CHAPTER III

EXPERIMENT

Adsorbents

6 types of zeolite were used in this experiment : commercial 4A, synthesized 4A, NaZSM-5, NH_4ZSM-5, HZSM-5 and 13X. Crystals of synthesized 4A and ZSM-5 were synthesized at the Chemical Engineering department laboratory , Chulalongkorn University. While commercial 4A and 13X were supplied by Union Carbide Corporation (Thailand).

A. Preparation

ZSM-5

ZSM-5 crystals were synthesized using the standard hydrothermal technique. The Si/Al ratio of the ZSM-5 crystals was about 40 based on the initial synthesis composition. The reagents used summarized and the preparation procedures are illustrated in Table 3-1 and Figure 3-1, respectively.

Table 3-1 Reagents used for the ZSM-5 preparation

Reagents for the gel preparation		Reagent for the decant solution preparation	
Solution G1		Solution S1	
$AlCl_3$ (g)	1.1101	$AlCl_3$ (g)	1.1101
TPABr (g)	5.72	TPABr (g)	7.53
NaCl (g)	11.95	Distilled water (ml)	60
Distilled water (ml)	60	H_2SO_4(conc.) (ml)	3.4
H_2SO_4(conc.) (ml)	3.4		
Solution G2		Solution S2	
Distilled water (ml)	45	Distilled water (ml)	45
Water glass (g)	69	Water glass (g)	69
Solution G3		Solution S3	
TPABr (g)	2.16	NaCl (g)	26.27
NaCl (g)	40.59	Distilled water (ml)	104
NaOH (g)	2.39		
Distilled water (ml)	104		
H_2SO_4(conc.) (ml)	1.55		

