CHAPTER - 4

EXPERIMENTAL TECHNIQUES

SYNTHESIS OF MONOMER AND ITS CO-POLYMERS

The present section deals with the synthesis of dihydroxy coumarin which were then subjected to the polycondensation.

Maleic acid, Sebacic acid, phthalic acid, Isophthalic acid, Terephthalic acid used for polymerisation were AR grade. Phloroglucinol required for synthesising the monomer of dihydroxy coumarin was also AR grade. All the chemicals were claimed to be pure to 99% by the manufacturers.

SYNTHESIS OF 5-7 DIHYDROXY-4-METHYL COUMARIN (1)

An ice-cold mixture of Ethylacetoacetate and conc. H SO was prepared. The proportionate quantity of phloroglucinol was added slowly to the ice cold mixture by maintaining the temperature between 0 to 5°C. The reaction mixture was left undisturbed overnight. Next day, it was poured on in the ice cold water. The solid was separated out by filtering and dried. The solid obtained was recrystallized by alchohol for purification. Structural formula of the 5-7 dihydroxy 4-Methyl coumarin is show in fig. 4.1

SYNTHESIS OF POLYMER

The synthesis of polymer involves the steps, first step is the preparation of acid chloride and second is polymerization.

PREPARATION OF ACID CHLORIDE (2)

Thionyl Chloride is used for synthesizing acid Chloride from acid. 1:2 proportion of acid and thionyl chloride was refluxed on water both for 5 to 6 hours. A drop of pyridine was added as an catalyst in the preparation of acid chloride. Excess of thionyl chloride was distilled off.

Acid chlorides of maleic acid, sebacic acid, phthalic acid, isophthalic acid and terephthalic acid were prepared by above method. After the preparation of acid chloride, they are immediately used for polymerisation. Acid chlorides were used instead of acids for preparation of polymers due to their higher reactivity. Structural formulae for all the acid chlorides are shown in fig. 4.2

POLYMERISATION (3)

For synthesising the polymer, monomers must be bifunctional. The monomer used for synthesising the polymer is 5,7-dihydroxy-4-methyl Coumarin and dibasic acids. Both the monomers satisfy the condition of polymerisation, that they have two reactive sites.

Polymers were prepared by condensing acid chlorides of dibasic acid with 5,7 dihydroxy-4- methyl coumarin.

An appropriate acid chloride was dissolved in dry pyridine and cooled in an ice-bath. Then 5,7- dihydroxy-4- methyl coumarin dissolved in pyridine, was added with stirring. The reaction mixture was stirred continuously by magnetic stirrer for one and half hour. After the stirring, the mixture was kept overnight. Nextday, 1:1 ice-cold water and HCl solution is added to the mixture. The white precipitate was separated, filtered and washed with alcohol. The precipitate was purified by solvent-nonsolvent method. DMF was used as solvent and alcohol as non-solvent.

During the synthesis extreme care was taken with regard to the cleanliness and the purity while preparing and handling the specimens. All the glasswares used during synthesis were cleaned by acetone. After cleaning they were dried at 60°C.

The structural formulae for the monomer (M) and its copolymers P1, P2, P3, P4 and P5 have been shown in figure 4.3

INFRARED SPECTRA

Infrared spectra (IR) is principally of use in detecting functional groups and in disclosing the identity of a unknown compound. In coumarin, IR spectra has revealed the cojugated lactone apart from the identification of functional groups. The IR spectra for different coumarin derivatives reported elsewhere (4,5,6,7) give the idea about the structure. The carbonyl stretching frequency is observed in the region 1700-1750 cm^{-1} while the weak to medium intensity bands in the region 3025-3175 cm-1 is due to C-H strething vibration. The C=C skeletal vibration give rise to band at 1613-1639 cm^{-1}. Other band also present at 1410 cm^{-1} was attributed to tertiary -OH deformation. The different IR freqencies are noted down for coumarin and its copolyesters.

IR SPECTRAL DATA

M	P1	P2	P3	P4	P5
1640	1740	1700	1750	1680	1745
3400-3000	2900	2800	2900	3000	2800
1340	1610	1610	1605	1575,1510	1610
1310	1390	1430	1470	1430	1450
1190	1250	1300	1300	1280	1390
1060	1080	1240	1230,1150	1110	1215
800	860	1060	745	780	1070
760	710	720	720	730	720

In monomer M, the presence of broad band at 3400-3000 cm^{-1} confirms the presence of -OH group while such a broad band was found out to be absent in all polymers indicate that no -OH group

is present but the bands in all polymers near 3000 cm^{-1} are due to the -CH stretching(4). The band near 1700 cm^{-1} in all specimens confirms the presence of carbonyl group (4). The C=C stretching gives rise to the bands near 1600 cm^{-1} .

C-O stretching vibration are seen by the bands present at 1250 and 1000 cm^{-1} . The presence of 3500 cm^{-1} in M and absence of the same in all polymer specimen proves that no hydroxyl group is present in polymer which can be confirmed by looking at the structure.

The IR spectra for the monomer M and polymer specimen P1, P2, P3, P4, and P5 are represented in figure 4.4 to 4.9 respectively.

VISCOSITY

The usefulness of solution viscosity as a measure of polymer molecular weight has been recognised ever since the early work of Staudinger (8). Solution viscosity is basically a measure of the size of polymer molecule. It is empirically related to the molecular weight of linear polymers. The simplicity of the measurements and usefulness of the viscosity molecular weight correlation are so great that the viscosity measurement constitutes an extremely valuable tool for the molecular size of polymers.

EXPERIMENTAL METHOD

The polymer solutions have been characterized by measuring their intrisic viscosity. Viscosity measurements are carried out in standardized Ostwald suspended level viscometer at room temp (27°C).

The solvent is introduced into the clean and dry viscometer held vertically upward. The efflux time is noted for solvent. Average

of three independent readings is noted. The viscosity for the solvent Dimethyl formamide (DMF) is calculated.

A powdered polymer is dissolved in the above solvent to make 1% solution. This solution is introduced in the viscometer and efflux time is noted. From the efflux time, the viscosity is determined.

Measurement (9) of solution viscosity are usually made by comparing the efflux time 't' required for a specified volume of polymer solution to flow through a capillary tube with the corresponding efflux time ' t_o ' for the solvent. The relative viscosity is given by the formula

$$\eta_{rel} = \frac{\eta}{\eta_o} = \frac{t}{t_o}$$

In the above equation η and η_o refer to solution and solvent viscosity each, which are proportional to the corresponding flow times t and t_o through the viscometer capillary.

Viscosity data for polymers

Solvent : Dimethyl formamide (DMF)
Concentration: 1%
Temperature : 27°C.

Polymers	P1	P2	P3	P4	P5
Relative Viscosity	1.038	1.041	1.048	1.042	1.039

PREPARATION OF SPECIMEN

A brief description of the preparation of the specimens used in present investigations is given in this section. The specimens are studied in as-received condition and also after subjecting them to mechanical as well as thermal treatments.

