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### CHAPTER III

### EXPERIMENTS

#### 3.1 Chemicals and Reagents

Chemicals used were of Analar grade except where specified. Kerosine was decolorized prior to use by filtering through activated charcoal. Standard solutions of metal ions were from Carlo Erba. Gas Chromatographic standards were from the Polyscience Corporation.

Deionized water was used throughout the chemical analyses and distilled water was used in other studies of this research.

#### 3.2 Instruments

Surface structures of diatomite and its products were analyzed with a Jeol scanning electron microscope JFC-35CF by which the gold particles were coated on the surface of the sample with a Jeol fine-coat machine JFC-10. The concentrations of metal ions in these samples were determined with a Shimudsu inductively coupled plasma spectrometer ICPS-50 and a Shimudsu atomic absorption/flame spectrophotometer AA-650. The flux calcination of diatomite was carried out in a Gallenkamp muffle furnace. In addition, the chromatographic behavior of the solid supports was studied with a Varian gas chromatograph model 4100 equipped with a data system Vista 401 and a flame ionization detector (FID).

### 3.3 Procedure

#### 3.3.1 Scanning Electron Microscopic Technique for Study of the Surface Structure of Diatomite and Its Products

A sample holder was painted with the conductive silver glue as a thin layer and a dry crushed sample was strewed on the glue. After it was dried in the air, the sample holder was placed in the fine-coat machine. The coating chamber was evacuated and the voltage of 5 kilovolts was applied. The gold particles from the coil in the coating chamber was then dispersed to coat the sample surface on the holder as a thin film. The instrument was turned off and the air was automatically released into the chamber. The coated sample holder was inserted into the sample position of the scanning electron microscope. The chamber was evacuated and the high voltage of 20 kV was applied. The coarse and fine bottons of the electron microscope were adjusted until the clear-cut image on the oscilloscope was achieved at the required magnification.

#### 3.3.2 Chemical Analyses of Diatomite and Its Products

The method of ASTM C323 (35) was modified to analyze the composition of Lampang diatomite and its products. The content of silica ( $\text{SiO}_2$ ) was determined by gravimetric method. Aluminium (Al), iron (Fe), magnesium (Mg) and calcium (Ca) ions were determined by inductively coupled plasma spectrometric method as well as sodium (Na) and potassium (K) ions were determined by flame emission spectrophotometric method.

##### 3.3.2.1 Gravimetric Determination of $\text{SiO}_2$

A sample was dried in an oven at  $105^\circ\text{C}$  for 1-2 hours and kept cool in a desiccator. A 0.5 g of the moisture-free

sample was weighed accurately in a platinum crucible containing about 5 g of the carbonate mixture (5:7 w/w of  $\text{Na}_2\text{CO}_3:\text{K}_2\text{CO}_3$ ). The solid was mixed thoroughly and then covered with a little carbonate mixture. The crucible was heated gradually to full heat by a burner and maintained in the muffle furnace at  $1000^\circ\text{C}$  for about 1 hour. After the melt was cool the crucible was placed in a  $250\text{-cm}^3$  beaker containing  $30\text{ cm}^3$  concentrated HCl. The beaker was warmed on a hot-plate heated until the solution was complete. Then the crucible was rinsed with deionized water. The solution and precipitate obtained were evaporated to dryness and so on baked for 1 hour. A  $30\text{ cm}^3$  1:1 HCl and  $50\text{ cm}^3$  water were added. After the beaker was warmed for 10 minutes, the precipitate was allowed to settle and then transferred to a Whatman filter paper No. 42. A policeman was used to help all  $\text{SiO}_2$  removed from the beaker. The precipitate was washed several times with hot water until it was free from salts. The filtrate and the washed water were collected into a  $250.00\text{ cm}^3$  volumetric flask. The precipitate was dried and put into a platinum crucible. The crucible was gradually heated to burn off the filter paper and the residual  $\text{SiO}_2$  was ignited to constant weight in the furnace at  $1100^\circ\text{C}$ . Then the crucible was kept cool in a desiccator and weighed. The residue was moistened with 1:1  $\text{H}_2\text{SO}_4$  and  $10\text{ cm}^3$  concentrated HF were added. The solution was evaporated to dryness and the residue was ignited to constant weight in the furnace at  $1100^\circ\text{C}$ . The loss in weight from the original silica residue represented the silica content.

The residue obtained after the evaporation of HF was fused with 1 g of potassium pyrosulfate ( $\text{K}_2\text{S}_2\text{O}_7$ ) and then dissolved in a small amount of water. The solution obtained was

kept with the filtrate which was collected from the silica determination and then the volume was made up to 250.00 cm<sup>3</sup>. This solution was reserved for the determination of Al, Fe, Mg and Ca ions.