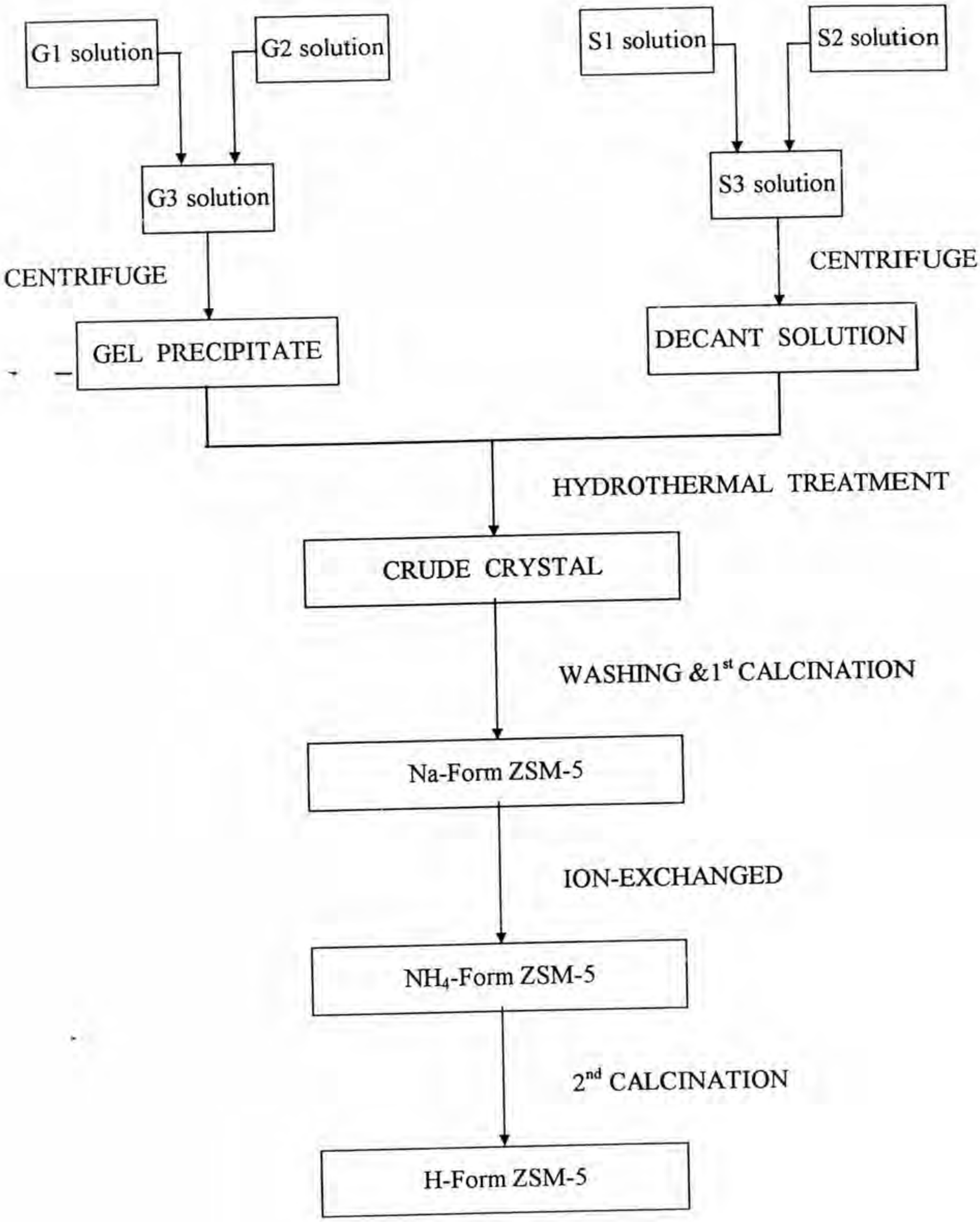

Figure 3-1 Procedure for the preparation of ZSM-5 zeolite

1. Preparation of Decantation Solution and Gel Precipitation

Firstly, a decant solution was prepared by adding 60 ml of G1-solution and 45 ml aqueous solution of G2-solution to 104 ml of G3-solution while stirring with a magnetic stirrer. G1-solution was added by a microfeeder at a volumetric flow rate 12.0 ml/min and G2-solution was added from a 50 ml burette by the manual control to keep the pH of the mixed solution in the range of 9-11. Upon the complete mixing, the precipitating gel was then removed from the supernatant solution by a centrifuge and the supernatant solution was kept for mixing with gel precipitate. On the other hand, another gel mixture was prepared by adding 60 ml of S1-solution to 208 ml of S3-solution. The method and condition of mixing were similar to the preparation of decantation solution. The precipitate from solution was separated by centrifuge and then milled by a powder mill.

2. Crystallization

The milled gel and the supernatant solution were mixed together. The mixture was heated for crystallization in an autoclave from room temperature to 160 °C in 90 min and from 90 °C to 210 °C in 4.2 hrs. under the nitrogen atmosphere of 3 kg/cm^2 (gauge). The hot mixture was allowed to cool down to the room temperature in the autoclave. The product crystals were washed with distilled water, to remove Cl$^-$ out of the crystals and were separated using the centrifugal separator (about 15-20 min for each time). The washing step was repeated several times until the pH of washing water became about 7. Finally, the crystals were dried out in an oven at 110-120 °C for at least 3 hrs.

3. Calcination

The dry product crystals were placed in porcelain container then were heated in a furnace (under an air ambient) from room temperature to 540 °C in 60 min and then were kept at this temperature for 3.5 hrs. During this step, TPABr was burned out in order to create cavities and channels in the crystals. The calcined crystals were cooled to room temperature in a desiccator. After this step the so called "NaZSM-5" was obtained.

4. Ammonium Ion-exchange of NaZSM-5

About 1.5 g of the NaZSM-5 was mixed with 45 ml of 1 M NH_4NO_3 and heated on a stirring hot plate at 80 °C for 1 hr. The ion-exchange step was repeated. The ion-exchange crystal was washed twice with deionized water and was separated using a centrifugal separator. Then, ion-exchanged crystal was dried out at 110-120 °C for 3 hrs. in an oven. The Na-form crystal was thus changed to " NH_4ZSM-5 ".