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i. a) AS RECEIVED SPECIMENS

The synthesis of monomer has already been described earlier. The monomer was crystallized twice from alcohol to ensure purity of the specimen. The melting point of the purified monomer tallies with the one reported in the literature. The crystals of the monomer were then dried and powdered. The monomer specimen prepared in this manner is designated 'as received' monomer.

i. b) POLYMERS

All the polymer were accomplished by known method of poly condensation (3,10). The purification of polymers was carried out by solvent-nonsolvent method. The solvent in which the polymers are soluble and also insoluble are usually found out. It is found that all the polymers used here are soluble in Dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) but they are insoluble in alcohol. The polymers obtained by solvent-nonsolvent method were dried and powdered. The polymers obtained thus are called as received polymers.

ii) MECHANICALLY DEFORMED SPECIMENS

Powdered 'as received' specimen could be compressed to form the pellets. A stainless steel press was used for the compression. The pellets formed in this way were usually 1 cm in diameter and 0.1 mm thick. The average pressure applied to specimens under which they are compressed is around 2500 Kg. cm^{-2} . Such specimens are called 'Mechanically deformed' or 'Mechanically compressed' specimens.

iii) THERMAL TREATMENTS

Monomer and Polymer specimens are annealed in a muffle furnace at 60, 70 and 80°C. for one hour in a silica boat. On completion of

the annealing time, the specimen was quenched to room temperature by withdrawing the boat on a block of aluminium and by a blast of cold air. Such specimens are designated as 'Annealed and quenched' spcimens.

INSTUMENTATION

The instrument used for the study of Excitation and Emission spectra of polymers is Aminco-Bowman spectrophotofluorometer (SPF) supplied by American instrument Co. Inc. The SPF consists of an optical unit which includes an electrical panel, Xenon lamp with housing and a blower, two monochrometers, cell compartment, two slit holders (installed in monochromators) photomultiplier housing with manually operated rotary slit turret and filter holder with shutter control. The Xenon lamp power is supplied from D.C. power supply and sweep power circuit is energized by a mercury battery contained within the optical unit. The Xenon lamp operates on 19.8 volts DC. The photomultiplier microphotometer includes an electronic chesis, control panel and meters. The photometer operates on 115 volts A.C.

A) PRINCIPLE OF OPERATION

Light from Xenon lamp is dispersed by the excitation monochromater (grating type) into monochromatic radiation incident on the sample. Emitted light from the sample is dispersed by a similar monochromator into monochromatic radiation incident on the photomultiplier. The light is then transformed to a weak electrical signal and fed to the photometers, where it is amplified. The photometer output is indicated on the self contained meter. This output signal is connected to a strip chart Recorder.

The greatings are oscillated by motor driven cams to which are coupled graduated discs for visual observtion and adjustment of·

wavelength. Provision is also made to adjust the wavelength manually. Spring loaded arms follow the continuous cam rotation and oscillate the gratings. The maximum and minimumn angular positions of gratings correspond to the high and low points of cams and to the maximum and minimum wavelength of the monochromators namely, 800 and 200 nm respectively. The recorder could be started and stopped at any desired wavelength reading on the graduated scale. As the motoer driven cam moves with uniform speed, the intermediate wavelength valued between two extreme readings on the chart could be determined by equally dividing the linear distance betwen two end points into the number of wavelengths involved in the corresponding range. The peak position of an excitation or an emission peak read from the chart was found to be coinciding with the position of the corresponding peak are observed by the manual operation of the graduated disc.

B) OPTICAL UNIT

The optical unit incorporates two gratings monochromators of the basic type first described by Elbert. Properties of this mounting are discussed fully in two artides by W.G.Fastie. The schematic diagram of the optical system is shown in figure which illustrates the following.

i) The excitation monochromator selects light of monochromattic wavelength from the Xenon arc lamp and focuses it on sample holder. The light emitted from the sample is received by emission monochromator and directed on the photomultiplier tube.

ii) Monochromators are optically identical except for a difference in 'blaze' wavelength between the two gratings. The excitation grating is blazed at 300 nm (1st order) to strengthen the output from the Xenon lamp which decreases below 400 nm. The

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emission grating is blazed at 500 nm (1st order) to improve the response to the emission at wavelength from   400-600 nm.

iii))The Xenon arc lamp, located at the focus of the spherical mirror, MR-1 (vide figure a), produces a continuous spectrum peaking at 400 nm and again at 900 nm (beyond the range of the instrument). Light from the lamp indicated by the three rays, strikes MR-1, which renders it parallel and directs it to the plane grating. Dispersed light from the grating is redirected to the second mirror MR-2 (identical to MR-1) which focuses a monochromatic image of the lamp on the centre of the sample holder. The magnification of the system is unity; resulting in an image equal in size to Xenon arc (1.8 mm by 3.5 mm high). Emitted light from the sample is similrly dispersed by the emission monochromator and imaged on the photomultiplier slit. Five slit provisions are provided in an optical unit. Slits 2 and 3 determine the bandwidth and the resolution for excitation spectra, whereas, slits 4 and 5 decide the bandwidth and the resolution in the case of emission spectra. The photomultiplier slit turret controls the intensity. A convenient arrangement of the slits was found out by trial and error. This arrangement remains uncharged throughout all the measurement, thereby keeping the bandwidth and resolution constant.

A certain amount of scatter is always present in varying degree in any optical instrument. This is especially true for instruments which measure fluorescence. In the design of the equipment presently being used, though the scatter has been reduced to a practical minimum, a certain amount of scatter still exists. Thus, one observed scatter or reflection peaks whenever the excitation and emission wavelengths are equal. Due to uneliminated second order light from the gratings a noticeable amount of apparently spurious signal will frequently be present at high wavelengths. For example, if

emission is maximum at 300nm. there will be an indication at 600 nm. This spurious indication should be ignored, since it will usually not interfere with the shape of the peaks (both excitation and emission spectra). It can be eliminated with the use of suitable optical filters. Thus whether a given peak is genuine or not, can be verified by using the appropriate optical filters.

iv) A desicant chamber mounted on the sample housing of the SPF performs two functions. It serves as a light trap for the excitation wavelength and prevents condensation on the samples, especially under condtions of high humiity. The solid sample is fixed on the sample holder with the help of non-fluorescent grease, and placed diagonally in the sample compartment such that the sample faces both the excitation and emission monochromator slits. The sample holder is made of Ebonite, the surface being covered with black paper, further it does not show any excitation or emission peaks without the phosphor. The position of the sample holder is adjusted in such a way that it gives the maximum emission.

C) PHOTOMULTIPLIER MICROPHOTOMER UNIT

This assembly essentially consists of a light sensitive photomultiplir tube with associated circuitary and an amplifier which responds to a small curent produced by photomultiplier tube and registers the amplified current on a microphotometer. The photometer sensitivity is controlled by the metermultiplied switch which reduces the metr readings in the steps of 1,3,10,30,100,300 and 1000. he photomultiplier tube used into this setup is IP-21 with S4 spectral response.

