CHAPTER 4

APPARATUS, MATERIALS AND EXPERIMENTAL PROCEDURES FOR DETERMINATION OF THE RETENTION INDICES

In the experimental part, the CFC compounds with one and two carbon atoms, which are available from Solvay Laboratory Centre (as shown in table 4.1),will be examined by linear programmed-temperature gas chromatography to obtain the retention data. The measurements were performed on a model HRGC 5160 Carlo Erba Strumentazione Gas Chromatography equipped with a flame-ionization detector,an electron-capture detector and a Cryo 520 module cryogenic unit. Results were computer integrated by an installed CLAS System Perkin Elmer. The compounds are divided into seven families according to the number of carbon and hydrogen atoms in the molecule. Retention was measured on three capillary columns of different polarity, namely OV-1, DB-1701 and DB-210. The retention data will be converted into retention indices which are used in the correlation study. In the next part, the experimental equipments and procedures will be presented.

4.1 Experimental Equipments and Materials

4.1.1 Programmed-temperature gas chromatography

The instrument is a HRGC 5160 Carlo Erba Strumentazione (Italy) of the Mega Series gas chromatography. It comprises of five parts : Pneumatic circuits, Sampling systems, Oven, Multifunction controller MFC 500 and Detectors (Figure 4.1). The description of each part is as follow :-

4.1.1.1 Pneumatic circuit

The pneumatic circuits and their controls are shown in

Table 4.1 The CFC compounds with one and two carbon atoms

Code #	Formula	mol. wt.	b.p. °C	f.p. °C	Density (g/cc)/ °C
CHLOROFLUOROMETHANES					
10	CCl_4	153.8	76.8	-23	1.595/20
11	CCl_3F	137.4	23.8	-111	1.487/20
12	CCl_2F_2	120.9	-29.8	-158	1.293/30
13	$CClF_3$	104.5	-81.4	-181	1.298/-30
14	CF_4	88.0	-128	-183.6	1.33/-80
20	$CHCl_3$	119.4	61.2	-63.5	1.489/20
21	$CHCl_2F$	102.9	8.9	-135	1.354/30
22	$CHClF_2$	86.5	-40.8	-160	1.175/30
23	CHF_3	70.0	-82.1	-160	1.246/-34
30	CH_2Cl_2	84.9	40.1	-96.7	1.336/20
*31	CH_2ClF	68.5	-8.1	-133	1.271/20
32	CH_2F_2	52.0	-51.7	-136	1.100/20
40	CH_3Cl	50.5	-24	-97.7	0.920/18
41	CH_3F	34.0	-78.5	-141.8	0.8428/-60
CHLOROFLUOROETHANES					
110	CCl_3-CCl_3	236.8	185	186	2.091/20
*111	CCl_3-CCl_2F	220.3	137	100	1.740/25
112	CCl_2F-CCl_2F	203.8	92.8	23.5	1.637/30
112a	CCl_3-$CClF_2$	203.8	91.5	40.6	1.6488/20
113	CCl_2F-$CClF_2$	187.4	47.6	-35	1.533/30
113a	CF_3-CCl_3	187.4	45.7	14	1.579/20
114	$CClF_2$-$CClF_2$	170.9	3.6	-94	1.440/30
*114a	CCl_2F-CF_3	170.9	3	-56.6	1.454/29
115	$CClF_2$-CF_3	154.5	-38.7	-106	1.265/30
116	CF_3-CF_3	138.0	-78.1	-100.6	1.607/-78

see nomenclature of the code numbers in Appendix D

* non-available products

Table 4.1 (continued)

Code	Formula	mol. wt.	b.p. °C	f.p. °C	Density (g/cc)/ °C
120	$CHCl_2$-CCl_3	202.3	162	-29	1.709/90
121	$CHCl_2$-CCl_2F	185.8	116.6	-82.6	1.622/20
*121a	CHClF-CCl_3	185.8	116.5	-95.4	1.625/20
122	$CHCl_2$-$CClF_2$	169.4	71.9	-140	1.5447/25
*122a	CHClF-CCl_2F	169.4	72.5	glass	1.5587/20
*122b	CHF_2-CCl_3	169.4	73	glass	1.566/20
123	$CHCl_2$-CF_3	153.0	27.1	-107	1.475/15
123a	CHClF-$CClF_2$	153.0	28.2	-	1.498/0
*123b	CHF_2-CCl_2F	153.0	-	-	-
124	CHClF-CF_3	136.5	-12	-	-
*124a	CHF_2-$CClF_2$	136.5	-10.2	-117	1.379/20
125	CHF_2-CF_3	120.0	-48.5	-103	-
130	$CHCl_2$-$CHCl_2$	167.9	146.3	-43.8	1.600/20
130a	CCl_3-CH_2Cl	167.9	130.5	-68.1	1.588/20
131	$CHCl_2$-CHClF	151.4	102.5	-	1.5497/17
131a	CH_2Cl-CCl_2F	151.4	88	-104.7	1.4921/20
*131b	CH_2F-CCl_3	151.4	-	-	-
132	CHClF-CHClF	135.0	59	-155	-
*132a	CHF_2-$CHCl_2$	135.0	60	-	1.4945/17
132b	$CClF_2$-CH_2Cl	135.0	46.8	-101.2	1.4163/20
*132c	CCl_2F-CH_2F	135.0	-	-	-
*133	CHClF-CHF_2	118.5	17	-	1.365/10
133a	CF_3-CH_2Cl	118.5	6.1	-105.5	1.389/10
*133b	$CClF_2$-CH_2F	118.5	12	-	-
134	CHF_2-CHF_2	102.0	-19.7	-89	-
134a	CF_3-CH_2F	102.0	-26.5	-101	-

* non-available products

Table 4.1 (continued)

Code	Formula	mol. wt.	b.p. °C	f.p. °C	Density (g/cc)/ °C
140	$CHCl_2$-CH_2Cl	133.4	113.5	-36.7	1.334/20
140a	CCl_3-CH_3	133.4	74.1	-30.4	1.3249/26
141	CHClF-CH_2Cl	116.9	75.7	-	1.3814/20
*141a	$CHCl_2$-CH_2F	116.9	-	-	-
141b	CCl_2F-CH_3	116.9	32	-103.5	1.250/10
142	CHF_2-CH_2Cl	100.5	35.1	-	1.312/15
*142a	CHClF-CH_2F	100.5	-	-	-
142b	$CClF_2$-CH_3	100.5	-9.2	-130.8	1.096/30
143	CHF_2-CH_2F	84.0	5	-84	-
143a	CF_3-CH_3	84.0	-47.6	-111	0.942/30
150	CH_2Cl-CH_2Cl	98.9	83.5	-35.3	1.253/20
150a	$CHCl_2$-CH_3	98.9	57.3	-96.7	1.174/20
*151	CH_2F-CH_2Cl	82.5	53.2	-	1.1675/25
151a	CHClF-CH_3	82.5	16.1	-	-
*152	CH_2F-CH_2F	66.0	30.7	-	0.913/19
152a	CHF_2-CH_3	66.0	-24.7	-117	0.966/19
160	CH_2Cl-CH_3	64.5	13.1	-138.7	0.9214/0
161	CH_2F-CH_3	48.0	-37.1	-143.2	0.8716/-37