### 3.3.2.2 Inductively Coupled Plasma Spectrometric Determination of Al, Fe, Mg and Ca ions

Series of standard solutions of 10.00-120.00 mg/dm<sup>3</sup> Al, 2.00-10.00 mg/dm<sup>3</sup> Fe, 0-5.00 mg/dm<sup>3</sup> Mg and 0-5.00 mg/dm<sup>3</sup> Ca were prepared by diluting the appropriate amounts of the 1000.00 mg/dm<sup>3</sup> stock solution of each metal ion with deionized water in the 50.00 cm<sup>3</sup> volumetric flasks which contained 1.0 g of the carbonate mixture and 6.0 cm<sup>3</sup> 1:1 HCl.

The ICPS-50 instrument was set at the following condition:

#### RF Generator:

|                               |                          |
|-------------------------------|--------------------------|
| Frequency                     | 27.12 MHz                |
| Incident Power                | 1.4 kW                   |
| Reflected Power               | <5 W                     |
| Coolant gas flow rate Ar      | 14 dm <sup>3</sup> /min  |
| Plasma gas flow rate (Ar)     | 1.2 dm <sup>3</sup> /min |
| Aerosol carrier gas (Ar)      | 1.0 dm <sup>3</sup> /min |
| Observation height above coil | 15 mm                    |
| Sample solution uptake rate   | 2.4 cm <sup>3</sup> /min |
| Integration time              | 10 sec                   |

#### Wavelength:

|    |                        |
|----|------------------------|
| Al | 3090.50 <sup>o</sup> A |
| Fe | 2599.40 <sup>o</sup> A |
| Mg | 2795.55 <sup>o</sup> A |
| Ca | 3933.66 <sup>o</sup> A |

After the linearity of the ion concentrations against the detector responses was determined from a series of standard solutions. The high and low concentrations of the linearity of that metal ion was set at the instrument condition. Then the sample solution was drawn to the plasma of the instrument and the concentration of the sample solution was read.

### 3.3.2.3 Flame Emission Spectrophotometric Determination of Na and K ions

A 0.5 g moisture-free sample was weighed accurately in a platinum crucible. The sample was moistened with 1:1  $\text{H}_2\text{SO}_4$  and 10  $\text{cm}^3$  concentrated HF were added. This solution was evaporated to dryness. Then the residue was dissolved in 100  $\text{cm}^3$  1:50  $\text{HNO}_3$ . After the solution was warmed for 10 minutes, the precipitate was transferred on to a Whatman filter paper No. 42 and washed with deionized water until it was free from salts. The filtrate was collected into a 250.00  $\text{cm}^3$  volumetric flask and the volume was made up to the mark. The solution was reserved for the determination of Na and K ions.

Series of standard solutions of 0.10-0.50  $\text{mg}/\text{dm}^3$  Na ion and 0.50-2.50  $\text{mg}/\text{dm}^3$  K ion were prepared by diluting the appropriate amount of the 1000.00  $\text{mg}/\text{dm}^3$  stock solution of each metal ion with deionized water in the 50.00  $\text{cm}^3$  volumetric flasks which contained 20.0  $\text{cm}^3$  1:50  $\text{HNO}_3$ .

After the flame emission spectrophotometer was turned on, the compartments such as mode selector, fuel, oxidant, flame, wavelength selector (at 588.7 nm for Na and at 677.3 nm for K), slit width and sensitivity of the instrument were adjusted. Then the solutions of standards and samples were drawn to the

flame and the detector responses were recorded.

To obtain a calibration curve, the detector responses against the concentrations of the standard solutions were plotted and a linear line was drawn through most of points, using the least-square method. From the calibration curves the concentrations of Na and K ions in the samples were interpreted.

#### 3.3.2.4 Loss on Ignition

A 0.5 g dry sample was weighed accurately in a known weight platinum crucible. The crucible was ignited to constant weight in the furnace at 1100°C. The difference in weight of the sample between that before and that after ignition divided by the sample weight before ignition was the loss on ignition.

### 3.3.3 Beneficiation of Lampang Diatomite

#### 3.3.3.1 Mechanical Separation

This procedure was carried out to remove some soluble salts, clays and coarse minerals such as sand and iron oxide from the raw material. It was modified from the method of J. Visman and J.L. Picard (24). Since cyclone process was not suitable for a laboratorial scale, it caused the feed-loss, stirring, settling and decanting were used instead. The necessity of a dispersant was also studied. In addition, filtration and decantation were tried for the separation between diatomite and clays. Three methods for this separation were attempted, Method 1 with a dispersant and Methods 2 and 3 without any dispersant. In each method, a 200.0 g of raw diatomite having particle sizes ranged less than 1/4 inch was used.

