EXPERIMENT

The scope of experiment in this study was divided into two parts. The first part was concerned about synthesis of zeolite crystals whereas the second ones was characterization of the product crystals.

3.1 Crystals Synthesis Experiment

3.1.1 Apparatus and Reagents Used

Apparatus

a. High Pressure Autoclave

The high pressure autoclave was used in crystal synthesis under hydrothermal treatment and autogeneous pressure. Maximum allowable working pressure which this autoclave can be used is 60 kg/cm^2 gauge at temperature under 370 ^{O}C. Design and construction of high pressure autoclave were shown in appendix A., and fig.3.1 shows the scheme of high pressure autocleve set which consists of autoclave, furnace, N$_2$ bomb, and temperature readout device.

b. Homogenizer

The homogenizer was used to mix solutions in ultrafine particle level as shown in fig.3.2. Its speed was beween 8,000 and 24,000 rpm and was sold by JANKE & KUNNEL-IKA-Labortechnik.

c. Centrifuge

Centrifuge was used to separate ultrafine particle from solution. Its speed was up to 9,000 rpm and sold by DAMON/IEC Devision.

Reagents Used

Reagents used in catalyst preparation, solution for the gel preparation and decant solution preparation, and preparation

Table 3.1 Reagents for catalyst preparation

No.	reagent	formula	purposed	properties	grade	sold by
1	Aluminum nitrate-nonahydrate	$Al(NO_3)_3 \cdot 9H_2O$	source of aluminum-ion	MW.=375.13 g/mol	extra pure	E.Merck,F.R.Germany.
2	Sodium silicate solution (water glass)	-	source of silicon-ion	density=1.37 g/cm^3	extra pure	E.Merck,F.R.Germany.
3	Tetrapropylammonium-bromide	$N(C_3H_7)_4Br$	template of crystal	MW.=226.27 g/mol	pure	Fluka Chemie AG,-Switzerland.
4	Sodium chloride	NaCl	source of sodium-ion	MW.=58.44 g/mol	analytical	E.Merck,F.R.Germany.
5	Sodium hydroxide	NaOH	adjust pH of-solution	MW.=40.00 g/mol	analytical	E.Merck,F.R.Germany.
6	98% sulfuric acid	98% H_2SO_4	adjust pH of-solution	MW.=98.07 g/mol sp.gr.=1.84	analytical	BHD LimitedPoole,England.
7	distilled water	H_2O	make volume of-solution in required concentration	MW.=18 g/mol density=1.0 g/cm^3	analytical	Science Complex Limited,-Thailand.

procedure were shown in table 3.1, 3.2 and fig.3.2 respectively.

Table 3.2 Composition of A, B, and C solution [39]

Solution for the gel preparation	Solution for the decant-solution preparation
Solution A-1 $Al(NO_3)_3.9H_2O$ x g TPABr[a] 2.28 g NaCl 4.8 g distilled H_2O 24.0 ml conc. H_2SO_4 1.36 ml	Solution A-2 $Al(NO_3)_3.9H_2O$ x g TPABr[a] 3.0 g distilled H_2O 24.0 ml conc. H_2SO_4 1.36 ml
Solution B-1 water glass[b] 20.14 ml distilled H_2O 18.0 ml	Solution B-2 water glass 20.14 ml distilled H_2O 18.0 ml
Solution C-1 TPABr 0.88 g NaCl 16.34 g NaOH 0.96 g distilled H_2O 18.0 ml conc. H_2SO_4 0.4 ml	Solution C-2 NaCl 10.52 g distilled H_2O 18.0 ml