* non-available products

Table 4.1 (continued)

Code	Formula	mol. wt.	b.p. C	f.p. C	Density (g/cc)/ C
CHLOROFLUOROETHYLENES					
1110	$CCl_2=CCl_2$	165.8	120.8	-22.4	1.6311/15
*1111	$CClF=CCl_2$	149.4	71.0	-108.9	1.5460/20
1112-c	$CClF=CClF$	132.9	21.1	-130.5	1.4950/0
*1112-t	$CClF=CClF$	132.9	22	-110.3	1.4936/0
1112a	$CF_2=CCl_2$	132.9	19	-115	1.4385/20
1113	$CClF=CF_2$	116.5	-27.9	-157.5	1.3048/20
*1114	$CF_2=CF_2$	100.0	-76.3	-142.5	1.519/-76
1120	$CHCl=CCl_2$	131.4	88	-86.4	1.4556/25
1121	$CHCl=CClF$	115.0	35.1	-	1.4032/16
*1121a	$CHF=CCl_2$	115.0	37.3	-108.8	1.3833/20
1122	$CHCl=CF_2$	98.5	-17.7	-138.5	1.230/21
*1122a	$CHF=CClF$	98.5	-	-	-
1123	$CHF=CF_2$	82.0	-61	-78	1.265/27
1130-c	$CHCl=CHCl$	96.9	60.1	-80.5	1.291/15
1130-t	$CHCl=CHCl$	96.9	48.4	-50	1.265/15
1130a	$CH_2=CCl_2$	96.9	37	-	1.250/15
*1131-c	$CHF=CHCl$	80.5	16	-	-
*1131-t	$CHF=CHCl$	80.5	-4	-	-
1131a	$CH_2=CClF$	80.5	-25	-169	-
1132	$CHF=CHF$	64.0	-28	-	-
1132a	$CH_2=CF_2$	64.0	-82	-144	0.617/24
1140	$CH_2=CHCl$	62.5	-13.9	-159.7	0.9195/15
1141	$CH_2=CHF$	46.0	-72.2	-160.5	0.615/25

* non-available products

Figure 4.2 and 4.3. They include :

Fig 4.1 The HRGC 5160 Carlo Erba Strumentozione GC

- Carrier gas circuit for split/splitless (SSL) injection system for which helium (He) is used as carrier gas with pressures of about 240 KPa. It can be adjusted by using the carrier gas pressure regulator marked "PRESSURE" for SSL.

- Hydrogen circuit which is used for flame-ionization detector (FID) with pressures of about 50 KPa. It can be adjusted by using the hydrogen pressure regulator marked "H_2".

- Air circuit which is used for FID with pressures of about 150 KPa. It can be adjusted by the air pressure regulator marked "AIR".

- The make up circuit can be used for the detectors in order to achieve the highest sensitivity. Nitrogen (N_2) is used for this work with pressures of about 150 KPa. It can be adjusted by the make up pressure regulator marked "MAKE-UP".

