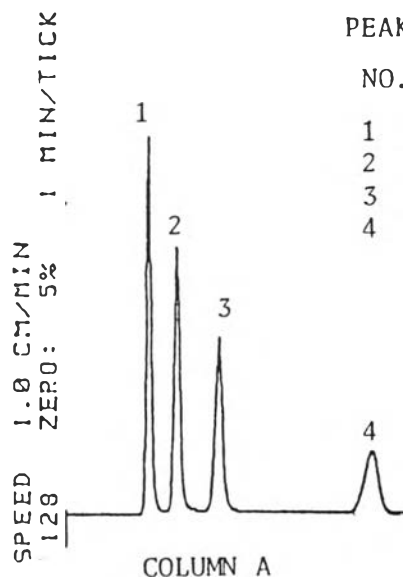
Varying the sample size for both columns was attempted and their results are shown in Table 4.18. The column of Gas Chrom Q provided a dependence of the sample size on the retention time of methanol. This indicated that sample molecules were able to be adsorbed on the column of 5% OV-101 coated on Gas Chrom Q. For the column of the prepared support, the retention time of methanol was independent of the sample size. This was because the prepared support might have more surface area than Gas Chrom Q had and using the 5% liquid phase could not cover all surface of the prepared support, i.e., some molecules passed through the support and other molecules passed over its surface. The counteraction of the porosity and the adsorption caused no difference of the retention times of methanol on various amounts. Comparing the results from the two columns, the column of the prepared support provided longer retention time than the column of Gas Chrom Q did. This meant that sample molecules were more adsorbed on the column of the prepared support than on the column of Gas Chrom Q. Peak tailing appeared because surface of the support was not all covered, so there was some interaction between sample molecules and the surface of the support which still had some active sites.

Table 4.18 Relationship between sample size and retention time of methanol under the same condition as in Figure 4.4 (c).

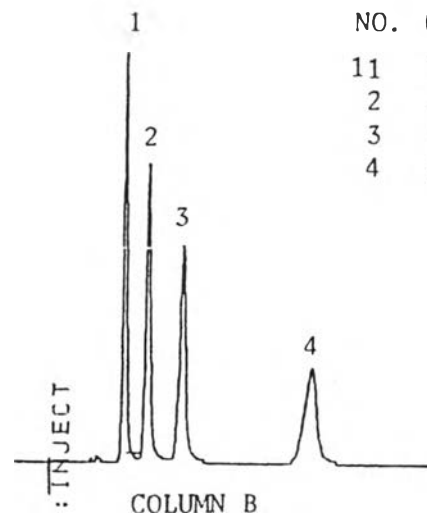
Sample size (nm ³)	Retention time of peaks (min)	
	Gas Chrom Q	The prepared support
0.1	0.32	0.37
0.5	0.33	0.37
1.0	0.34	0.37

4.8.3 Column Efficiencies in the Separation of Various Compounds

Column efficiencies were described in terms of resolution and HETP (Height equivalent to theoretical plate). The mixture of dodecane, tridecane, tetradecane and hexadecane was used as the test sample for the separation of hydrocarbons. The mixture of ethyl ethanoate, ethyl propanoate, ethyl butanoate, ethyl pentanoate and ethyl hexanoate was used as the test sample for the separation of esters as well as the mixture of 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol was used as the test sample for the separation of alcohols. The separations of hydrocarbons and esters were performed on the column of 5% OV-101 and the separation of alcohols was performed on the column of 10% Carbowax 4000. The chromatograms for these separations are shown in Figure 4.5, 4.6 and 4.7, respectively and the retention times as well as the peak width at half height of the peaks were recorded automatically from the instrument. Figure 4.5 showed that the peaks of hydrocarbons were completely separated on the column of Gas Chrom Q and these peaks were symmetrical. For the column of the prepared support, a small tail of each peak appeared but the peaks were completely separated. In the separation of esters, both columns provided the peak-tailing and in the separation of alcohols the peak-tailing still appeared in the chromatograms. The peak-tailing in all cases was owing to the adsorption of sample molecules by the active sites remaining on the support surface. The resolutions and column efficiencies for the separation of these compounds were calculated and compared in Table 4.19. The resolution of hydrocarbons from the column of the prepared support was 0.10 more than that from the column of Gas Chrom Q, so was the resolution of ethyl esters, while the resolutions of alcohols from both columns were equal. Considering the height equivalent to theoretical plates (HETP) which were