[a] Tetra-n-propylammonium Bromide, $[CH_3CH_2CH_2)_4N]Br$

[b] Composed of 9.3% Na_2O, 28.5% SiO_2

[x] Based on mole ratio of Si/Al, method of calculation see in appendix B

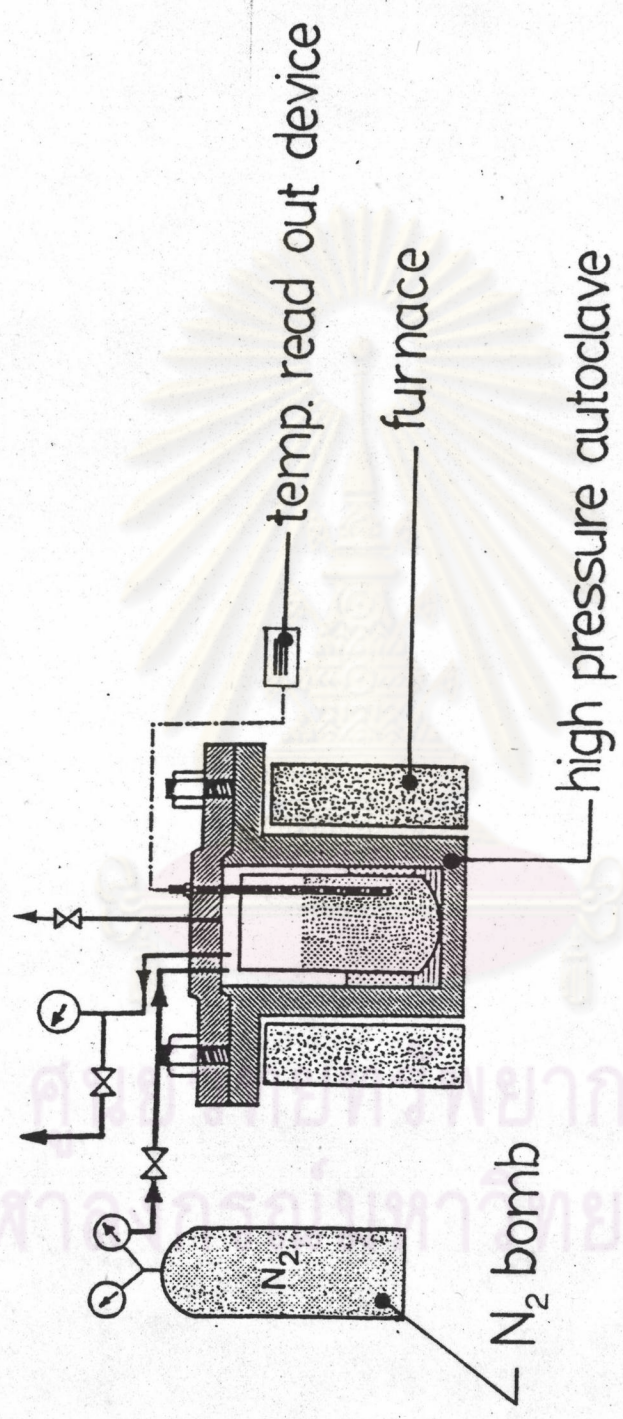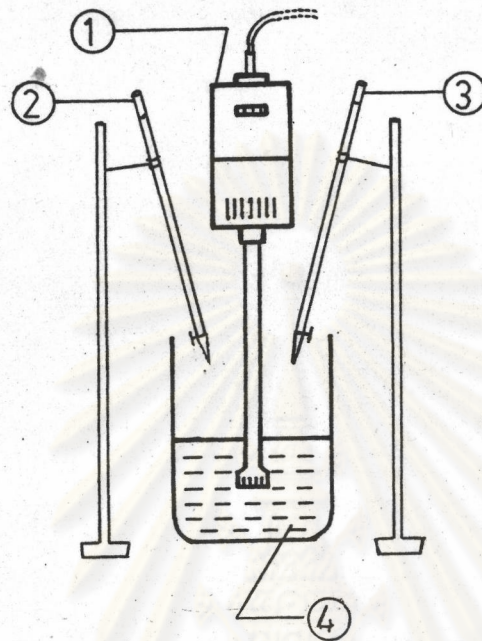The procedure and preparation method of zeolite crystal synthesis as