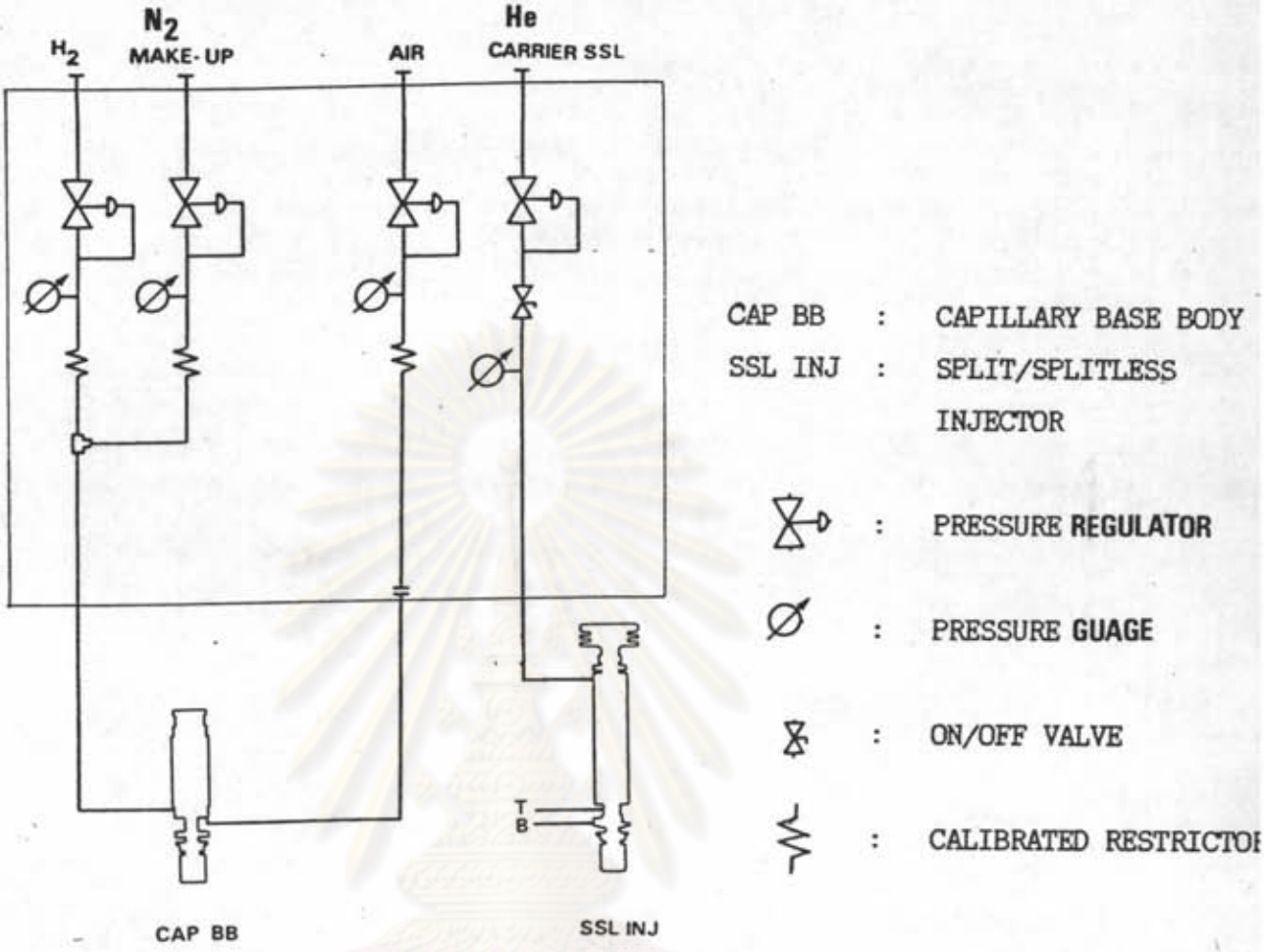

Fig. 4.2 Pneumatic circuit for the MEGA 5160 GC

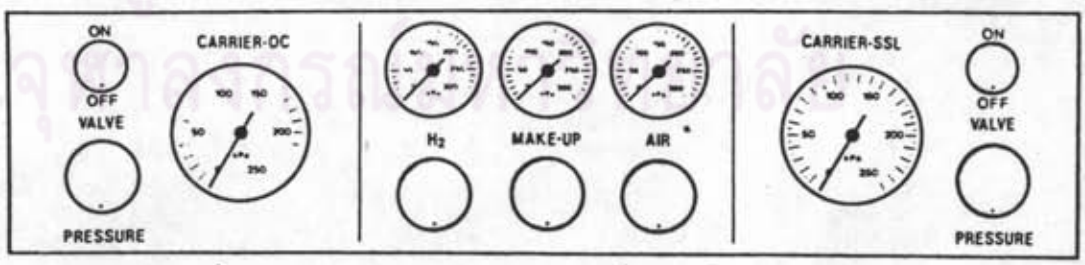

Fig. 4.3 Pneumatic controls for the MEGA 5160 GC

4.1.1.2 Sampling system

The injection device which is used in the experiments is the vaporizing split-splitless injector as shown in Figure 4.4. The liquid sample is introduced into the vaporization chamber, which is made of glass, by means of a microsyringe through the silicone septum. They can be heated in the range of 50 °C to 450 °C by 1 °C increments. In the split mode where the concentration is reduced prior to entrance into the column, the sample is split consistently by a fixed amount known as "split ratio". This is set by regulating the bottom split valve (1) and it is expressed as the ratio of the carrier gas flowing through the column to the carrier gas coming out the bottom split. In this work, the split ratio is about 1:150 to 1:180.

4.1.1.3 Base unit oven

The oven includes a column with a high thermal stability. The temperature in the oven has been optimized in air circulation based on a highly efficient fan. The inside configuration of the oven is shown in Figure 4.5.

Separation of moderately volatile components may be easily achieved at near ambient temperature especially when thick film stationary phase capillary columns are used. To match this requirement a "modulated cooling flap system" has been fitted into the oven in order to take the cool ambient air in and exhaust the hot air. This system allows accurate and reproducible operations at temperature about 5 °C to 10 °C above ambient temperature without the use of a cryogenic system. The temperature parameters are dictated from the Multifunction controller MFC 500 and the working temperature range for the oven fitted with this modulating flap is :