OPERATING PROCEDURE FOR RECORDING THE SPECTRA

Excitation spectra are obtained by recording the luminescence intensity at fixed wavelength as a function of the wavelength of

the exciting source. Whereas, emission spectra are records of the spectral distributions of luminescence at fixed excitation wavelength.

a) The photomultiplier shutter was opened after inserting the sample in the sample chamber.

b) The emission monochromator wavelength disc was then allowed to rotate slowly with the help of slow-fast control.

c) The photometer was set for high sensitivity. Subsequently the excitation wavelength disc was changed manually in steps if 20 nm at the completion of each emission scan until a maximum is indicated on the photomer.

d) When excitation wavelength was located, the emission scan was stopped and the emission wavelength was adjusted for maximum emission indicated on the meter.

e) The excitation wavelength disc was again adjusted until a new maximum on scale meter reading was obtained.

Knowing the excitation peak wavelength and placing the excitation monochromator wavelength disc at this known value, the emission spectrum was recorded. Similarly, knowing the emission peak wavelength, the emission monochromator wavelength disc was adjusted at this known value, and the excitation spectrum was recorded. During the above procedure the sensitivity was adjusted with the help of metermultiplier, so that the photometer reading was within the range of the meter.

Whenever, the instrument is switched ON for measurements a warm-up period of about half an hour was allowed for stability. The excitation and emission spectra were recorded immediately one after another to avoid the effect of voltage fluctuations. These

fluctuations were kept to a minimum with the help of a voltage stabilizer.

Fluorescence spectra were recorded for monomer M and Polymer P1 to P5 in as received condition. Above specimens are annealed quenched to room temperature. These Annealed quenched specimen were used for recording emission spectra. The emission spectra was also recorded for all the above specimens after they were mechanically compressed in the form of tablets. Emission spectra for all the specimens were taken at Excitation wavelength of 250 nm.

THERMOLUMINESCENCE GLOW CURVE READER

Modern Thermoluminescence (TL) recording unit can vary from the simple to the extremely sophisticated one. The basic requirement of all the various designs is sample holder cum heater, a temperature control unit, and a light detection system, but the design of each of these devices are plenty and varied TL glow curve read unit employed for present investigation system consisted of photomultiplier tube, a high negative voltage unit, a d.c. amplifier a temperature programmer cum controller and a X-Y chart recorder Block diagram of the unit is presented in fig (1).

The output signal of photomultiplier tube when plotted as a function of temperature gives the TL glow curve of the specimen. Sample holder used was a metallic kanthal strip which is an alloy of chromium (Cr)-23%m iron, (Fe)-72%, Aluminium-(Al) -3% and Cobalt (Co)-2% which also acted as a heater. The size of the kanthal strip used in the experiment was 30x15x0.25 mm^3. Because of the small size of kanthal heater, high temperature can be obtained with low power input, also faster cooling could be attained after switch off of the power supply. A chromel allumel thermocouple, spot welded at the centre on the lower side of the kanthal strip was used for the record of temperature. Kanthal strip was secured tightly between

two brass electrodes. These electrodes were fitted in 233x110x24 mm³ bakelite plates which could slide in and out of a lalumini7m guide box, at the top of which an EMI 9804 B photomultiplier tube was mounted. The photomultiplier tube was kept in a˜light tight brass cylinders. When the bakelite plates were fully inside the guide box, the specimen position (Kanthal strip) place vertically under the photomultiplier tube. To reduce the thermal back ground of the heater quartz filter was placed between the heater and photomultiplier tube. Specimen could be chanrged by sliding the aluminium guide box drawer half way out.

A negative voltage of 900 volts was applied to photomultiplier tube which defects the photon emission from the specimen.

Power for the heater plate was driven from the temperature programmer to heat the specimen at desired rate. The light emitted by the specimen on linear heating was collected by photomultiplier tube and output signal was subsequently amplified by a d.c. amplifier and recorder using X-Y chart recorder.

In the present work the heating rate kept, was 2°C/Sec. and the specimens are exposed to the β-radiation source having the dose rate 2.3 x 10² rad/min.
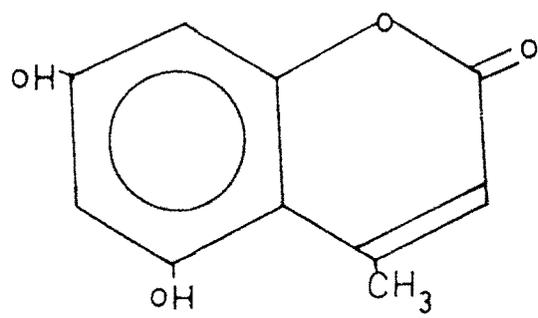
MONOMER M

FIGURE 4·1

1   SEBACYL CHLORIDE

$$ClOC - (CH_2)_8 - COCl$$
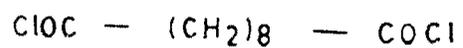
2   MALEIC ACID DI CHLORIDE

$$\begin{array}{ccc} CH & = & CH \\ | & & | \\ COCl & & COCl \end{array}$$

3   PHTHALOYL CHLORIDE
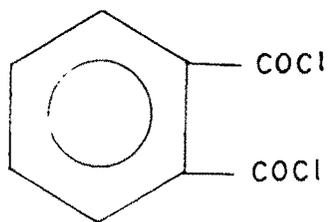
4   ISOPHTHALOYL CHLORIDE
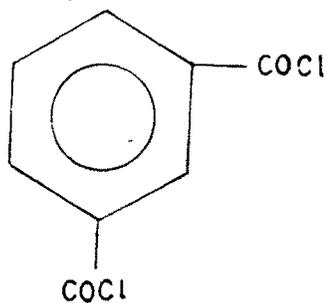
5   TEREPHTHALOYL CHLORIDE
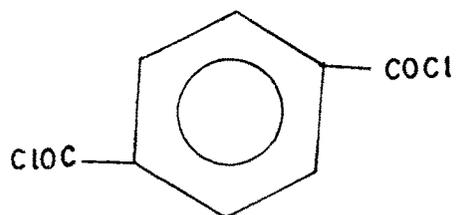
FIG. 4-2 STRUCTURAL FORMULAE FOR ACID CHLORIDES