Figure 3.1 The scheme of high pressure autoclave set

① Homogenizer

② Buret for acidic solution, A

③ Buret for basic solution, B

④ Beaker for C-solution

Figure 3.2 Mixing set

```
┌─────────────────────┐        ┌─────────────────────┐
│ HOMOGENIZED MIXING  │        │ HOMOGENIZED MIXING  │
│         OF          │        │         OF          │
│  GEL-PRECIPITATION  │        │   DECANT-SOLUTION   │
└─────────────────────┘        └─────────────────────┘
        │                                │
   ┌──────────┐                    ┌──────────┐
   │ CENTRIFUGE │                  │ CENTRIFUGE │
   └──────────┘                    └──────────┘
        │
   ┌──────────┐
   │  MILLING │
   └──────────┘
        │
   GEL-PRECIPITATE              DECANT-SOLUTION

       ┌──────────────────────────┐
       │  HYDROTHERMAL TREATMENT   │
       │       IN AUTOCLAVE        │
       └──────────────────────────┘
                   │
              ┌──────────┐
              │ WASHING  │
              └──────────┘
                   │
              ┌──────────┐
              │  DRYING  │
              └──────────┘
                   │
              ┌────────────┐
              │ CALCINATION │
              └────────────┘
                   │
                   ▼
              Na-form ZSM-5
```
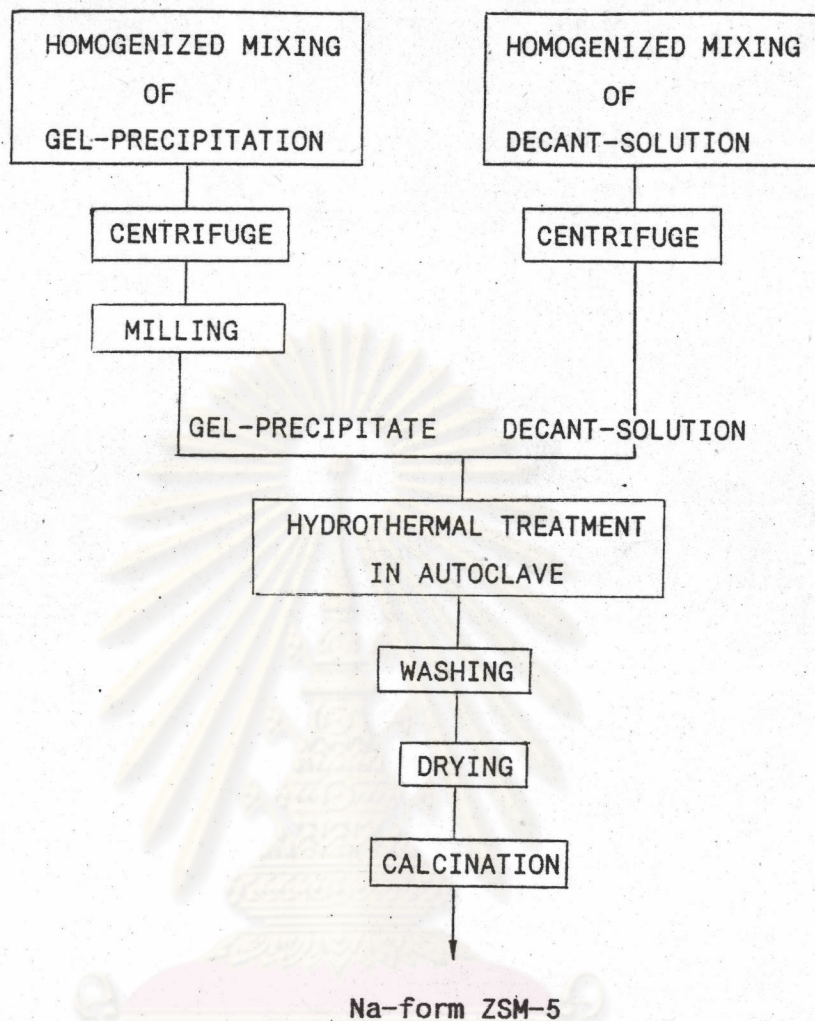
Figure 3.3   Procedure of zeolite preparation [19]

described above were used throughout. this study.

3.1.2 Preparation Condition

In preparation of the catalysts, reagents used and the preparation procedures were shown in table 3.2 and fig.3.3, respectively. Firstly, a gel mixture was prepared by adding solution A-1 and solytion B-1 into solution C-1 while maintaining a pH of 10 (solution A-1 and solution B-1 were contained in burets and solution C-1 was contained in a beaker) at room temperature and vigorously stirring with the homogenizer. the precipitate was separated from solution by centrifuge and then milled by using a manual porcelain motar until the precipitated gel became fine particles. Separately, a supernatant of decant-solution was prepared by adding solutions A-2 and B-2 into solution C-2, followed the separation of precipitate by centrifuge. The milling precipitate and the supernatant of the decant solution were mixed together and charged in an autoclave. The atmosphere in the autoclave was replaced by N_2 with pressure of 3 kg/cm^2 (gauge) and was heated from room temperature to 160 ^{O}C with a constant heating rate, 1.6 $^{O}C/min$, and then up to 210 ^{O}C with a heating rate of 12 $^{O}C/hr$ (temperature control lines of each experiments were shown in appendix C. These parameters were designed as a normal condition for this study. The produced crystals were washed with distilled water by using the centrifugal separator until no Cl ions were detected by $AgNO_3$ solution. The crystals were dried at 120 ^{O}C for at least 3 hr., and then calcined at 540 ^{O}C for 3.5 hr.