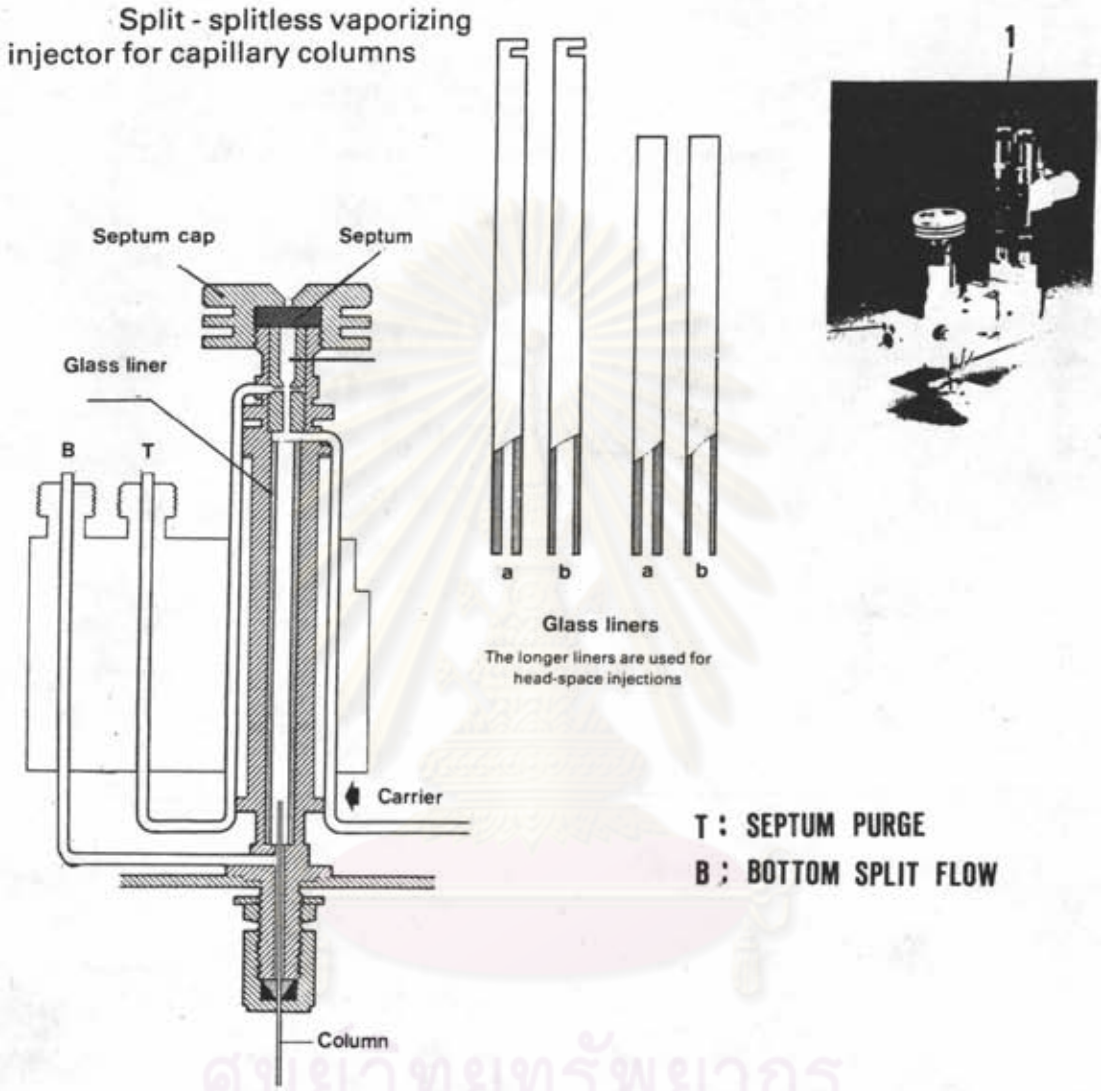

Fig. 4.4 Split/splitless vaporizing injector for capillary column

Minimum temperature : 5 - 10 °C above ambient

Maximum temperature : 450 °C

Programmed rates : 0 - 45 °C/mim in 0.1 °C/min accuracy

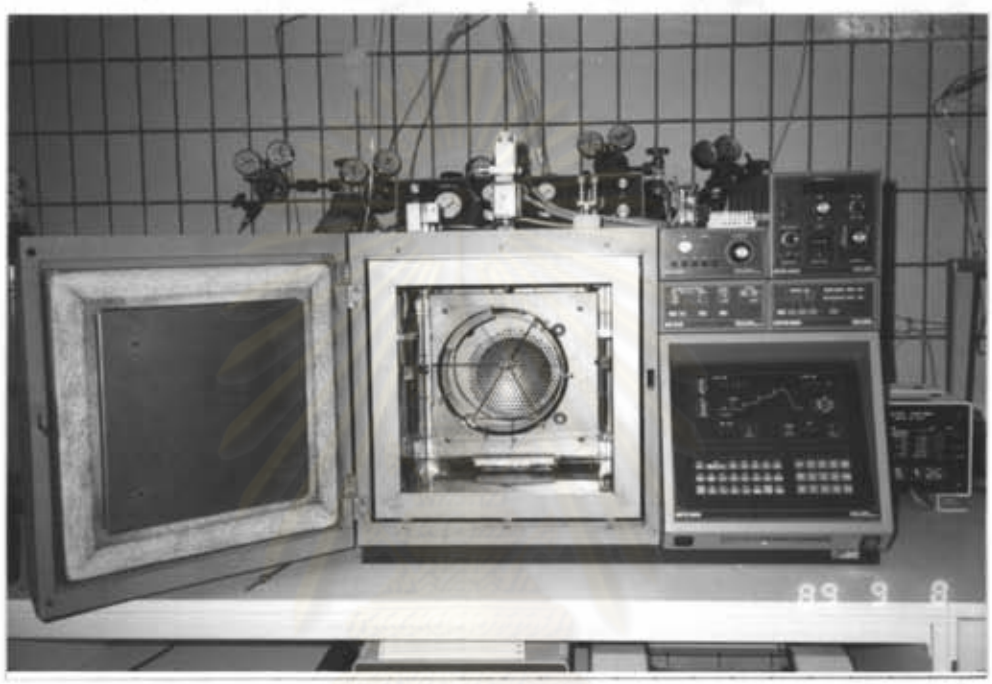

Fig. 4.5 MEGA 5160 GC Oven, showing column installed inside

4.1.1.4 Multifunction controller MFC 500

The MFC 500 is the controller of the MEGA Series GC featuring a membrane-type keyboard (Figure 4.6) where all chromatographic parameters are clearly indicated on each key. This controller consists of :

- Address keyboard
- Numeric keyboard
- Graphic array
- Column limit protection (2) It ensures that the column

maximum temperature will not be exceeded. Setting is independent from temperature program.

- ON/OFF power supply switch (3)

Fig. 4.6 MFC 500 featuring the membrane keyboard and graphic array

4.1.1.5 Detectors

There are 2 detectors used in the experiments. One is a Flame-Ionization detector (FID). It can be used for the mojority of organic compounds. Specifically, the detector measures only C-H containing molecules and gives no response for H_2O, CO_2 or inorganic compounds. For organic compounds containing heteroatoms, FID will give a lower response than with hydrocarbons. The experimental results are mainly based on this detector. The other detector used is the Electron-Capture detector (ECD). It has a high sensitivity for

compounds containing highly electronegative atoms, such as Cl, but gives no response for hydrocarbons. In this work, this type of detectors is used to help identifying the sample peaks.

4.1.1.5.1 Flame-Ionization detector with EL-480 controller

In this detector the effluent from the column is mixed with hydrogen and the resultant mixture is then burnt with a flow of air at a metal jet which acts as an electrode. The second electrode is in the form of a metal collar and surrounds the flame. When pure carrier gas leaves the column, the flame contains few ions. But when compounds burn in the flame, positive ions and electrons are produced and a higher current passes between these two electrodes. This current is measured by a high input impedance amplifier which is used to detect compounds present in the carrier gas. Normally, to avoid condensation of the components being eluted from the column, the detector base body temperature should be set about 50 °C higher than the column operating temperature but should not exceed the temperature limit of the column. The configuration of FID and controller are shown in Figure 4.7 and 4.8, respectively.

The Electrometer Control EL-480 consists of :-

1. The switch "ATTENUATION" (4) to change the sensitivity of the electrometer

2. Push-button polarity switch (5) to set the polarising voltage

3. Push button "IGNIT" (6) to ignite the flame

4. Power indicating lamp (7), lights up when power is "ON" and the intensity decreases when the IGNITER is depressed.

5. Zero knob (8) with three steps control (9), a continuously adjustable potentiometer for baseline setting in recorder or integrator.