Method 1 The weighed sample was washed with 1 dm<sup>3</sup> distilled water by a gently stirring for 5 minutes and the suspension was allowed to settle overnight. Then the supernatant liquid was decanted off. This washing step was repeated for other 2 times. The wet diatomite was transferred into a 10-dm<sup>3</sup> dispersion tank by 6 dm<sup>3</sup> distilled water and a 0.3750 g dispersant (1:2 w/w of Na<sub>2</sub>SiO<sub>3</sub>:Na<sub>2</sub>CO<sub>3</sub>) was added. This suspension was stirred for 30 minutes and allowed still for 1 minute to settle coarse minerals. Then the diatomite and clay which suspended in the supernatant liquid were decanted into another 10-dm<sup>3</sup> glass tank. The supernatant was divided into 2 equal portions. Portion 1 was filtered on to a Whatman filter paper No. 1 through a Buchner funnel equipped with a vacuum pump. Portion 2 was allowed to settle for minimum 5 hours then the clay in the supernatant liquid was decanted. The solid remained in portion 1 and portion 2 were then dried in the oven at 105<sup>o</sup>C and weighed. The clean diatomite was chemically analyzed by the method in section 3.3.2.

Method 2 This method was performed as Method 1 except no dispersant was used and only 1 dm<sup>3</sup> instead of 6 dm<sup>3</sup> distilled water was used in the process occurring in the dispersion tank.

Method 3 This method was performed as Method 1 except no dispersant was used and only decantation was done for the removal of clay from diatomite.

The flow diagrams of the beneficiation of diatomite were shown in Figure 3.1.

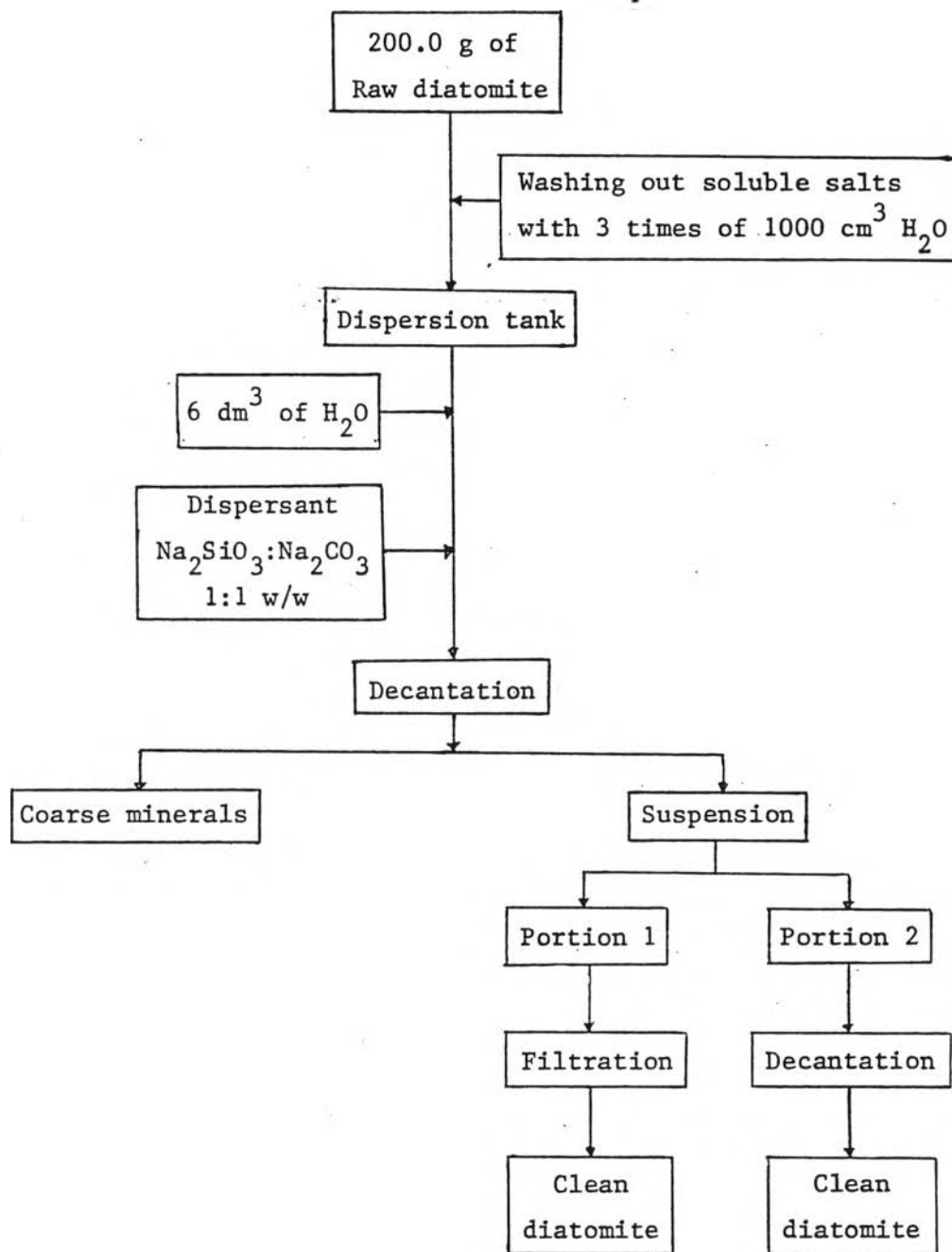


Figure 3.1 Flow diagrams of the beneficiation of diatomite Method 1.