3.1.3 Variation of Synthetic Factors and Conditions

The purpose of study in this thesis was to know the effects of synthetic factors and conditions on structure of synthetic crystal. Therefore, in the catalyst synthesis under conditions section, the interesting effics were chemical compositions of crystal, initial

pressures in the autoclave, pH of mixing solution, temperature rates in crystal synthesis, and temperatures and times in calcination process.

3.1.3.1 Chemical Compositions of Crystal

Chemical compositions of crystal were studied by the variation of Si/Al mole ratio in the range of 20 and 200. By fixing of Si mole ratio, the amounts of waterglass used in this sytudy were all constant and Al mole ratio was varify with amounts of $Al(NO_3)3.9H_2O$ as shown in table 3.3.

Table 3.3 Amounts of $Al(NO_3)_3.9H_2O$ used related with mole ratio of Si/Al

mole ratio of Si/Al	20	40	100	140	200
$Al(NO_3)_3\ 9H_2O$, g	9.820	4.900	1.962	1.401	0.982

3.1.3.2 Initial Pressure in the Autoclave

The crystallizer was a clesed system reactor, when it was heated by furnace, the pressure in the system was increased itself and was called " Autogeneous pressure". Different initial pressure caused different final pressure so and because final pressure was the pressure of the system in crystallization step which was suggested to be effected on crystal synthesis. Therefore, initial pressure was varied in the range of 1 to 5 kg/cm^2 gauge.

3.1.3.3 The pH of Mixing Solutions

However, one of the most important factors in the synthesis of zeolite crystal was pH effect [28]. For the more understanding of the effect, pH of mixing solution was varied as shown in table 3.4.

Table 3.4 SiO_2/Al_2O_3 mole ratio and mixed pH used in 3.1.3.3.

Si/Al mole ratio	mixed pH
2	6, 8, 10, 12
100	6, 8, 10, 12
200	6, 8, 10, 12
400	4, 6, 8, 9, 10, 12

3.1.3.4 Temperature Rates in Crystal Synthesis

Crystal formation in the synthesis step was — effected by temperature rate. Only the optimum temperature rate, complete crystal would be formed, so there were study both teperature rate change and crystal formation at various times when temperature rate was changed. The detials of study were shown in table 3.5 and fig 3.3.

Table 3.5 Heating rate and times detected data in section 3.1.3.4.

1st heating rate (°C/min.)	heated from (°C to °C)	detected data at (hr:min)
1.6	room temp. -> 160	0:43.5, 1:03, 1:21, 3:51, 5:30
1.2	room temp. -> 130	same
2.0	room temp. -> 190	same