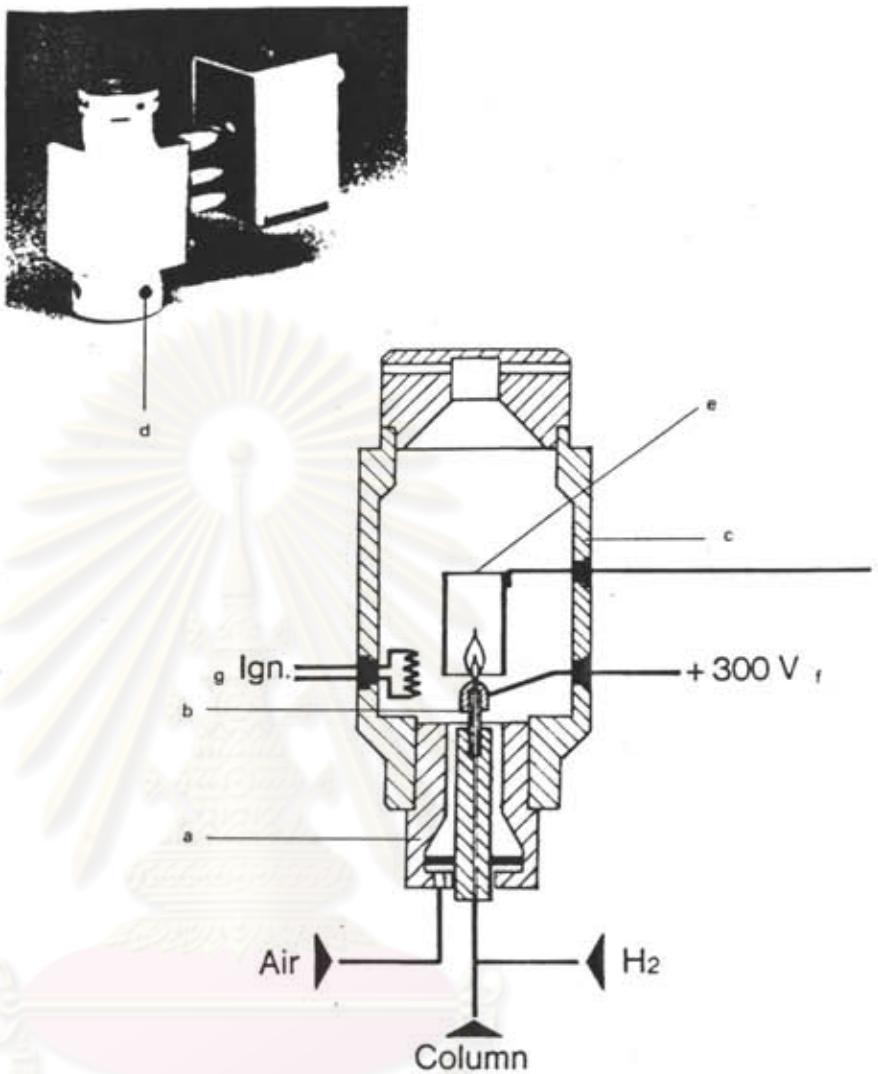

Fig. 4.7 The flame-ionzation detector FID-40

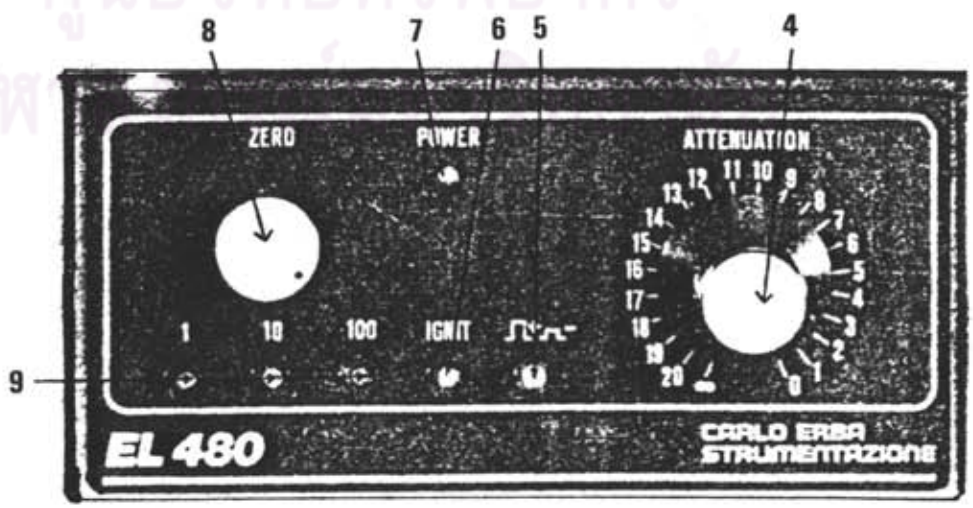

Fig. 4.8 Electrometer control module EL-480

4.1.1.5.2 Electron-Capture detector with ECD-400 controller

The ECD operates on the principle of gas phase absorption of free electrons by electron capturing molecules. It consists of an ionization chamber with two electrodes. Carrier gas flows through this chamber and an ionizing radioactive source, Ni^{63} beta-emitting, produces free electrons through a gas ionization process. When an electron capturing substance passes through the detector, the electric current is reduced owing to the absorption of electrons. The electron affinity of the molecule influences the sensitivity and selectivity of response of the ECD. The detector can operate in two modes : Constant Frequency (CF) mode, this yields the best results from a sensitivity point of view, and Constant Current (CC) mode, which allows the linearity of ECD reponse to be increased by a factor of 100 compared to the CF mode and this work is based on the CC mode. The configuration of ECD and controller are shown in Figure 4.9 and Figure 4.10.

The ECD-400 control module comprises of the following functions :-

1. Push button to select CF mode (10) and CC mode (11) operations.

2. Dual function knob (12) used as zero control and digital frequency meter (13) giving direct frequency readout (KHz) for both modes of operations.

3. Five-turn double functions potentiometer (14), used to select the reference current (nA) in CC mode and baseline zero set with the standing current readout (nA) in CF mode.

4. Binary step output attenuator (15)

5. Detector temperature thumbwheel switch (range 0-399 °C) (16).

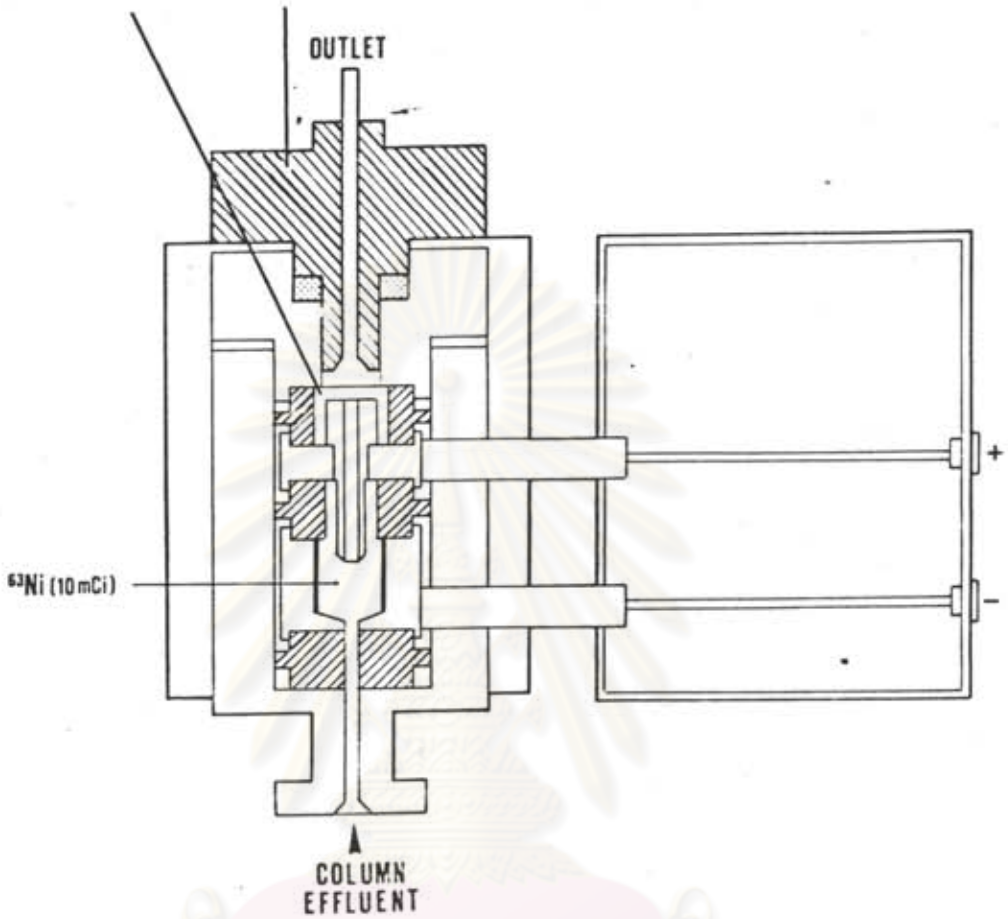

Fig. 4.9 The Electron-Capture Detector ECD-40

6. Detector heating LED (17)

- blinking when the temperature controller is regulating the detector temperature
- full intensity during detector heating phase
- half intensity when detector temperature is higher than the present one

7. Detector alarm (18) Light switch from green to red(with subsequent power cut off) in case of detector overheating or when the detector connector is disconnected.