PEAK NO.	t_R (MIN)	$W_{0.5}$ (SEC)	AREA %
1	1.11	3.70	31.76
2	1.48	4.75	28.24
3	1.02	6.15	23.87
4	4.02	11.20	16.14



PEAK NO.	t_R (MIN)	$W_{0.5}$ (SEC)	AREA %
11	1.00	3.00	32.53
2	1.31	3.85	27.84
3	1.78	5.05	23.62
4	3.48	9.60	16.00

Figure 4.5 Chromatograms for the separation of hydrocabons: dodecane (1), tridecane (2), tetradecane (3) and hexadecane (4), Column A, 5% OV-101 coated on Gas Chrom Q 80/100 mesh 1.99 m x 2 mm I.D. and Column B, 5% OV-101 coated on the prepared support 80/100 mesh, 1.98 cm x 2 mm I.D. Conditions: columns, 180°C; injector, 200°C; FID, 230°C; N₂ carrier gas, 15 cm³/min; sample size, 0.5 nm³; detector range, 8 x 10⁻⁹ AFS.

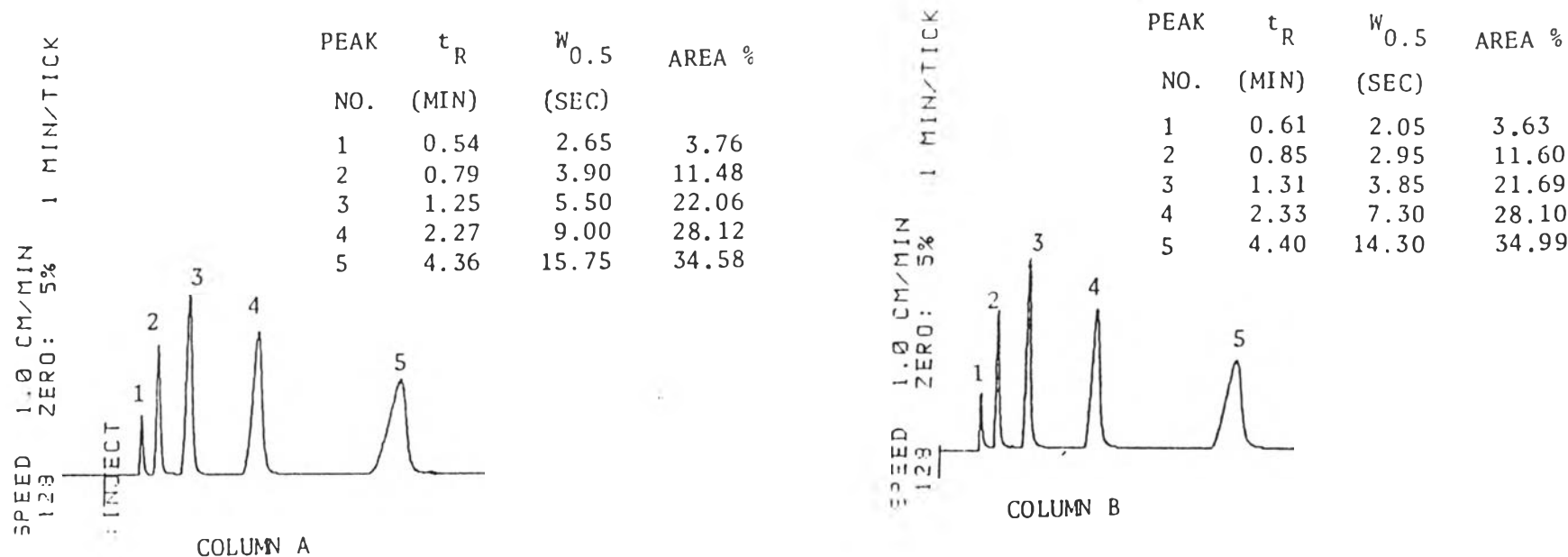


Figure 4.6 Chromatograms for the separation of esters: ethyl ethanoate (1), ethyl propanoate (2), ethyl butanoate (3), ethyl pentanoate (4) and ethyl hexanoate (5). Column A, 5% OV-101 coated on Gas Chrom Q 80/100 mesh, 1.99 m x 2 mm I.D. and Column B, 5% OV-101 coated on the prepared support 80/100 mesh 1.98 m x 2 mm I.D. Conditions: columns, 80°C; injector and FID 150°C; N₂ carrier gas, 20 cm³/min sample size, 0.4 nm³; detector range, 8 x 10⁻⁹ AFS.