3.1.2.5 Temperature and Time in Calcination Process

The effect of temperature and times in calcination process was studied by variation of conditions as shown in table 3.6 and for constant compositions of crystal, Si/Al mole ratio was fixed at 140.
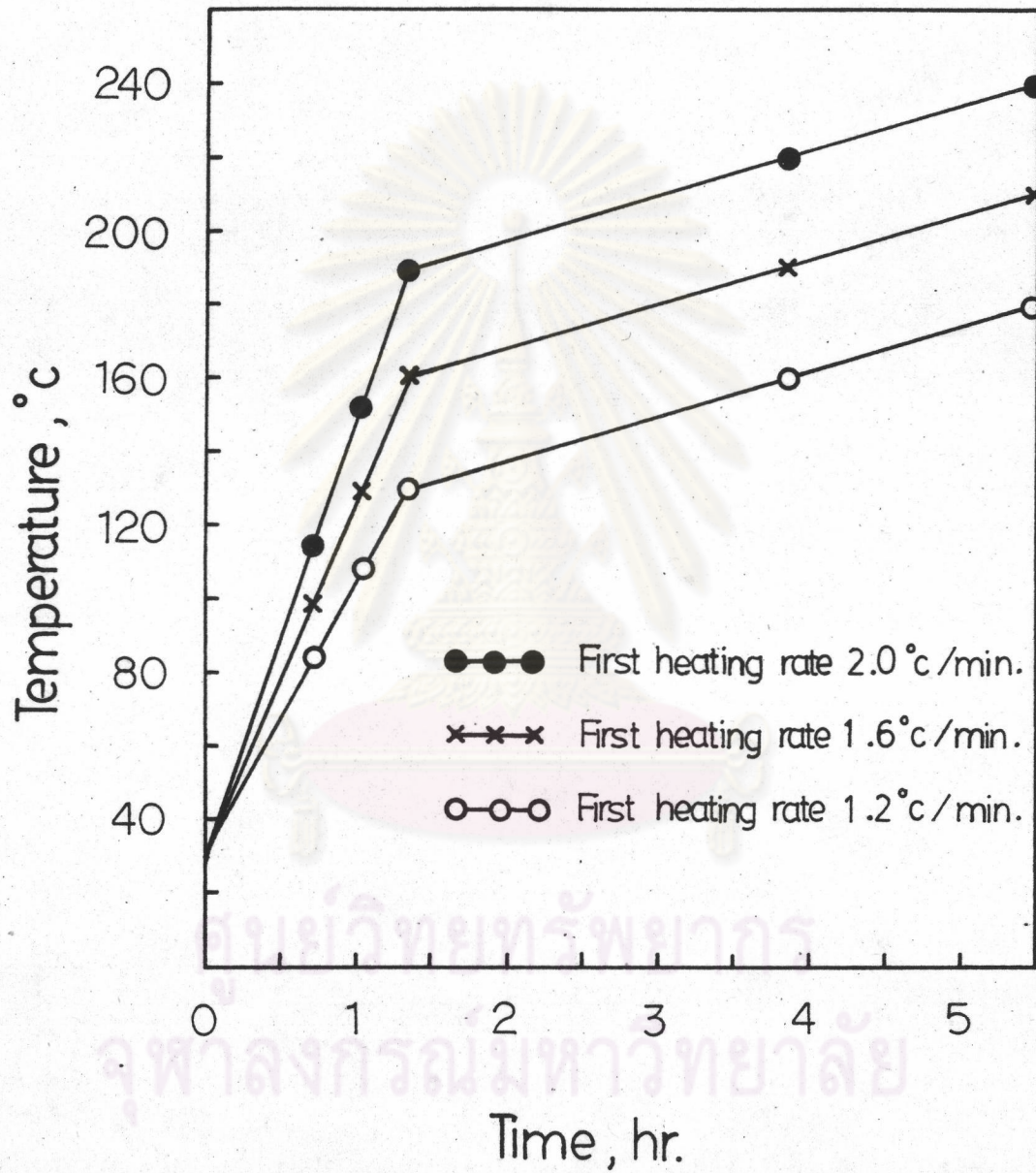
Figure 3.4   Operating lines for various heating rates in crystallization step.

Table 3.6 Temperatures and times used times used in calcination process

Temperature (^oC)	Time (hr)
450	3.5
540	1.5, 2.5, 3.5
630	3.5

3.2 Characterizations of the Product Crystals

Crystal characterizations were parted into four sections as follows : crystallinity analysis, external structure analysis, functional group analysis, and chemical elements analysis.

3.2.1 Crysallinity Analysis

Crystallinity of zeolite crystal was determined by X-ray diffraction (XRD) spectroscopy. The used type was PW1390 channel control and supplied by Philips. The intensity of crystal pattern range was set at 10^3 counter/sec. Time constant was equal to 1 and Cu-light source was used and give wave length, at 1.542 Å.

Procedure

1. Mill crystals until they become ultrafine particles. Pack in the tray and put the tray into goniometer and close the window.

2. Start up X-ray source, adjust the speed of detector to 2 ^{o}/min., set speed of graph paper on recorder at 1 cm./min.