8. Five-turn potentiometer (19) to adjust pulse amplitude in the range of 0 to 50 V and pulse width push button selector (μsec) (20) which selects 1 μs when operating with nitrogen or 0.1 μs when using argon/methane.

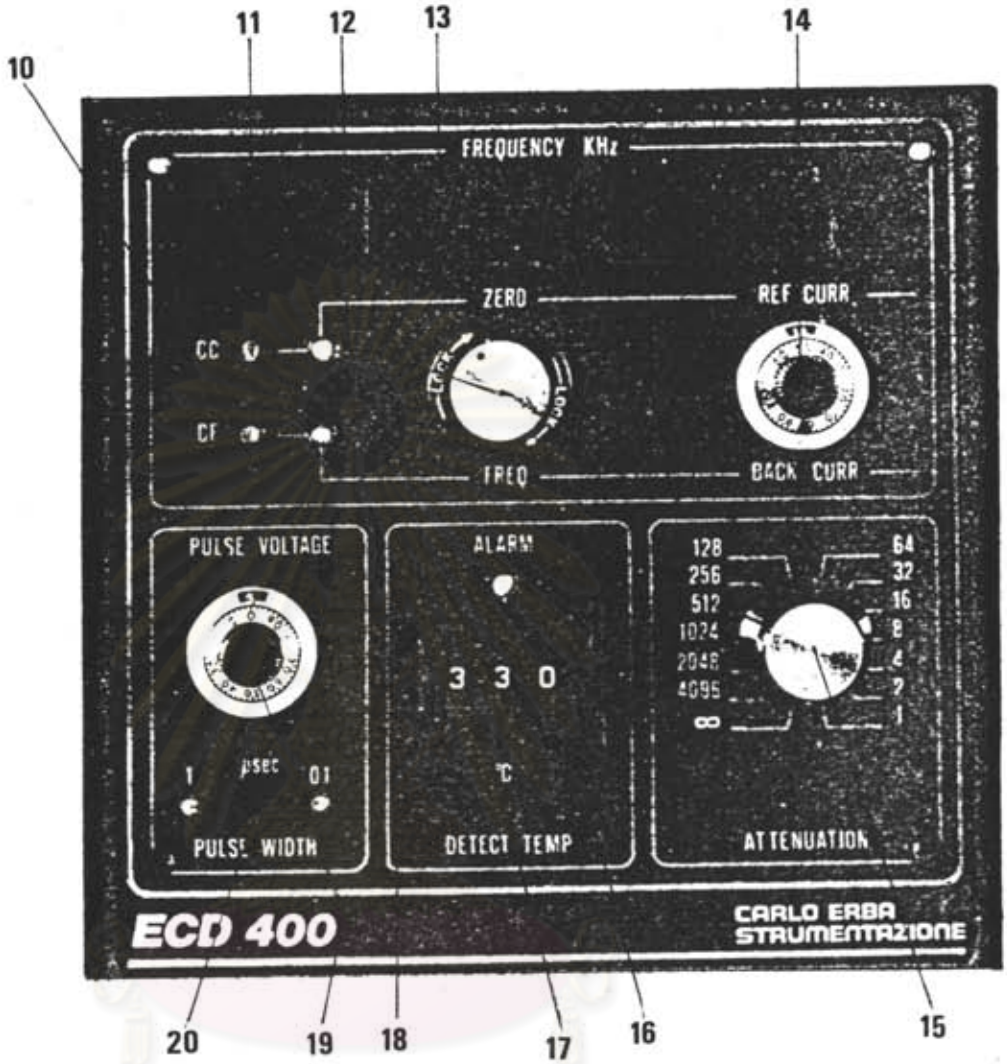

Fig. 4.10 The ECD Control Module 400

4.1.2 Cryogenic system (Cryo 520 Module)

The cryogenic unit has been developed to perform sub-zero temperature operations of the column by introducing liquid carbon dioxide (LCO_2) or liquid nitrogen (LN_2) inside the oven. In this experiment liquid nitrogen is used as coolant.

The Cryogenic unit 520 comprises the following parts :-

- Control Module Cryo 520 communicates with the MFC 500 controller

- The coolant system which comprises the valve and pneumatic acessories for LN_2

4.1.2.1 Cryo 520 control module

The front panel of the control module is shown in Figure 4.11 and consists of the following functions :

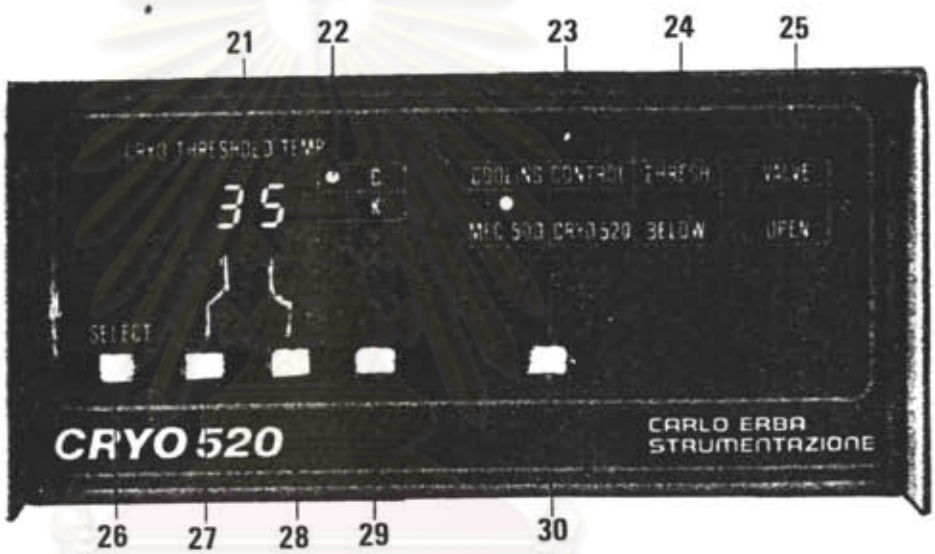

Fig. 4.11 Front panel of CRYO 520 Unit

- A "CRYO THRESHOLD TEMP" display (21) and LEDs (22) to indicate the temperature scale chosen. This cryo threshold is the selectable temperature at which the cryo unit activates the valves, closes the cooling oven flap of the MEGA GC and starts cooling. The coolant valve delivers LN_2 according to pulses. Frequent and short pulses are performed when the setting temperature is nearly reached.