5. Calcination

The NH_4ZSM-5 was calcined in a furnace by heating from room temperature to 540 °C in 60 min and then kept at this temperature for 3.5 hrs. After this step the ZSM-5 obtained was called " HZSM-5 ".

4A

4A crystals were synthesized with the principle of rapid crystallization. The molar composition of the modified zeolite charged was Si/Al = 1 and Na_2O/Al_2O_3 = 5. The aluminium source was sodium aluminate while the silica source was water glass. Another reactant was sodium hydroxide. Detailed procedures was described with the corresponding Figure 3-2 as follows : 11.70 g of $NaAlO_2$, 18.45 g of NaOH and 13.65 g of water glass were dissolved in 50, 50 and 100 ml of distilled water, respectively. They were then mixed together while stirring vigorously for about 2 min until a uniform gel was formed. The gel was milled for 15 min. This gel was transferred into a closed glass bottle and placed in an oven at 85 °C. The sample was allowed to crystallize and then washed with distilled water until the pH of washing water became about 7 , and it was dried overnight at 110 °C. Finally, the sample was calcined at three different temperatures of 550, 750 and 800 °C for 1 hr. in air.

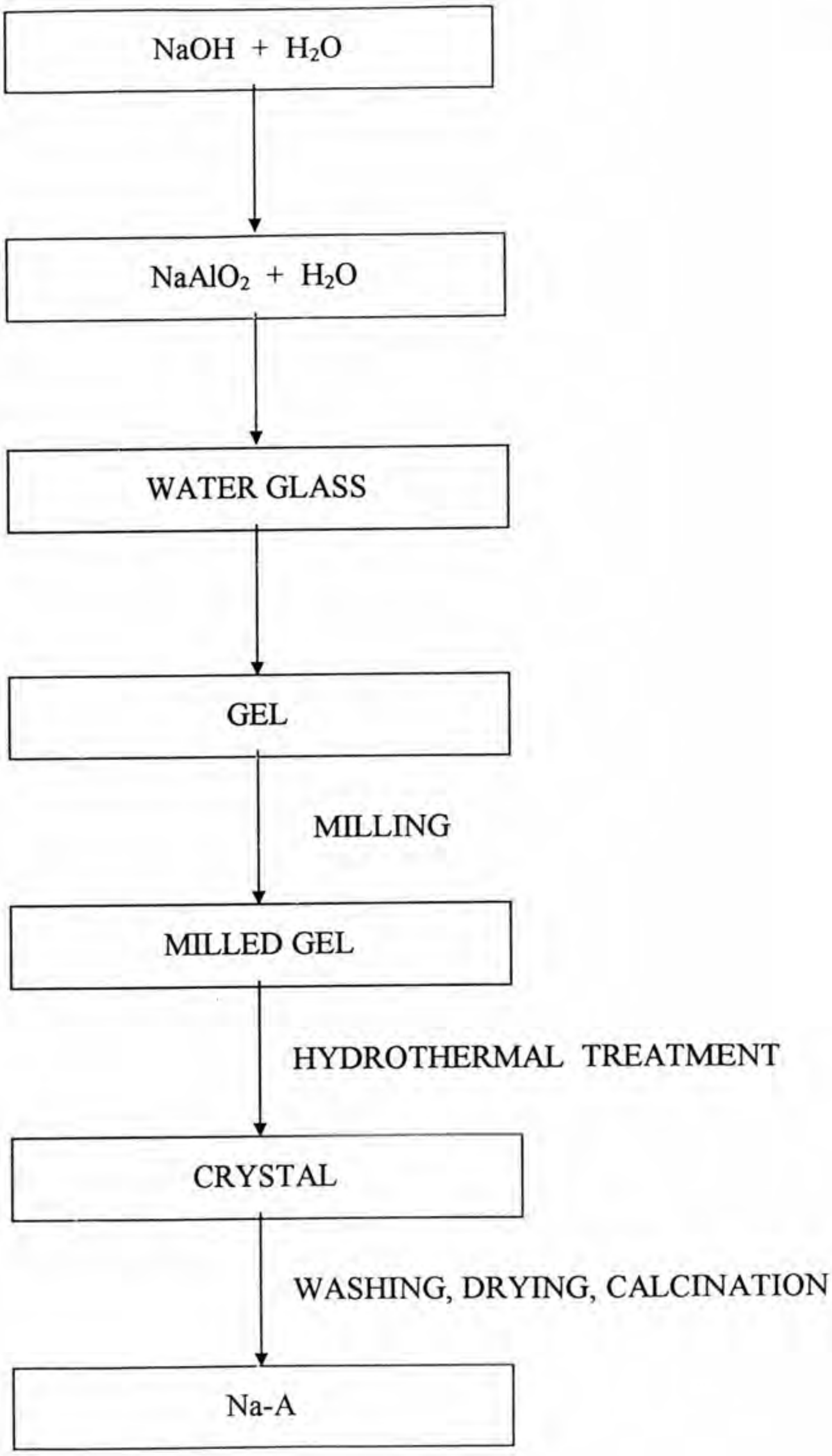

Figure 3-2 Procedure for the preparation of A-type zeolite

The synthesized crystals of 4A and ZSM-5 were palletized by compressing with hydraulic press. After that, the pressed pellets were crushed and sieved to 60-80 mesh size. The Commercial 4A and 13X were supplied in form of 1/16 inch cylindrical shape. They were also crushed and sieved to 60-80 mesh size.