3. Set the starting angle at 6 ^{o} and note it on the graph paper.

4. Switch on the goniometer and recorder at the same time.

5. After get the data, bring the value of 2θ of 3 maximum peaks to calculate plane of pareallel, d.

6. Use these 3 d-values to check the data from Powder

diffraction file [29] which gave name of crystal.

Method of Calculation for d-value (plane of parallel) [30]

From the equation of Braggs Law. : $n\lambda = 2d\sin\theta$

$$\text{For } n = 1, \quad \lambda_{Cu} = 1.542 \text{ Å}$$

$$\underline{\text{Example}} \text{ at } 2\theta \text{ (from graph paper)} = 40^{\circ}$$

$$= 20^{\circ}$$

$$d = n\lambda / 2\sin\theta$$

$$= \frac{(1)(1.542)}{2\sin(20^{\circ})}$$

$$= 2.254 \text{ Å}$$

3.2.2 External Structure Analysis

Scanning Electron Microscope, SEM was used to study external structure and size of zeolite crystal. This type was Jeol model JSH-35CF.

Procedure

1. Dry and calcine crystal at optimum temperature and times (120 $^{\circ}$C 3 hr and 540 $^{\circ}$C 3.5 hr., respectively).

2. Touch the copper stub with two-face tape and pressed it on the dry crystal.

3. Coat the stub together with sample with gold and then put it into the chamber of SEM .

4. Switch on the system of SEM , choose the picture of crystal at optimum multiplication, and take the SEM photograph.

From SEM photograph, it shows the multiplication of the picture and the micron length units which can use to estimate size of crystal.

3.2.3 Functional Group Analysis

Infrared spectrophotometer, IR was used to analyze functional group of crystal. The used type was Shimadzu 440.

An infrared spectrophotometer provides the following functions; to obtain a spectrum of monochromatic IR radiation radiated from the light source, to irradiates infrared rays to a sample by continuously changing the wavelength, to measure the intensity of infrared rays transmitted through the sample, to record the percent transmittance according to wavelength or wave number scan, and to record the IR spectrum on the chart [31].

Almost all the types of infrared spectrophotometers available on the market can automatically record a percent transmittance curve in terms of wave number. Photometric system is based on double-beam, optical null method. The functional principle of the double beam, optical null method is shown in fig.3.5.

Tablet Method for Sample Preparation

After fully grinding about 1 mg of a solid sample in a mortar, add 200 mg of KBr crystal to the powdered sample, and fully mix them with each other. Use a die as illustrated in fig.3.6 to make this mixture into a tablet by pressing with the weight of 8 tons while removing water vapor contained in the sample after reducing the pressure to 1 mmHg by means of a vacuum pump. The diameter of the tablet is usually about 13 mm.