MONOMER M
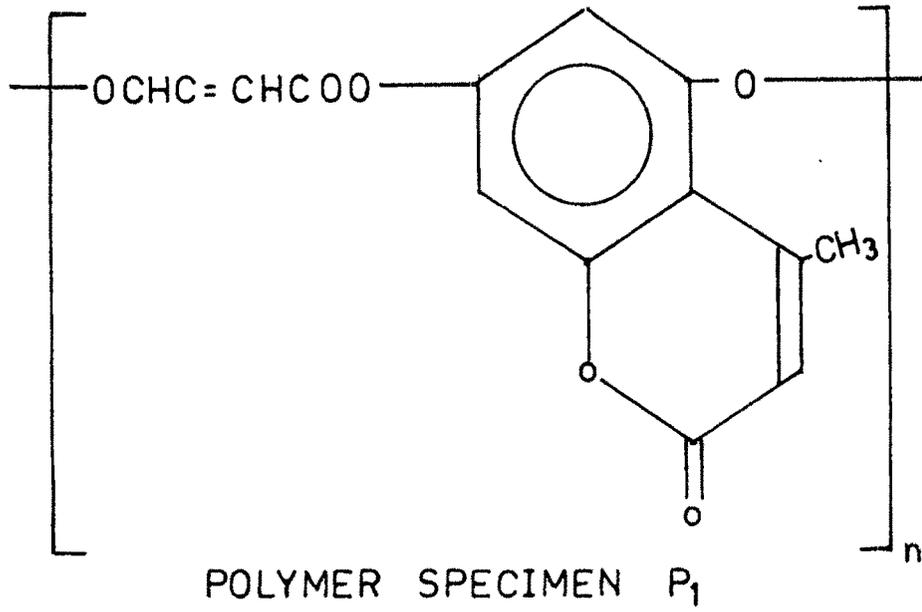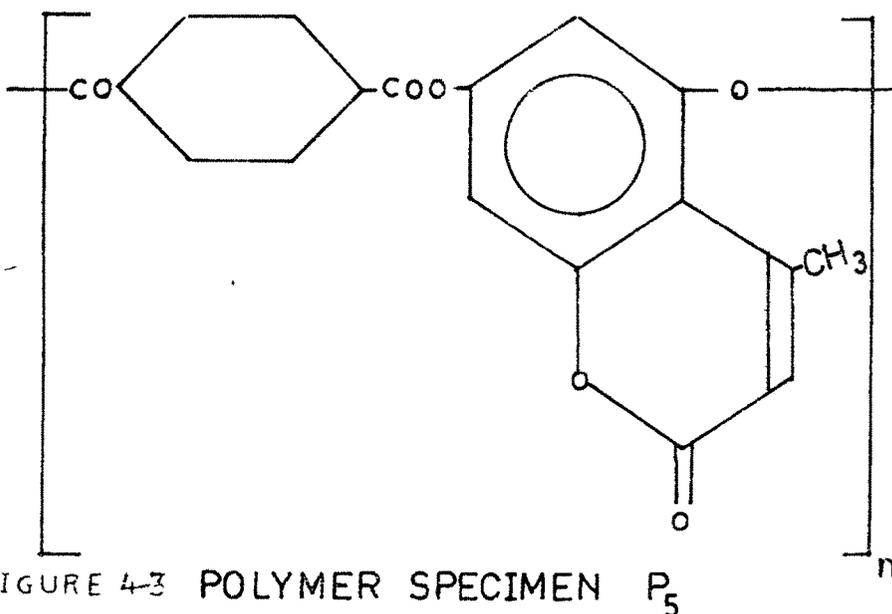
POLYMER SPECIMEN P_1