- "COOLING" control LEDs (23) to indicate the option of cooling operation under the control of MFC 500 or under the control of the CRYO 520 unit. This control under the MFC 500 may reach oven temperatures of up to 5-10 °C above room temperature, it ispossible to reach sub-ambient oven temperatures by selecting the control under the command of CRYO 520.

- "THRESH BELOW" LED (24) to indicate that the oven temperature is under the set threshold temperature

- "VALVE OPEN" LED (25) to indicate that the coolant valve is activated and coolant is being taken into the oven

- "SELECT" key (26-30) to address and select the functions 21 to 23. This key must be depressed and remains depressed while entering the selected value for threshold temperature (27-28), the temperature scale (29) and the cooling control command (30).

4.1.2.2 Coolant valve and pneumatic accessories for LN_2

The coolant system consists of a coolant valve, the pneumatic lines and a coolant container which is shown in Figure 4.12

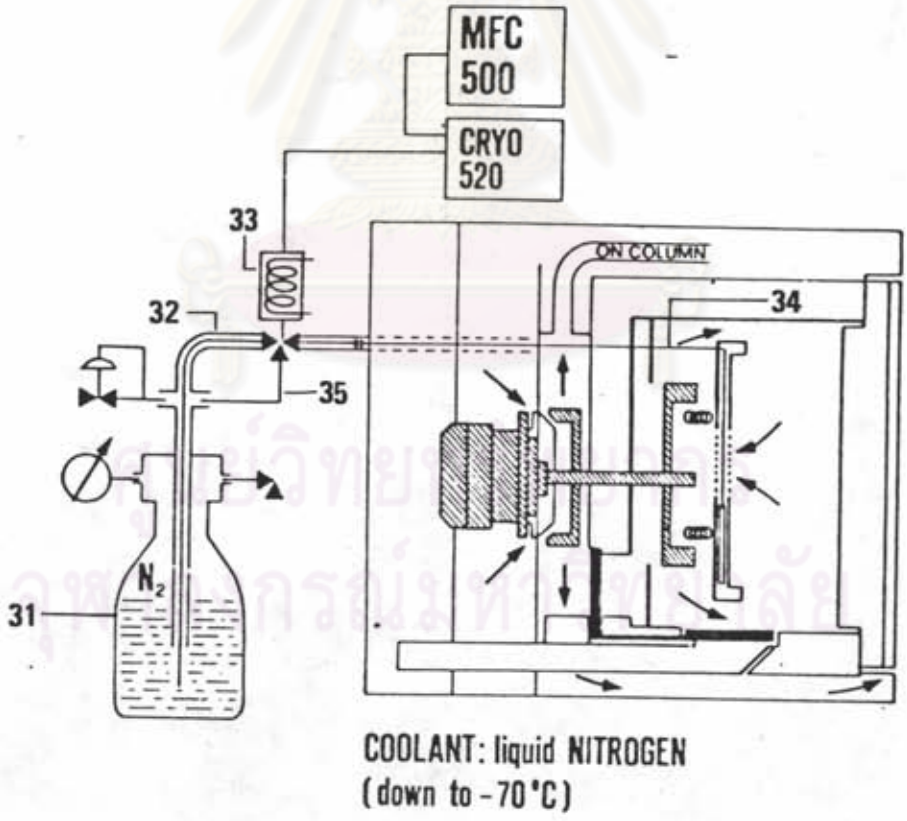

Fig. 4.12 Schematic diagram for components of CRYO 520 unit using LN_2

- A liquid nitrogen container (31) with a minimum pressure of 0.4-0.5 bar. It is extremely important to operate with this constant pressure for accurate temperature regulation

- Pneumatic line (32) of teflon 4*2 mm with an outer copper tube of 12 mm OD connects the liquid nitrogen container to the 3 way coolant valve (33), which is used for liquid nitrogen intake into the oven

- Stainless steel pneumatic lines (34) of 4*3 mm and 6*5 mm that connect the coolant valve to the diaphram internal cavity of the oven

- A pneumatic line (35) that connects the coolant valve to the liquid nitrogen container. This overflow connector will help to keep the pressure constant inside the container

Proper insulation of the pneumatic lines is essential in order to get the coolant into the GC in liquid form.

4.1.3 Capillary columns

The columns used in the experiments are wall-coated open tubular (WCOT) capillary columns. They are made of fused-silica capillary tubing (0.05 to 0.53 mm internal diameter) with a film (0.1 to 8.0μm) of stationary phase uniformly applied to the inside of the capillary wall. WCOT capillary columns offers high efficiency for the difficult separation of a large number of sample constituents. In this work,three columns of different stationary phases and polarities are used, they are

4.1.3.1 Non-polar column, **OV-1**

It has 100% dimethyl polysiloxane as stationary phase. The specifications of this column are as follow :-

- column length = 50 m
- column diameter = o.22 mm
- film thickness = 0.5 μm
- operating condition = -60 °C to 375 °C

4.1.3.2 Slightly or medium polar column, DB-1701

It has 7% phenyl, 7% cyanopropyl and 86% methylsilicone as stationary phase. The specifications of this column are as follow :-

- column length = 60 m
- column diameter = 0.255 mm
- film thickness = 1 μm
- operating condition = -20 °C to 300 °C

4.1.3.3 High polarity column, DB-210

It has 50% methylsilicone and 50% fluoropropyl as stationary phase. The specification of this column are as follow :-

- column length = 30 m (two columns)
- column diameter = 0.25 mm
- film thickness = 0.5 μm
- operating condition = -20 °C to 260 °C

4.1.4 Column installation

The column configuration with the right support and fittings are shown in Figure 4.13

To install the column in the injector side, put the column about 4 cm. deep into the injector. For the detector side, put the end of the column about 1 mm under the detector inlet. Then fasten