When carrying out the measurement a tablet of KBr which contains no sample powder should be placed in the reference beam to compensate both scattering loss of infrared radiation caused by the tablet and water adsoebed by KBr which is apt to adsorb moisture. Since KBr is free from absorption between 2 and 25 μ, this method possesses the merit that the whole wavelength range can be measured with only KBr
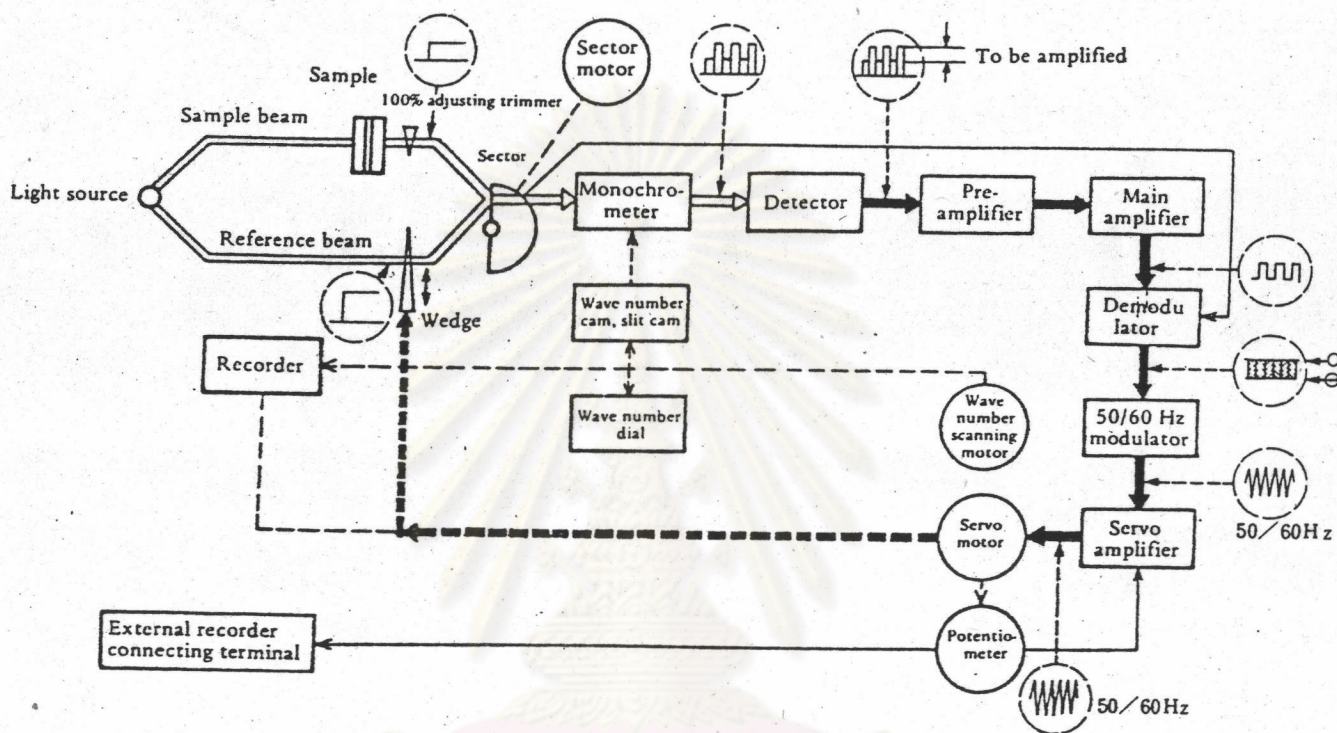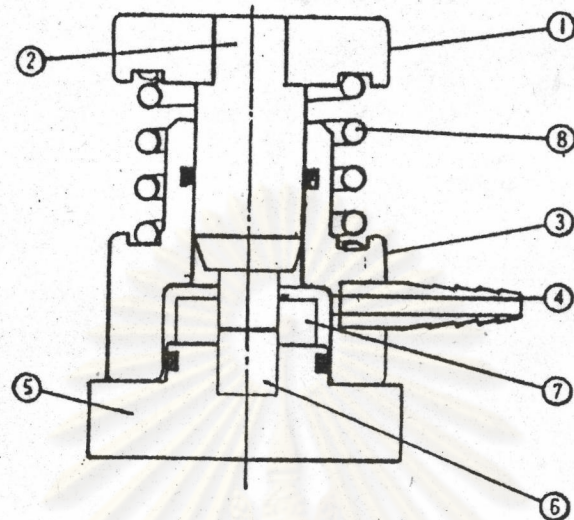
Figure 3.5 Block diagram of a double beam IR spectrophotometer system.

① Plunger upper plate   ⑤ Base
② Plunger   ⑥ Sample receiver
③ Plunger guide metal   ⑦ Tablet frame
④ Air vent   ⑧ Coil spring

Figure 3.6   KBr Die

tablet.

3.2.4 Chemical Element Analysis

Atomic absorption spectrophothmeter, Varian Techtron model Spectra 30/40 was used to determine chemical element.

The principle components of the IL551 were [32] :

-Cathode-ray tube (CRT) display

-Micromomputer

-Optical system composed with lenses, beam splitter, rotary modulator and monochromator.

-Photomultiplier tube and associated digital elextronics.

-Premix and burner systems.

-optimal components.

Principle of Atomic absorption

Atomic absorption spectroscopy makes use of the fact that neutral or ground state atoms of an element will absorb electromagnetic radiation over a series of very narrow, sharply defined wavelengths. In flame atomic absorption spectroscopy, the dissolved sample is aspirated as a fine mist into a flame where it is converted to an atomic vapor. As an atomic vapor, most of the atoms remain in the ground state and are therefore capable of absorbing electromagnetic radiation of characteristic wavelengths. This discrete radiation is usuallysupplied by a hollow cathode lamp, which is a sharp line source consisting of a cathode containing the element to be dertermined along with an anode (usually tungsten). When a sufficient voltage is impressed across the electrodes, the filler gas is ionized and the ions are accelerated towards the cathode. As these ions bombard the cathode, they cause the cathode material to "sputter" and form an atomic vapor in which atoms exist in an excited electronic state. When the excited atoms return to the groung state, the characteristic spectra of the analyte elements are

emitted and pass through the flame where they may be absorbed by the atomic vapor.