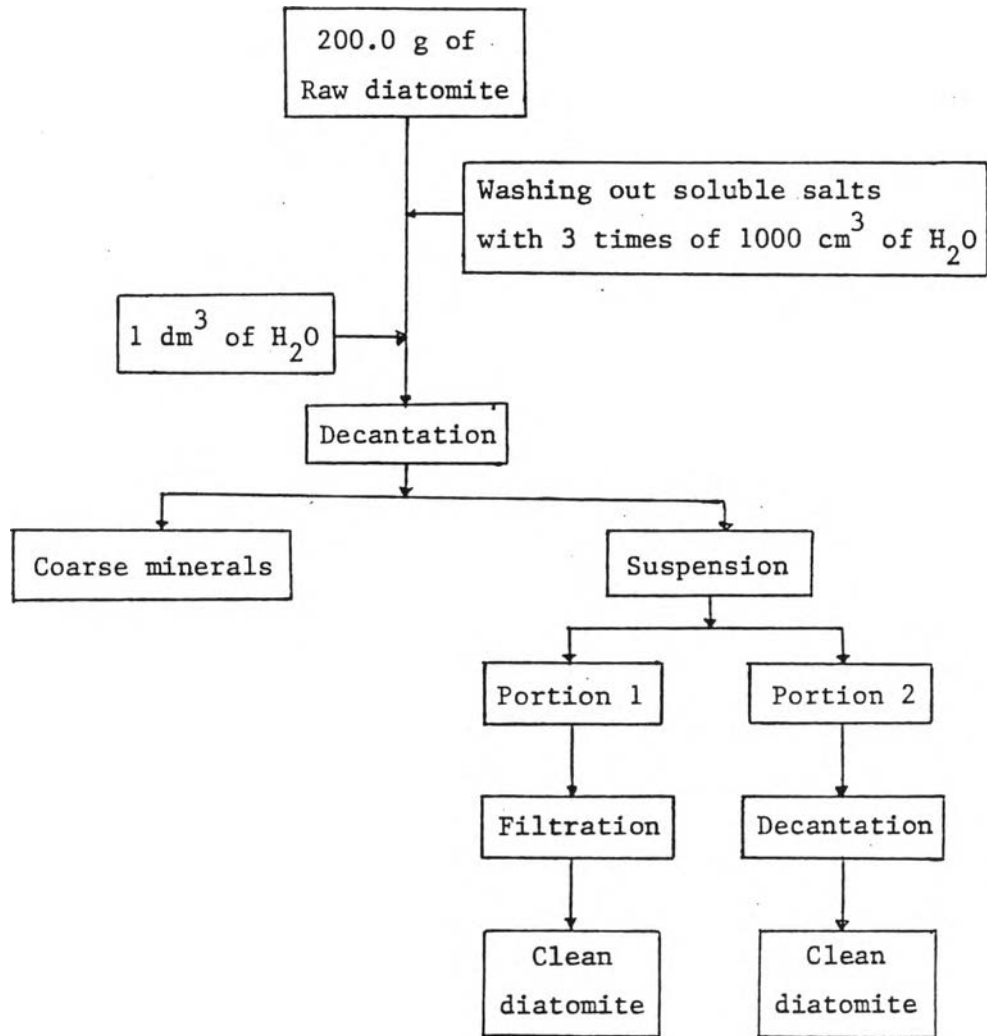


Figure 3.1 (continued) Method 2

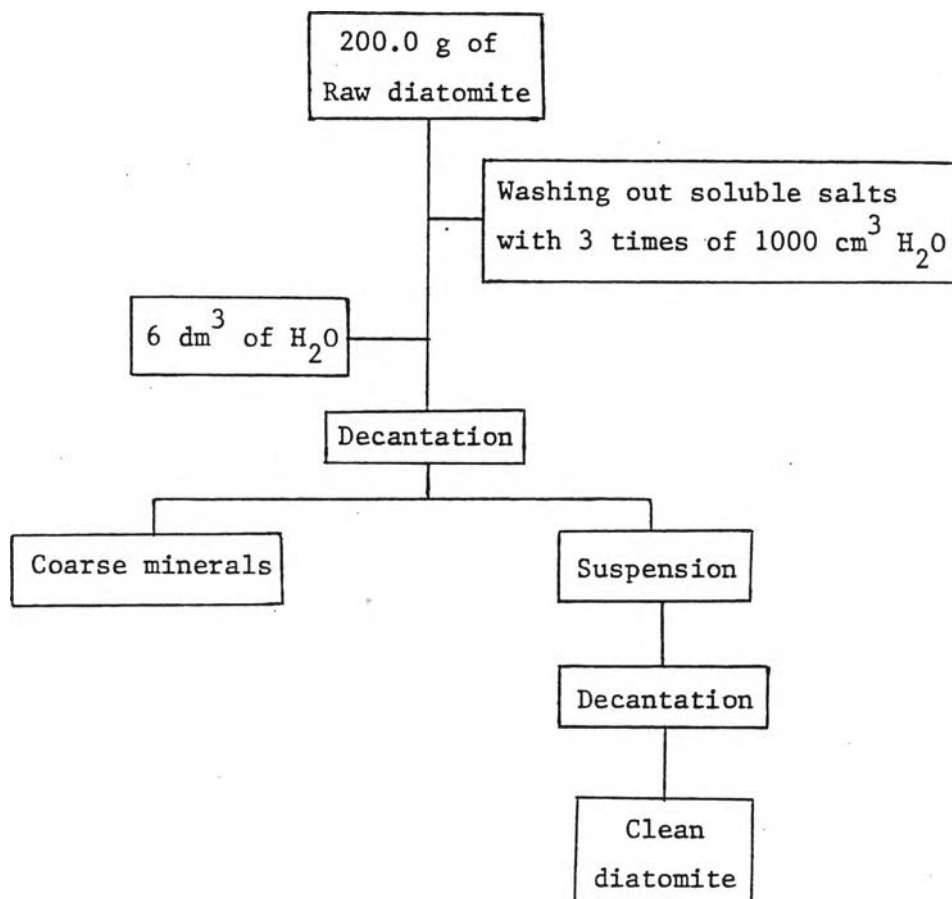


Figure 3.1 (continued) Method 3

### 3.3.3.2 Chemical Treatment

This procedure was carried out to remove the remaining iron by using the acid treatment. Many variations were performed such as the number of extraction (from one to four extractions), the concentration of HCl (10%, 20% v/v HCl and concentrated HCl), the volume of HCl (1000 cm<sup>3</sup> and 500 cm<sup>3</sup>) and time for extraction (2 to 3 hours for warming the mixture of diatomite at 90<sup>o</sup>-95<sup>o</sup>C and standing overnight). A 200.0 g diatomite from portion 2 of Method 2 in section 3.3.3.1, crushed into the particle-size range than of 1/4 inch, was used for each acid treatment. The product obtained from the extraction was washed to neutral and dried in an oven at 125<sup>o</sup>C. The final products were chemically analyzed by the method in section 3.3.2.

#### 3.3.3.2.1 Varying Number of Extraction

For each extraction, the sample was treated with 1000 cm<sup>3</sup> 20% (v/v) HCl and warmed at 90<sup>o</sup>-95<sup>o</sup>C for 3 hours. After each extraction the sample was washed with distilled water until neutral solution obtained. Four times of extraction were attempted.

#### 3.3.3.2.2 Varying Concentration of HCl

The concentrations of HCl used were 10%, 20% (v/v) and concentrated. One-time extraction was performed by using 1000 cm<sup>3</sup> HCl solution and warmed at 90<sup>o</sup>-95<sup>o</sup>C for 3 hours except for concentrated HCl which the treatment was performed at the ambient temperature overnight.

#### 3.3.3.2.3 Varying Volume of HCl

The volume of 10% HCl used were 500 cm<sup>3</sup>.  
One-time extraction was performed at 90<sup>o</sup>-95<sup>o</sup>C for 3 hours.

#### 3.3.3.2.4 Varying time of Extraction

The sample was one-time treated with  
1000 cm<sup>3</sup> 10% HCl and warmed at 90<sup>o</sup>-95<sup>o</sup>C for 2 or 3 hours.