B. Characterization

Both crystals of synthesized 4A and ZSM-5 were verified by X-ray diffraction.

A micromeritics BET (model ASAP 2000) was used to determine the surface area of all types of zeolites. Adsorption of nitrogen gas was carried out at the liquid nitrogen temperature, 77 K. The Brunaur-Emmett-Teller (BET) equation was employed to estimated the amount of nitrogen adsorbed for monolayer coverage (Yang, 1987). The surface area was taken as the area for monolayer coverage based on the nitrogen molecular area, 16.2 Å, obtained by assuming liquid density and hexagonal close packing.

C. Adsorption Column Preparation

The 60-80 mesh size of zeolite particles were packed in the 1/4 inch stainless steel tubes except the columns which were 0.1 cm bed length, they were packed in 0.38 cm ID glass tubes. The suitable bed length of each adsorbent was verified. It depended on the shape of the chromatogram which could be measured the area precisely. The characteristics of packed columns are summarized in Table 3-3. Both ends of the columns were plugged with glass wool.

Toluene and o-xylene vapors Preparation

Toluene and o-xylene vapors were prepared in a closed volumetric flask illustrated in Figure 3-3. The flask was filled with 200 ml liquid toluene or o-xylene. Then, it was sealed and kept in room temperature for several days in order to achieve the vapor-liquid equilibrium.