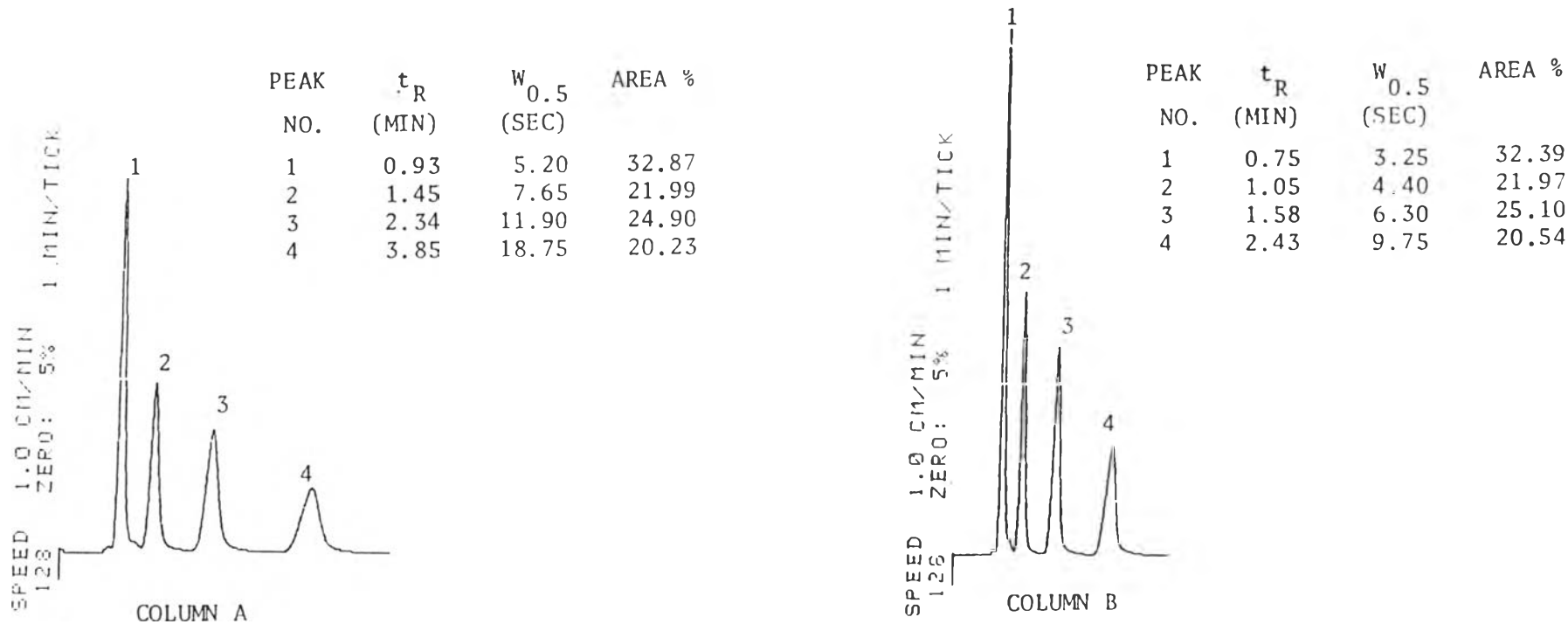


Figure 4.7 Chromatograms for the separation of alcohols: 1-butanol (1), 1-pentanol (2), 1-hexanol (3) and 1-heptanol (4). Column A, 10% Carbowax 4000 coated on Gas Chrom Q 80/100 mesh, 1.97 m x 2 mm E.D. and Column B, 10% Carbowax 4000 coated on the prepared support 80/100 mesh, 1.99 m x 2 mm I.D. Conditions: Columns, 100°C; injector and FID, 130°C; N₂ carrier gas, 20 cm³/min; sample size, 0.4 nm³; detector range, 8 x 10⁻⁹ AFS.