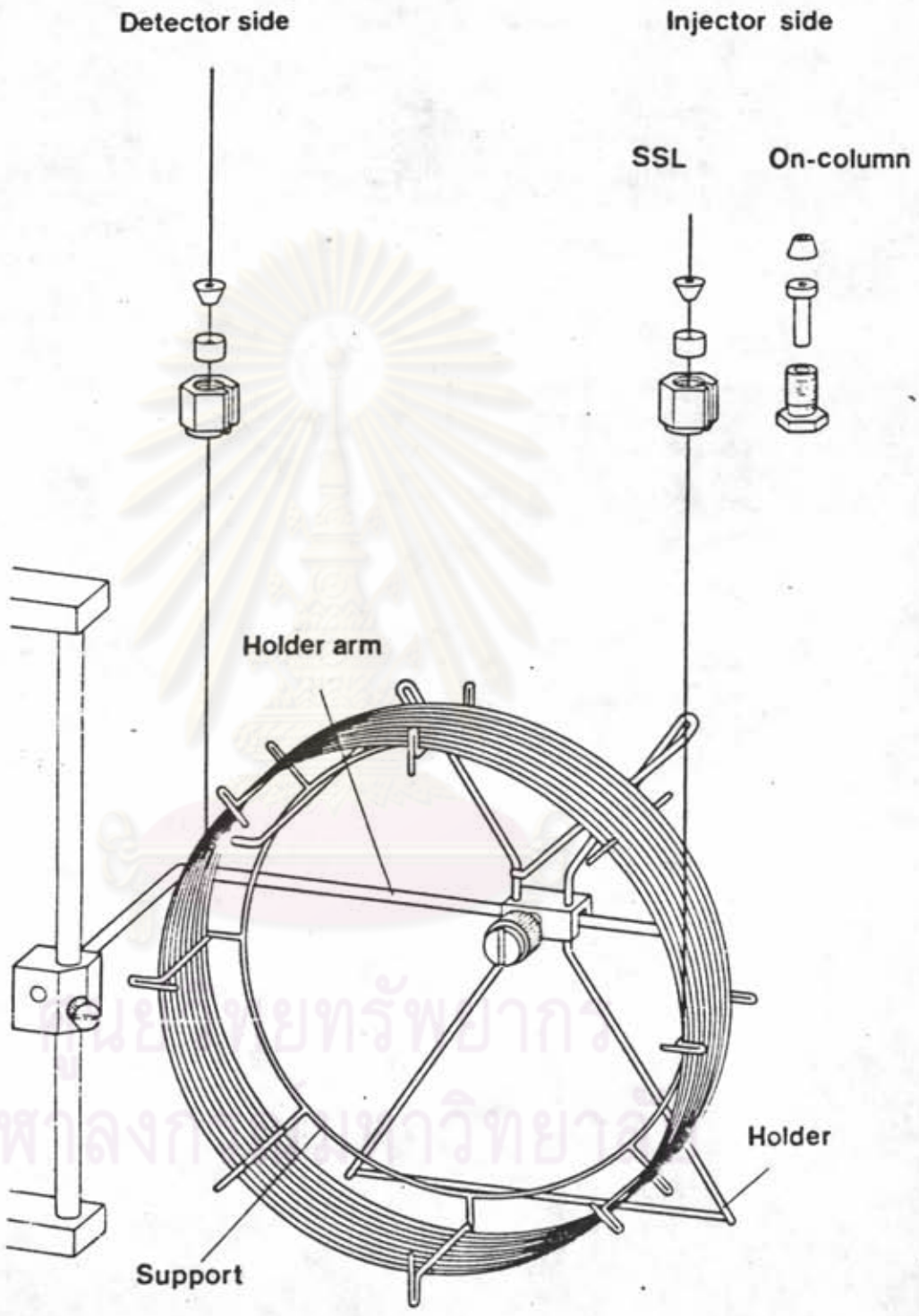

Fig. 4.13 Fused silica capillary column installation on the injector and the detector

the fitting tightly enough to be sure that the column will not move.

4.1.5 Column conditioning

A freshly deposited liquid phase will retain residual traces of solvents, along with lower molecular weight liquid phase fractions. These products progress through the column and emerge at the detector to yield a baseline offset and extraneous peaks. Therefore preconditioning of the column is necessary. In addition, periodic conditioning of older columns may be necessary due to the accumulation of non-volatilized material from the sample or an impure carrier gas. Selection of the conditioning temperature should take into consideration the operating temperature of the gas chromatography and the temperature limit of the liquid phase. High conditioning temperatures achieve stable baselines more rapidly but shorten column lifetime. Lower conditioning temperatures may prolong column life, but longer conditioning time is needed to achieve stable baselines. Overnight conditioning at normal flow rate and medium temperature (150 °C-200 °C) is optimum. It is recommended that the column should be disconnected from the detector during conditioning to minimize condensation of the liquid phase materials and contaminants at the detector. Before heating above 50 °C, the new column should be purged for 5 minutes with pure carrier gas at normal flow rates to removed any adsorbed oxygen. Columns are destroyed quickly by exposure to high temperatures without a flow of carrier gas.

4.2 Experimental Procedures

During the experiments, all the compounds will be divided into 7 families and examined on three different columns as shown in Table 4.2

Table 4.2 Classification of CFC compounds examined

FAMILY	COMPOUNDS	NO. OF COMPOUNDS
1	CFCs with 1 carbon atom and mixed hydrogen atoms	13
2	CFCs with 2 carbon atoms and no hydrogen atom	8
3	CFCs with 2 carbon atoms and one hydrogen atom	7
4	CFCs with 2 carbon atoms and two hydrogen atoms	7
5	CFCs with 2 carbon atoms and three hydrogen atoms	7
6	CFCs with 2 carbon atoms and four, five hydrogen atoms	6
7	CFCs with carbon double bonds and all hydrogen atoms	16

The procedures for each family are as follow :-

1. The mixtures of CFC compounds are prepared in a suitable solvent with the concentration for each compound of 0.001-0.005 cm^3/cm^3 solvent. The solvent being used should not show interactions with the stationary phase but should show high solubility towards the compounds. In this case the solvents that have been chosen are o-xylene, dichloromethane, acetone and toluene. When the same compounds were tested with these four types of solvents, the retention times obtained were nearly the same. This means that these solvents can replace one another to avoid solvent peaks overlapping

compound peaks.

2. The total mixture consists of :

- Hydrocarbons,which are n-alkanes,starting from methane (CH_4) to the alkanes which elutes after the highest boiling point compound.

- CFCs for each family. In each run, two or three compounds with different concentrations and different boiling points are mixed together or added to the existing mixture in order to facilitate the peak identification.

3. The experimetal conditions are :

- pressure of helium = 240 KPa
- pressure of hydrogen = 50 KPa
- pressure of air = 150 KPa
- pressur of nitrogen = 150 KPa
- split ratio = 1:150 to 1:180
- injector temperature = 50 °C
- detector temperature = 280 °C
- initial and final temperature of columns are different depending on the limit for each column
- temperature increasing rate = 2 °C/min for every column

4. Before injection, be sure that everything is ready. The temperature-program and the processing system are already set. The flame is already ignited and it does not extinguish. To ignite the flame, reduce the air pressure to one-third of normal required and depress the "IGNIT" on Electrometer Control Module EL-480 for a few seconds until a slight "POP" is heard. Then the "ZERO" knob will be adjusted to zero in order to obtain the chromatogram with a good baseline.

5. The quantity of sample injected is 1μl. After injection, depress the "PROG START" on the MFC 500 to start working. Meanwhile, the processing system (CLAS System) of the Solvay Laboratory, which is linked with the gas chromatography, will collect and record all the data until the experiment is finished. Then the results will be printed and the chromatogram will be plotted. The results will show the retention time and the area for each peak. The peaks of the CFCs can be identified according to the different concentrations and different retention times.