### 3.3.4 Preparation of Solid Support

#### 3.3.4.1 Flux Calcination

The optimum conditions of flux calcination of diatomite (19-20, 23, 25) depended on the nature of diatomite from each deposit and on the required surface area of the solid support. To obtain the optimum condition for Lampang diatomite many trials were performed and the final products were physically checked first by using the scanning electron microscope. On account of lack of a fused silica tray, a common fire-resistance tray was used. For prevention of any fusion of the tray during calcination an asbestos sheet was placed in the tray before transferring the sample in the tray. Raw diatomite and all products from the beneficiation in section 3.3.3 were crushed into sample sizes of -10 mesh and a 100.0 g of sample was used for each flux calcination. The calcination of diatomite was performed by varying temperature (1000<sup>o</sup>C, 1100<sup>o</sup>C and 1200<sup>o</sup>C), period of calcination (1 to 6 hours) and amount of flux (5.00% and 8.55% Na<sub>2</sub>CO<sub>3</sub>). For each calcination, the sample was mixed with 40 cm<sup>3</sup> of the flux solution containing 8.55 g of Na<sub>2</sub>CO<sub>3</sub> except only one of calcination using 5.0 g of Na<sub>2</sub>CO<sub>3</sub>. Then the mixture was tumbled for 30 minutes to distribute the flux evenly on the crushed diatomite, the well-mixed sample was

transferred into the fire-resistance tray and inserted into a furnace which was preheated to the operating temperature. After required period of calcination the sample was removed from the furnace. Then each flux-calcined product was physically studied by using the scanning electron microscope.

#### 3.3.4.2 Acid and Base Washing

This method was performed as that of the preparation of Gas Chrom Q (29). The flux-calcined support which was white and partially fused was crushed into 60/80 mesh, 80/100 mesh and 100/120 mesh. Each 50.0 g of them was transferred into a 2-dm<sup>3</sup> beaker containing 500 cm<sup>3</sup> concentrated HCl. The slurry was gently swirled and allowed to stand in a cleaned hood for minimum 16 hours. The acid was decanted and the support was washed to neutral with distilled water. Then the support was washed again with 500 cm<sup>3</sup> 2.0% KOH solution in the same manner of HCl washing. Then it was washed with distilled water until the supernatant liquid was clear and neutral.

#### 3.3.4.3 Silanization

The method of silanization of Gas Chrom Q (27) was modified to deactivate the silanol groups on the surface of the solid support. Washing the support with tap water can cause impurities to be trapped or adsorbed on the support surface. Therefore, distilled water was performed in this study.

A 50.0 g of the acid-washed and base-washed support was poured slowly into a beaker containing 500 cm<sup>3</sup> concentrated HCl. The mixture was swirled and permitted to stand for 19-22 hours. The acid was decanted and the support was washed by slurring with distilled water and decanting; fines were effectively

removed by this method. The wet support was slurried again and poured into a Buchner funnel fitted into a suction flask. The support was then washed in the funnel until the filtrate was no longer acidic. After the bulk of the final filtrate came through the funnel, 250 cm<sup>3</sup> absolute methanol were added to the support and the methanol was filtered off. The vacuum line was then disconnected from the filter flask and another 250 cm<sup>3</sup> absolute methanol was poured on the support to slurry it. After 30 seconds, any floating particles were siphoned off with an aspirator hose equipped with eyedropper tip. Additional methanol was added as necessary to keep the level of methanol above the support for 10 minutes. The vacuum line was reconnected for removal of the methanol remained. The support was washed again with 250 cm<sup>3</sup> methanol and suction was continued for 10 minutes after the bulk of the methanol had come off. The support was dried in an oven at 105°C.

A solution of 5% v/v DMCS in toluene was prepared just prior to the treatment. The hot support was quickly poured into the solution and gently slurried for 10 minutes. The excess solution was decanted and the support was washed twice with 500 cm<sup>3</sup> of toluene by decantation to remove any fine particles remaining in the support. An additional 250 cm<sup>3</sup> toluene was poured on the support for making it slurried and the slurry was poured into the Buchner funnel. The vacuum line was connected to the suction flask. The support was then washed for four additional times in the funnel with 250 cm<sup>3</sup> of toluene. When toluene in the slurry was filtered off the support surface, 250 cm<sup>3</sup> methanol were gently poured on top. After the bulk of methanol had come through the funnel, the vacuum line was disconnected from the suction flask

and 250-300 cm<sup>3</sup> methanol were added quickly to the support. All floating materials were removed as mentioned on page 82. Methanol was added during this stage to keep the support covered with the solvent for at least 10 minutes. The vacuum line was reconnected to the suction flask and a final rinse was performed with 250 cm<sup>3</sup> methanol. After suction was continued for 15 minutes, the prepared support was transferred to a clean 250-cm<sup>3</sup> beaker and dried in an oven at 105°C.

### 3.3.5 Determination of Physical Properties of the Supports

#### 3.3.5.1 Free fall density (36)

An empty 25.0 cm<sup>3</sup> measuring cylinder was accurately weighed. Through a small filter funnel, a support was poured into the cylinder as tapping the funnel neck with a rubber tubing but not trembling the cylinder until the volume of support was accurately 10.0 cm<sup>3</sup>. The cylinder containing the support was weighed. The weight of the support divided by its volume, 10.0 cm<sup>3</sup>, was the value of free fall density.