Table 4.19 Comparisons of resolutions of Peak No. 1 and Peak No. 2 and column efficiencies for the separations of hydrocarbons, ethyl esters and alcohols between Column A (Gas Chrom Q) and Column B (the prepared support)

	Column A	Column B
1) Separation of Hydrocarbons		
Resolution	3.10	3.20
Numbers of plates for Peak No. 2	1939	2313
HETP	0.10	0.09
2) Separation of Ethyl esters		
Resolution	2.70	2.80
Numbers of plates for Peak No. 2	819	1658
HETP	0.24	0.12
3) Separation of Alcohols		
Resolution	2.87	2.87
Numbers of plates for Peak No. 2	717	1137
HETP	0.27	0.18

also listed in Table 4.19, the HETP for the separation of hydrocarbons from both columns were about the same. This was because hydrocarbons were non-polar compounds which could not form hydrogen bond to the support surface. Thus the column efficiencies for both columns were not different. For the separation of ethyl esters which were more polar than hydrocarbons, the HETP of the column of the prepared support was 0.12 less than that of the column of Gas Chrom Q. This meant that the prepared support provided better column efficiency for intermediately polar compounds than Gas Chrom Q did. For the separation of polar compounds, alcohols, the HETP of the prepared support column was 0.09 less than that of the Gas Chrom Q column. This indicated that the prepared support provided better column efficiency for polar compounds than Gas Chrom Q did.

In the case of separation of esters on the column of 5% OV-101 which was non-polar phase, the retention times of the peaks from the prepared support column were longer than those from the Gas Chrom Q column. This was because sample molecules were more adsorbed by the prepared support than by Gas Chrom Q. For the column of 10% Carbowax 4000, the retention time on the prepared support column was shorter than that on the Gas Chrom Q column. This resulted from that the prepared support had more porosity and it tended to have larger surface area than Gas Chrom Q. Therefore, the liquid phase was spreaded out as a thinner film than Gas Chrom Q did, on the other hand, the thickness (df in van Deemter equation) of liquid phase on the surface of the prepared support was smaller than that of Gas Chrom Q. This resulted in that the resistance to mass transfer on the former was smaller than the latter, i.e., peaks were eluted from the column of 10% Carbowax 4000 coated on the prepared support at faster rate than those from the column of 10% Carbowax 4000 coated on Gas Chrom Q. Having smaller value of C term (resis-

tance to mass transfer) in van Deemter equation, the column of the prepared support provided the smaller HETP's than the column of Gas Chrom Q did, i.e., it had better efficiency than Gas Chrom Q.

Mentioning that the prepared support was likely to have larger surface area than Gas Chrom Q, the 5% loading of liquid phase might not be enough to coat the surface of the prepared support since it was evident that there was more tailing on the column of the prepared support than on the column of Gas Chrom Q.

4.8.4 Quantitative behavior

In Figure 4.5, 4.6 and 4.7 the percentages of peak areas were also reported. It was illustrated that the peak areas of each compound studied from both the prepared support column and the Gas Chrom Q column were insignificantly different. This meant that the prepared support column had the sensitivity for hydrocarbons, esters, and alcohols as the Gas Chrom Q column did.

The silanized solid support prepared from this research was named "Diatochrom L". From all results mentioned above, Diatochrom L can be used as a solid support for gas chromatography because its physical properties and chromatographic behaviors are close to those of Gas Chrom Q. The advantages of Diatochrom L comparing to Gas Chrom Q are that Diatochrom L costs about 900 baht/50 grams (this value comprises chemical and energy costs but does not comprise instrument and equipment cost) while the sale-price of Gas Chrom Q in Thailand is 4700 baht/50 grams, it is about five folds of Diatochrom L. In addition, Diatochrom L provides the better efficient column for the separation of polar and intermediately polar compounds as well as it provides faster analysis for the right column. The disadvantages of Diatochrom L are that it has more surface area than Gas Chrom Q, so the higher loading of liquid phase is required. For the separation of non-polar compounds, both supports are replaced to each other.