Since, generally, only the test element can absorb this radiation, the method becomes very specific in addition to being sensitive.

Sample Preparation[33]

1. Weight 0.1g sample in Ni-crucible.

2. Add NaOH 0.3g.

3. Dissolve with 30 ml distilled water in the beaker.

4. Add 10ml HCl 1:1 and warm on water bath.

5. Add approximate 3 drops of H_2O_2 slowly until the solution is clear.

6. Make volume to be 100 ml in volumetric flask by adding distilled water.

7. Filtere and keep in the bottle.

Conditions for Silicon Detections :

instrument mode	absorbance
calibration mode	concentration
measurement mode	integration
lamp position	7
lamp current (mA)	10
slit width (nm)	0.5
slit height	normal
wavelength (nm)	250.7
flame	N2O-acetylene
sample introduction	manual
delay time (sec)	5
time constant	0.05

measurement time (sec)	3.0
replicates	2
background correction	off
N2O flow (L/min)	11.0
acetylene flow (L/min)	6.0
recalibration rate	0
reslope rate	0

Calibration curve of silicon and aluminum were shown in fig.3.7 and 3.8, respectively.

Conditions for Aluminum Detections :

|	
instrument mode	absorbance
calibration mode	concentration
measurement mode	integration
lamp position	4
lamp current (mA)	10
slit width (nm)	3.5
slit height	normal
wavelength (nm)	237.3
flame	N2O-acetylene
sample introduction	manual
delay time (sec)	5
time constant	0.05
measurement time (sec)	3.0
replicates	2
background correction	off
N2O flow (L/min)	11.0
Acetylene flow (L/min)	6.0
recalibration rate	0
reslope rate	0
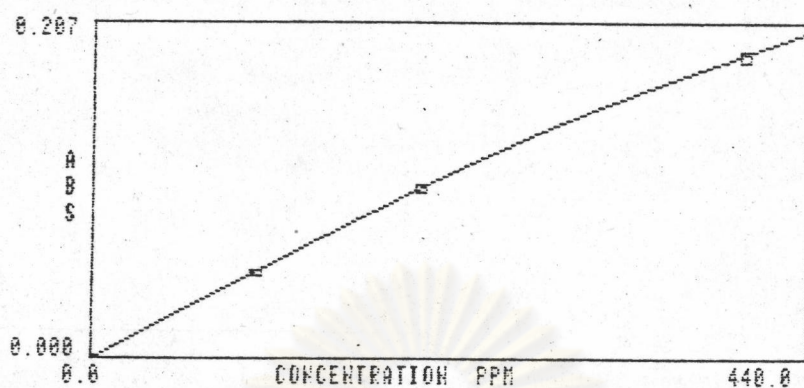
Figure 3.7 Calibration curve for silicon
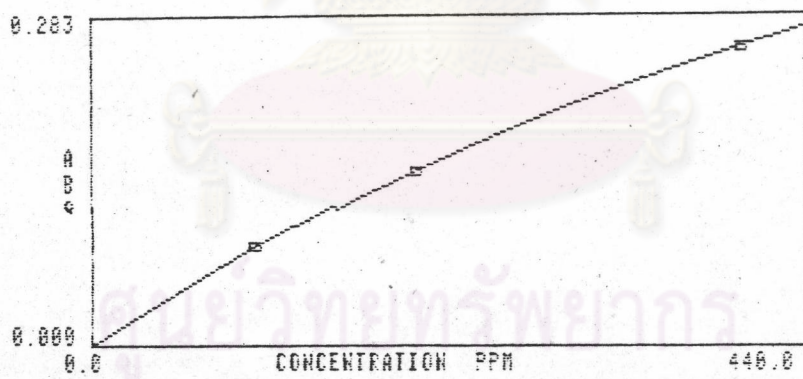
Figure 3.8 Calibration curve for aluminum