#### 3.3.5.2 Packed column density and hardness

No instrument can be used to determine the hardness of the material occurring in the form of particles. Therefore, an indirect method was used herein.

A dry clean glass column was accurately weighed. An amount of the 80/100 mesh support was resieved with a 100-mesh sieve. The support remaining on the sieve was packed into the column equipped to a vacuum line by vibrating method. The exact length of the support packed in the column was measured. After the pieces of glass wool at both ends of the column were removed,

the packed column was weighed. The weight of the support packed in the column divided by the volume of packed portion was the value of packed column density.

The support was removed from the column into a clean beaker and resieved through the 100-mesh sieve. The support which passed through the sieve was collected and weighed. The hardness was achieved by

$$\text{Hardness} = \frac{W_1 - W_2}{W_1} \times 100 \quad 3.1$$

where  $W_1$  was the weight of the 80/100 mesh support packed in the column and  $W_2$  was the weight of the support passing through the sieve after it was removed from the column.

#### 3.3.6.3 Specific gravity and porosity

The silanized supports were hydrophobic, thus their specific gravities were determined by replacing kerosine (37) instead of water. Porosity of the support was determined by both the wet method (36) and the dry method (38).

An empty dry pycnometer was weighed accurately. The pycnometer was filled up with kerosine and weighed. The kerosine was then poured out and the wet pycnometer was weighed. After cleaning and drying the pycnometer, it was filled up with distilled water and weighed. The weight of kerosine divided the weight of water filled in the pycnometer was the specific gravity of kerosine.

A 0.2 g of a support was weighed accurately in the dry pycnometer. Kerosine was poured into the pycnometer about a half of the pycnometer. The pycnometer was connected to the



vacuum line, the pressure in the pycnometer was gradually reduced to vacuum. When no air-bubbles appeared, it took about 30 minutes, the pycnometer was disconnected from the vacuum line. After arising to the ambient temperature, it was filled up with kerosine, wiped with dry clean cloth and weighed. The weight of the support divided by the weight of kerosine replaced by the support and multiplied by the specific gravity of kerosine was the specific gravity of the support.

The nonsorbed kerosine was poured out and the wet support was weighed. The porosity (P) by the wet method was determined by the equation.

$$P = \frac{W-D}{(W-D) + W_k} \quad 3.2$$

where W = the weight of wet support

D = the weight of dry support

$W_k$  = the weight of kerosine replaced by the support. This was identical to the true volume, not the total volume, of the support.

The porosity (P) by the dry method was determined by using the data for packed column density and the equation

$$P = \frac{V-(W/S)}{V} \times 100 \quad 3.3$$

where V = the total volume of the packed portion of the support in the column

W = the weight of the support packed in the column

S = the specific gravity of the support

### 3.3.7 Determination of Chromatographic Behavior of the Supports

There were 3 pairs of packed columns. Each pair contained the packing materials which were treated in the same manners. The columns of each pair only differed in the type of the supports, e.g., column A was for Gas Chrom Q and column B was for the prepared support. One pair of the columns were packed with the bared or non-coated supports and used for the determination of inertness of the supports. Another pair of them were packed with 5% OV-101 coated on the supports and used for the determination of tailing factor of the various-polarity-sample peaks. The other pair of them were packed with 10% Carbowax 4000 coated on the supports and used for the separation of alcohol mixture. The particle size of 80/100 mesh of the supports and the glass columns having 2 m length and 2 mm inner diameter were used throughout these studies.

Each column was preconditioned overnight by connecting one end of the column to the injector of the gas chromatograph, and disconnecting the other end of the column to the detector. For the columns of non-coated supports,  $N_2$  carrier gas was passed through the columns at the flow rate of  $15 \text{ cm}^3/\text{min}$ , the injector and column oven were heated to  $150^\circ\text{C}$  and the instrument was maintained at this condition overnight. For the columns of 5% OV-101, the injector and column oven were heated to  $260^\circ\text{C}$  with no flow of carrier gas and the instrument was maintained at this condition overnight. Then  $N_2$  carrier gas was gradually adjusted to  $30 \text{ cm}^3/\text{min}$  and this was maintained for 2 hours. For the columns of 10% Carbowax 4000,  $N_2$  carrier gas was passed through the columns at the flow rate of  $30 \text{ cm}^3/\text{min}$ , the injector and column oven were heated to  $170^\circ\text{C}$  and the instrument was maintained at this condition overnight. After preconditioning the instrument was cool to the ambient temperature while the carrier gas was still passed through the column. The free end

of the column was connected to the detector and the instrument was set at the operating condition below.