POLYMER SPECIMEN P_2

FIGURE 4-3

POLYMER SPECIMEN P$_3$

POLYMER SPECIMEN P$_4$

FIGURE 4-3 POLYMER SPECIMEN P$_5$

WAVENUMBER CM^{-1}
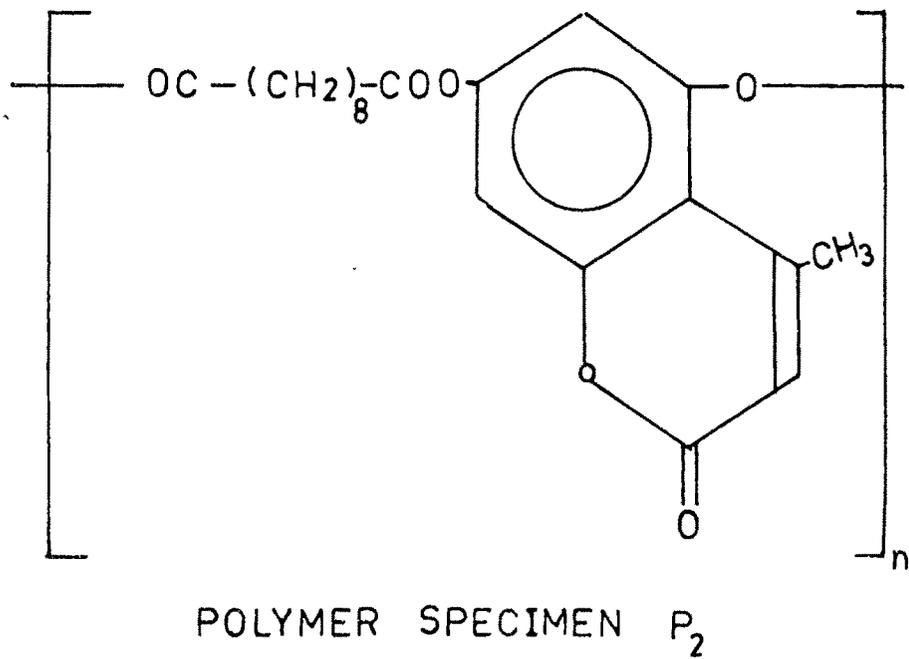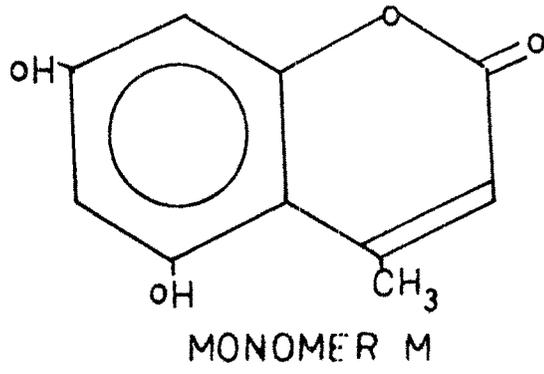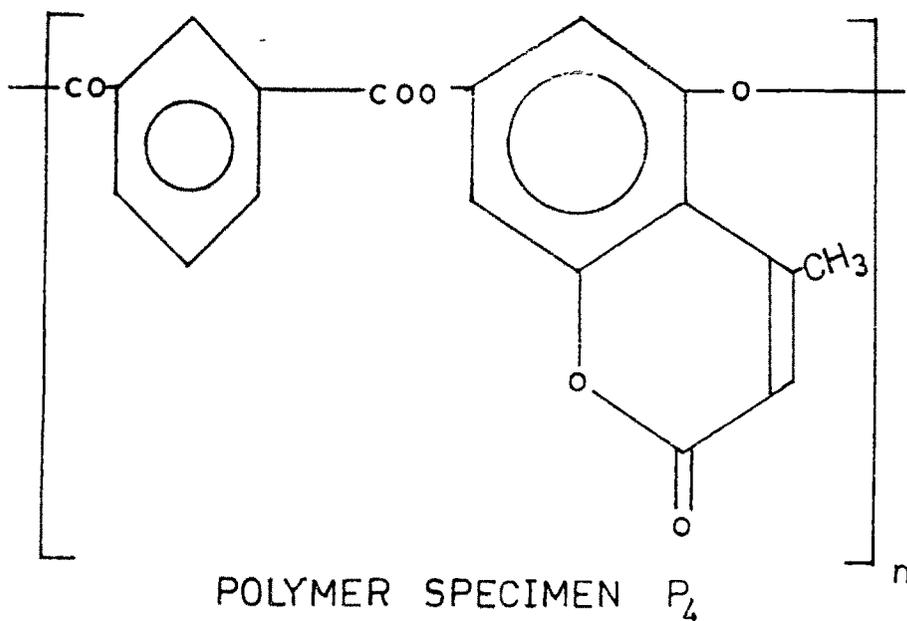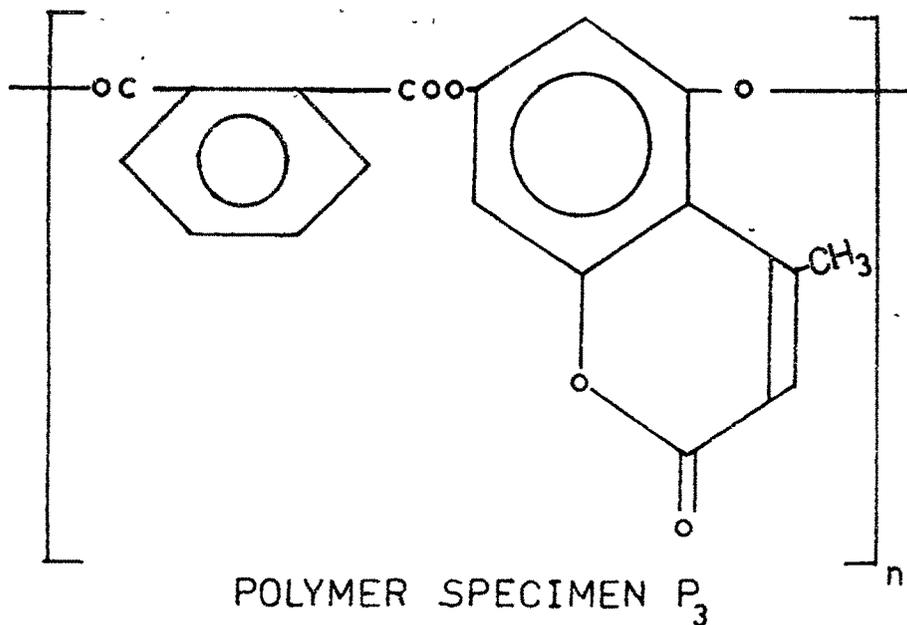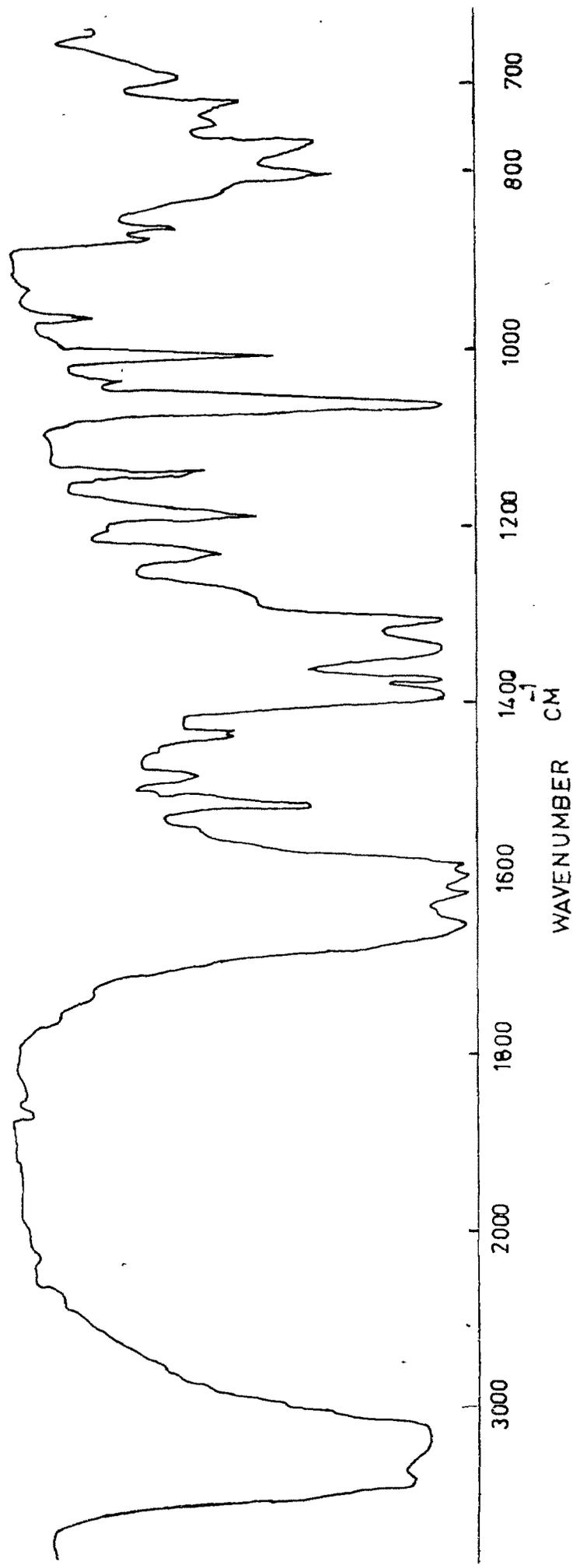
FIGURE 4·4 IR SPECTRA FOR SPECIMEN M

WAVENUMBER CM^{-1}
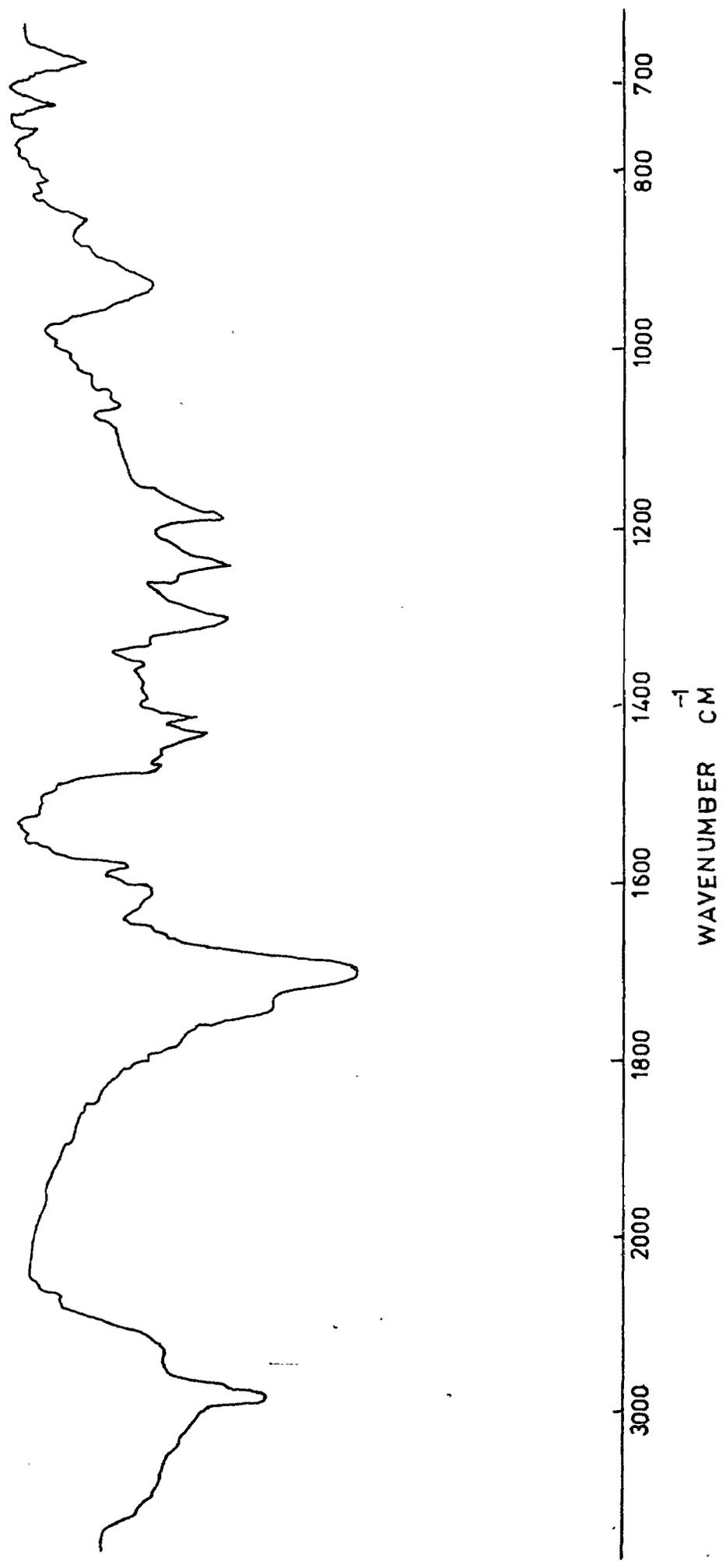
FIGURE-4.5 IR SPECTRA FOR SPECIMEN P1