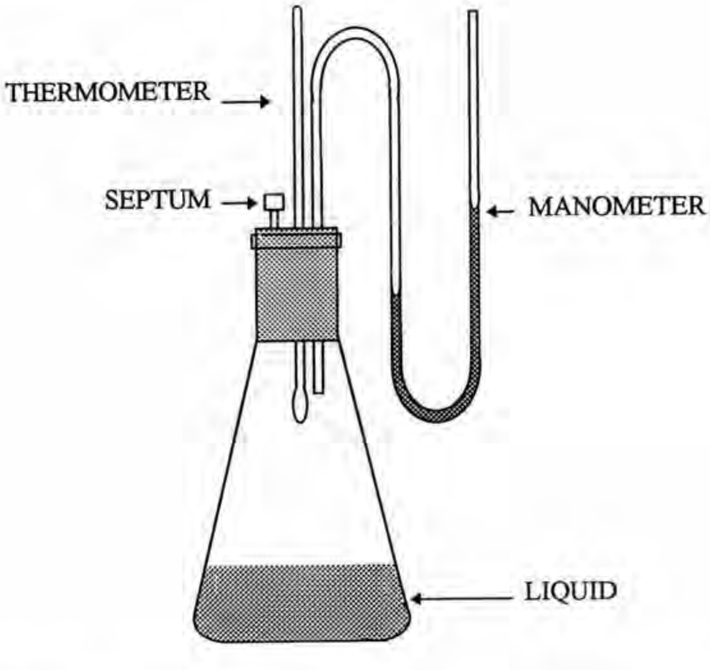

Figure 3-3 Closed volumetric flask used to prepare vapors

Table 3-3 Characteristics of packed columns

Adsorbate - Adsorbent	Weight of zeolite (g)	length of packed bed (cm)	Particle density (g/cm^3)	Bed porosity
Toluene - 4A(synthesized)	0.3049	3.0	1.148	0.461
Toluene - 4A(commercial)	0.1052	1.0	1.252	0.488
Toluene - NaZSM-5	0.0234	0.3	1.138	0.401
Toluene - NH_4ZSM-5	0.0080	0.1	1.060	0.335
Toluene - HZSM-5	0.0088	0.1	1.085	0.285
Toluene - 13X	0.0080	0.1	1.311	0.462
O-xylene - 4A(synthesized)	0.3049	3.0	1.148	0.461
O-xylene - 4A(commercial)	0.1052	1.0	1.252	0.488
O-xylene - NaZSM-5	0.0234	0.3	1.138	0.401
O-xylene - NH_4ZSM-5	0.0344	0.3	1.060	0.341
O-xylene - HZSM-5	0.0242	0.2	1.085	0.321
O-xylene - 13X	0.0306	0.3	1.311	0.526

The vapor composition was estimated from the vapor pressure and total pressure of the system which was measured with conventional manometer. The toluene and o-xylene vapor compositions were about 5 and 0.5 % by volume, respectively. The physical properties of toluene and o-xylene vapors are shown in Table 3-4.

Table 3-4 Physical properties of toluene and o-xylene vapors

Property	Toluene	O-xylene
Molecular weight	92.13	106.16
Liquid density (g/cm^3)	0.866	0.880
Boiling point (^{o}C)	110.6	144.4
Vapor pressure (mmHg, at 30 ^{o}C)	38.80	9.12
Heat of condensation (kJ/mol, at b.p.)	33.5	36.8

Adsorption Experiment

A Perkin-Elmer gas chromatograph (model 8700) with a flame ionization detector (FID) was used to measure the adsorption equilibrium constants and mass transfer coefficients. The carrier gas is helium. The flow rate of carrier gas was measured by a soap bubble meter at the exit of the detector during each run. One end of the zeolite column was connected to the injector and the other was connected to the detector. Each adsorbent was pretreated by passing helium through the packed column for 3 hrs. at 250 °C in order to purge all adsorbed species and then was brought to the desired temperature and flow rate.

The injections of small pulse of adsorbates were carried out manually with a gas-tight syringe into the carrier gas at various flow rates. For each column of zeolite, the temperatures of the column was altered in the range of 80-225 °C and for each temperature, flow rates of the carrier gas were varied 10-80 ml/min.

Both weighted mean retention times and variances of each chromatogram were measured by the method of moments in order to measure :

- the adsorption equilibrium constant of toluene and o-xylene on various types of zeolite molecular sieves

- the overall mass transfer coefficients of toluene and o-xylene on such zeolite molecular sieves.

- the heat of adsorption of toluene and o-xylene on such adsorbents.