### 3.3.7.1 Inertness of the support

The determination of inertness of the supports was based on that samples having different polarity but equivalent boiling points should have equivalent retention time on the column of the non-coated supports. Such compounds having the most equivalent boiling points (39) were 2-butanol (99°C), 2-pentanone (102°C) and 1-heptane (98°C) and they were used as the test samples for studying inertness of Gas Chrom Q and the prepared support. The gas chromatograph was set at the following condition:

|                             |                          |
|-----------------------------|--------------------------|
| Column limit                | 200°C                    |
| Column temperature          | 80°C                     |
| Injector temperature        | 130°C                    |
| Detector temperature        | 130°C                    |
| Detector range              | $8 \times 10^{-9}$ AFS   |
| Carrier gas: N <sub>2</sub> | 15 cm <sup>3</sup> /min  |
| Chart speed                 | 1.0 cm <sup>3</sup> /min |

This instrument was warmed until the gas flow rate was stable. A 1.00 nm<sup>3</sup> of each test sample was injected onto the columns and those of retention time were recorded.

### 3.3.7.2 Tailing factor

The determination of tailing factor of various-polarity compounds such are dodecane, ethyl ethanoate and methanol on the column of non-polar phase, 5% OV-101 was performed at the following conditions:

|                            |                          |
|----------------------------|--------------------------|
| Column limit               | 300°C                    |
| Column temperature for     |                          |
| dodecane                   | 180°C                    |
| ethyl ethanoate            | 80°C                     |
| methanol                   | 80°C                     |
| Injector temperature for   |                          |
| dodecane                   | 200°C                    |
| ethyl ethanoate            | 150°C                    |
| methanol                   | 150°C                    |
| Detector temperature for   |                          |
| dodecane                   | 230°C                    |
| ethyl ethanoate            | 200°C                    |
| methanol                   | 200°C                    |
| Detector range             | 8 x 10 <sup>-9</sup> AFS |
| Carrier gas:N <sub>2</sub> |                          |
| dodecane                   | 15 cm <sup>3</sup> /min  |
| ethyl ethanoate            | 20 cm <sup>3</sup> /min  |
| methanol                   | 20 cm <sup>3</sup> /min  |
| Chart speed                | 10.0 cm/min              |

The instrument was warmed until the gas flow rate was stable. The amounts of 0.10 nm<sup>3</sup> of dodecane, 0.10 nm<sup>3</sup> of ethyl ethanoate and 0.10 nm<sup>3</sup>, 0.50 nm<sup>3</sup> and 1.00 nm<sup>3</sup> of methanol were injected onto the columns and the chromatographic peaks were recorded.

### 3.3.7.3 Separation of hydrocarbon mixture

A mixture of dedecane, tridecane, tetradecane and hexadecane was separated on the columns of 5% OV-101 at the following condition:

|                            |                          |
|----------------------------|--------------------------|
| Column limit               | 300°C                    |
| Column temperature         | 180°C                    |
| Injector temperature       | 200°C                    |
| Detector temperature       | 230°C                    |
| Detector range             | 8 x 10 <sup>-9</sup> AFS |
| Carrier gas:N <sub>2</sub> | 15 cm <sup>3</sup> /min  |
| Chart speed                | 1 cm/min                 |

The instrument was warmed until the gas flow rate was stable. A 0.40 nm<sup>3</sup> of the hydrocarbon mixture was injected onto the columns and the chromatograms were recorded.

#### 3.3.7.4 Separation of ester mixture

A mixture of ethyl ethanoate, ethyl propionate, ethyl pentanoate, ethyl hexanoate and ethyl heptanoate was separated on the columns of 5% OV-101 at the following condition:

|                            |                          |
|----------------------------|--------------------------|
| Column limit               | 300°C                    |
| Column temperature         | 80°C                     |
| Injector temperature       | 150°C                    |
| Detector temperature       | 150°C                    |
| Detector range             | 8 x 10 <sup>-9</sup> AFS |
| Carrier gas:N <sub>2</sub> | 20 cm <sup>3</sup> /min  |
| Chart speed                | 1.0 cm/min               |

The instrument was warmed until the gas flow rate was stable. A 0.40 nm<sup>3</sup> of the esters mixture was injected onto the columns and the chromatograms were recorded.

#### 3.3.7.5 Separation of alcohol mixture

A mixture of 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol was separated on the columns of 10% Carbowax 4000 at

the following condition:

|                             |                         |
|-----------------------------|-------------------------|
| Column limit                | 200°C                   |
| Column temperature          | 100°C                   |
| Injector temperature        | 130°C                   |
| Detector temperature        | 130°C                   |
| Detector range              | $8 \times 10^{-9}$ AFS  |
| Carrier gas: N <sub>2</sub> | 20 cm <sup>3</sup> /min |
| Chart speed                 | 1.0 cm/min              |

The instrument was warmed until the gas flow rate was stable. A 0.40 nm<sup>3</sup> of the alcohol mixture was injected onto the columns and the chromatograms were recorded.