WAVENUMBER CM^{-1}
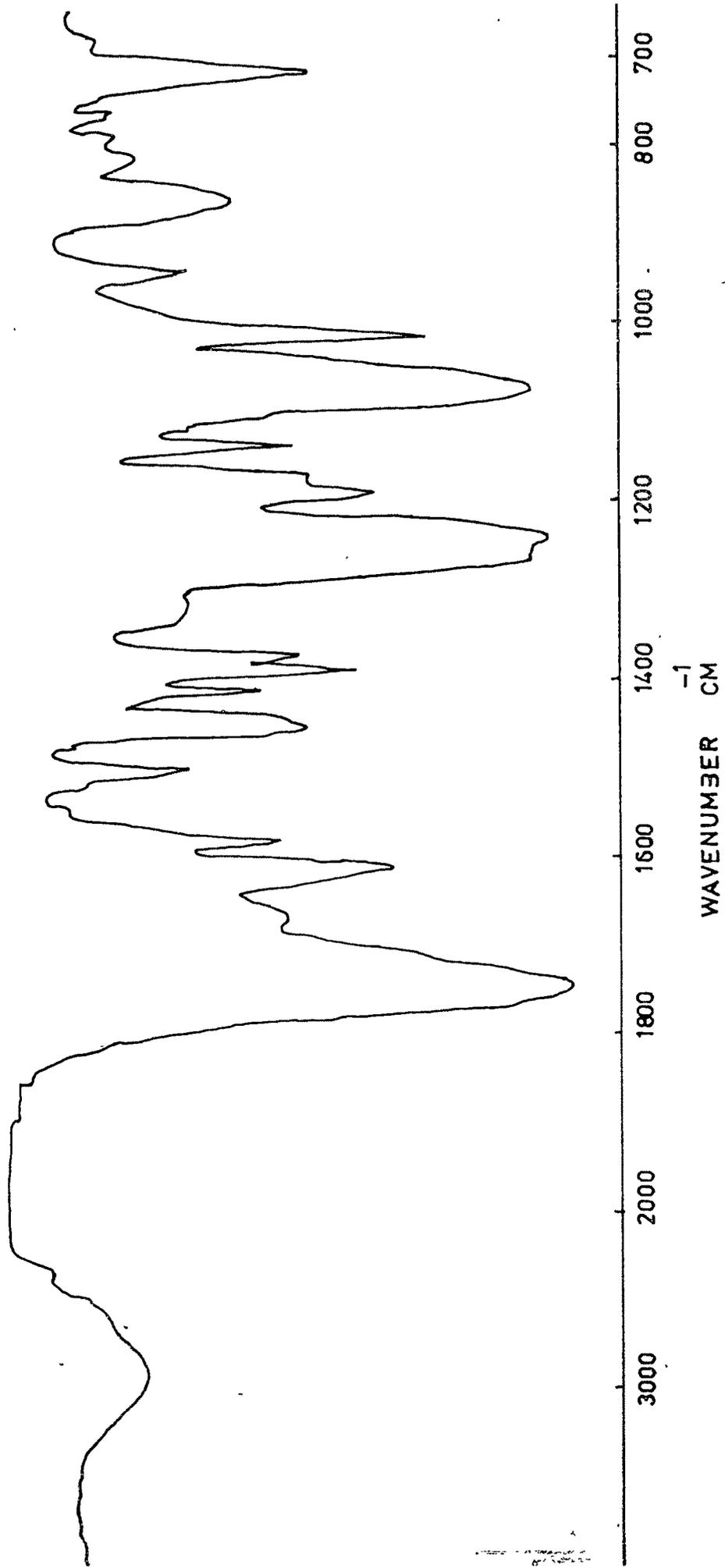
FIGURE-4.6 IR SPECTRA FOR SPECIMEN P$_2$