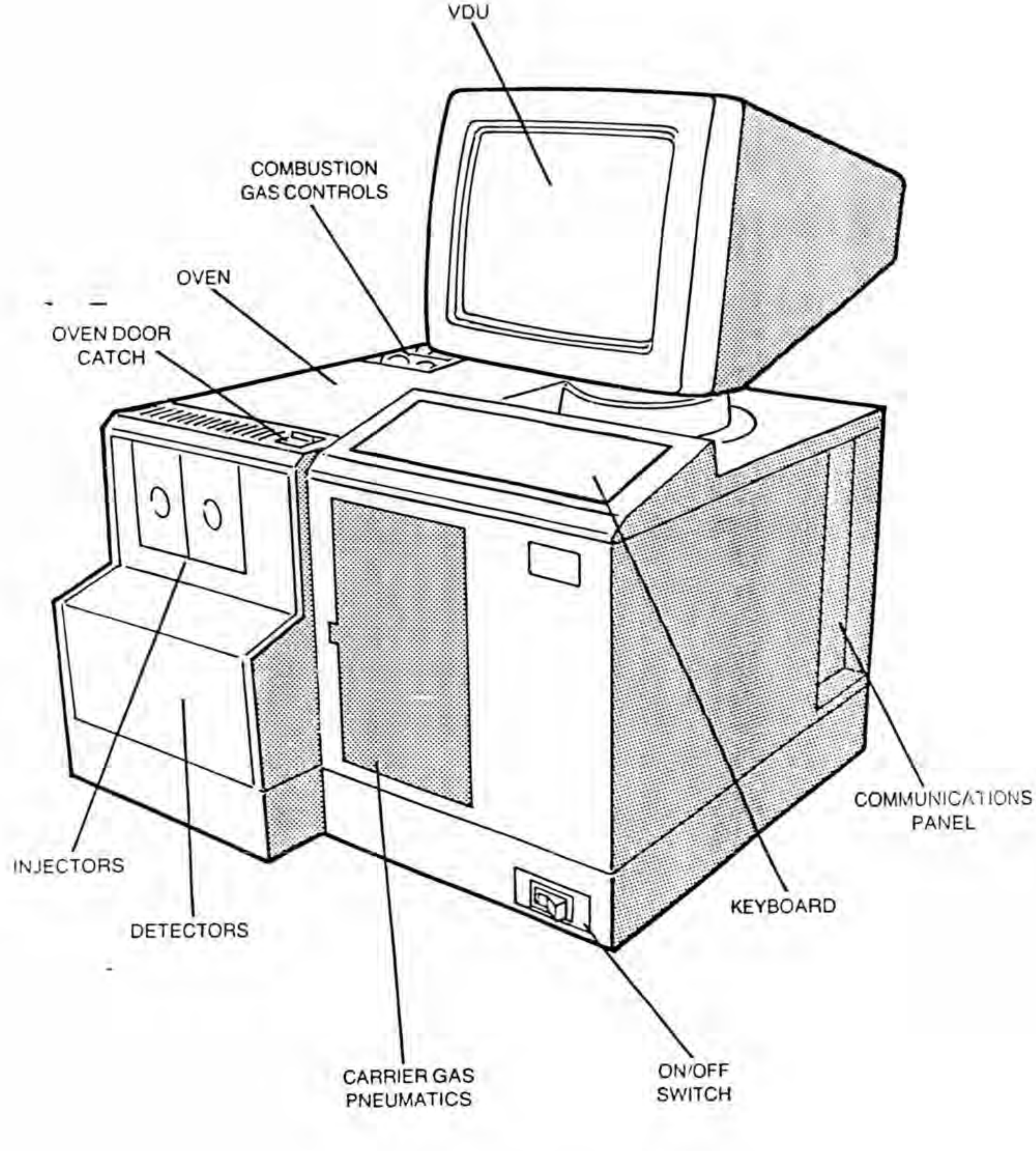

Figure 3-4 Physical features of Perkin Elmer gas chromatograph