WAVENUMBER CM^{-1}
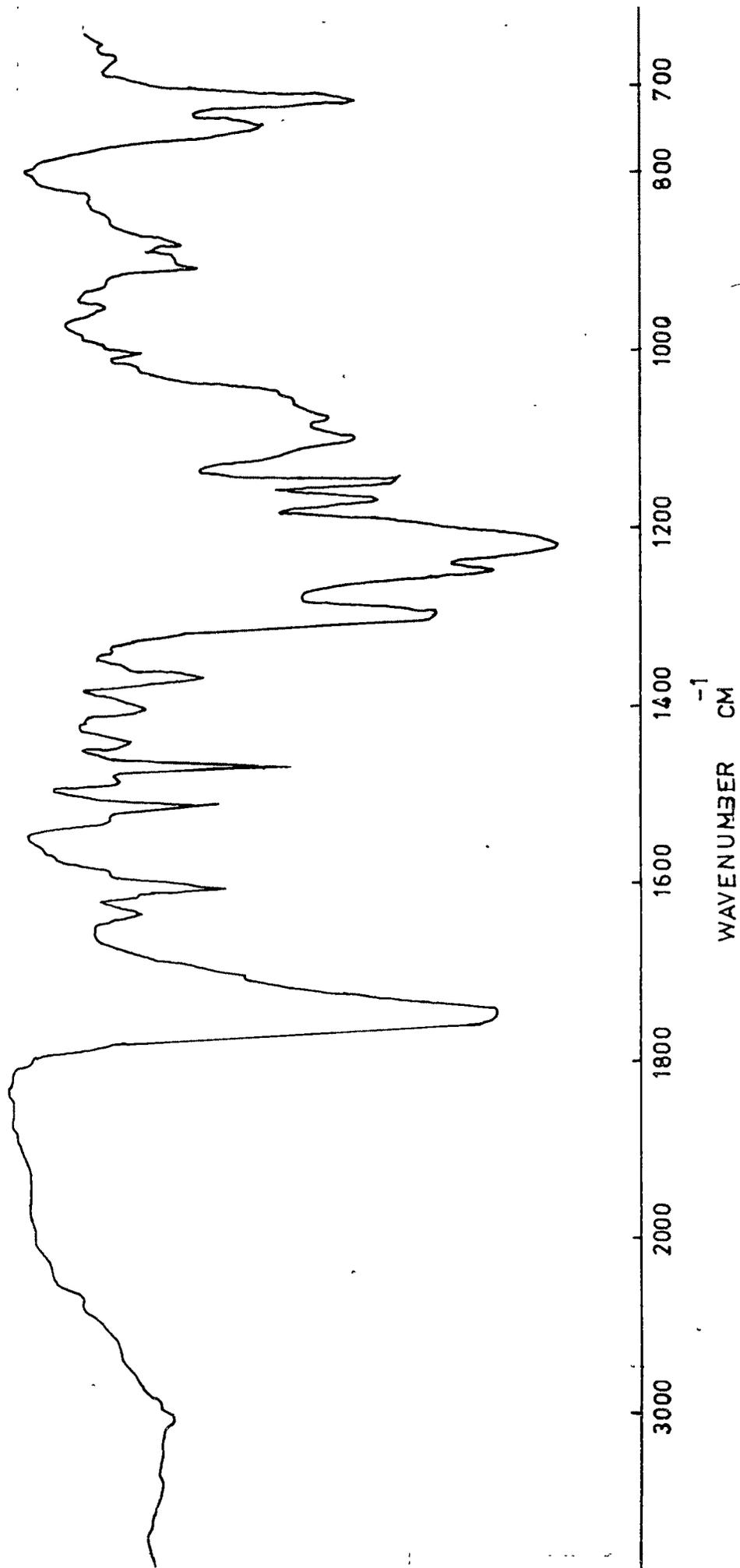
FIGURE-47 IR SPECTRA FOR SPECIMEN P3

WAVENUMBER CM^{-1}
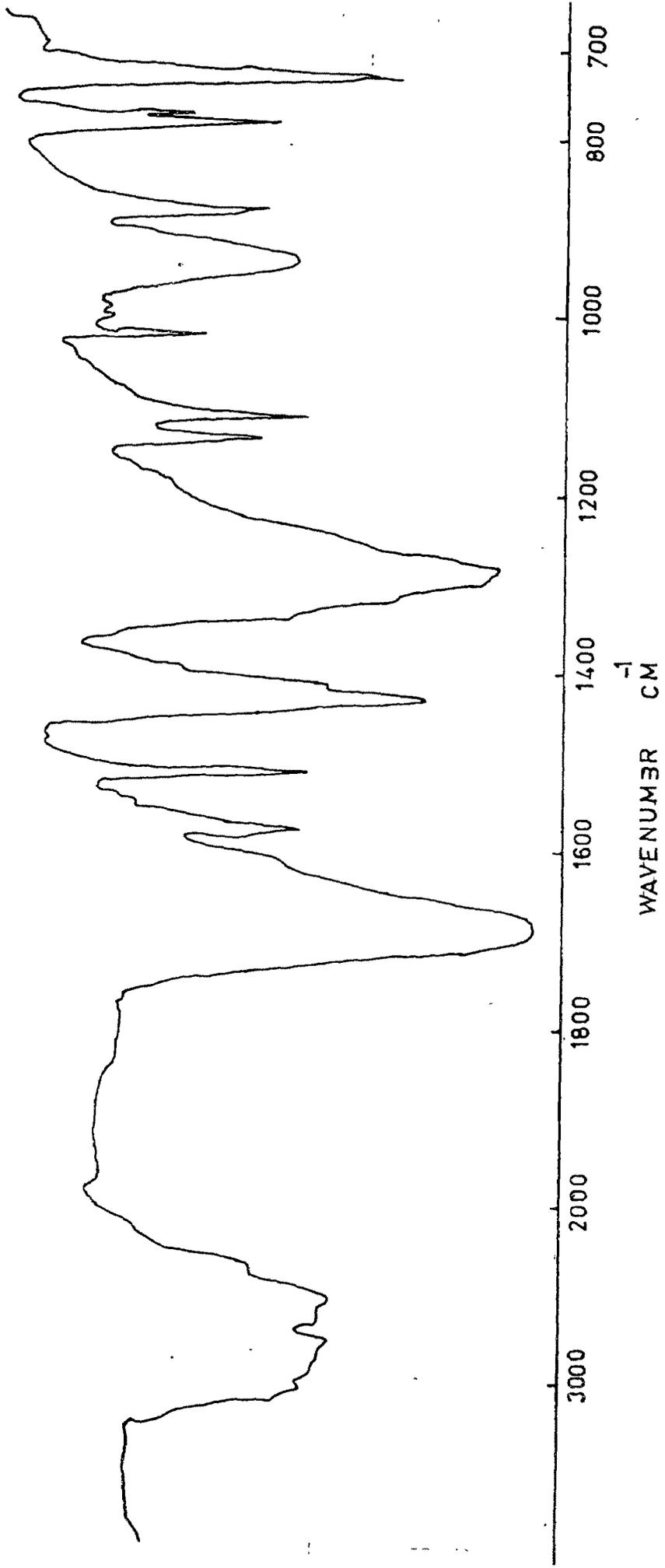
FIGURE-4.8 IR SPECTRA FOR SPECIMEN P$_4$

WAVENUMBER CM^{-1}
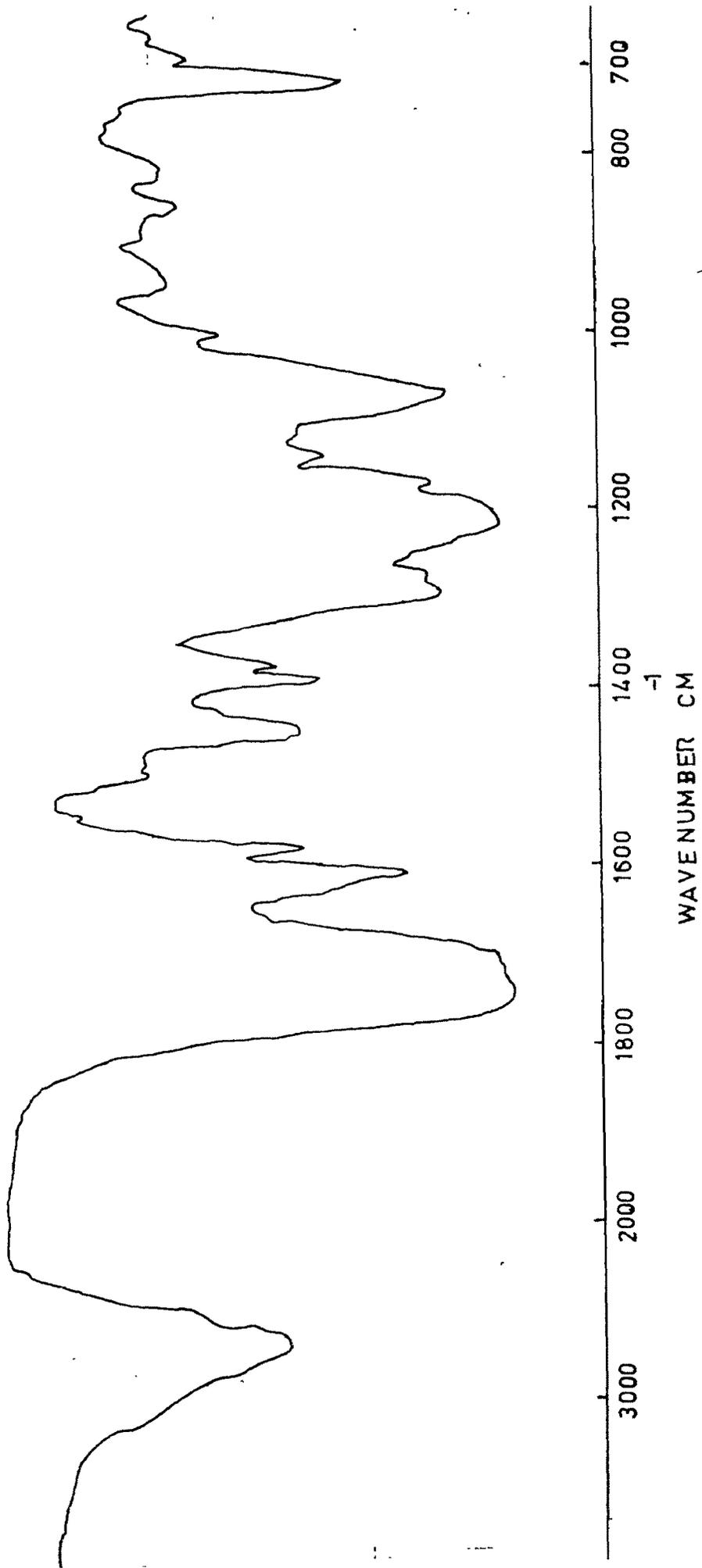
FIGURE-4.9 IR SPECTRA FOR SPECIMEN P$_5$

Labels (left side, top to bottom):
SLIT 4
CELL
SLIT 3
SLIT 2
XENON ARC LAMP
GRATING G-1
EXCITATION MONOCHROMATOR
MR-1
MR-2

Labels (right side, top to bottom):
SLIT 5
LIGHT TRAP AND DESICCANT CHAMBER
PHOTOMULTIPLIER TUBE
PHOTOMULTIPLIER TURRET SLIT 7
PHOTOMULTIPLIER SHUTTER & FILTER HOUSING
GRATING G 2
EMISSION MONOCHROMATOR
MR-4
MR-3
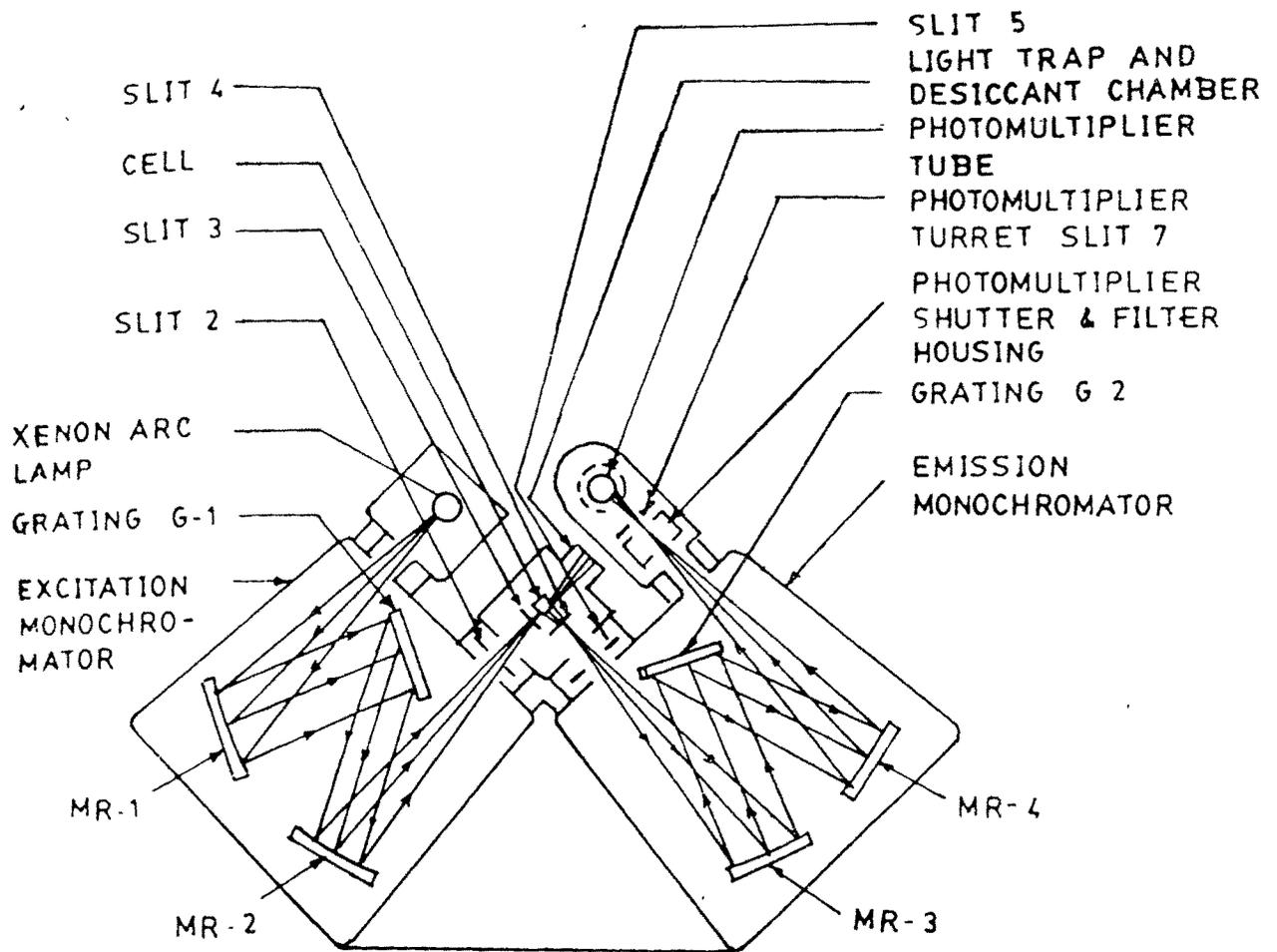
FIG·4-10 OPTICAL UNIT SHOWING POSITION OF SLITS

Fig-4.11 Block diagram of TL unit

D C Amplifier

Recorder

Thermocouple

-900V H T

Photomultiplier
Tube 9804 B

Quartz filter

Kanthal strip

Heater plate

Temperature
Programmer
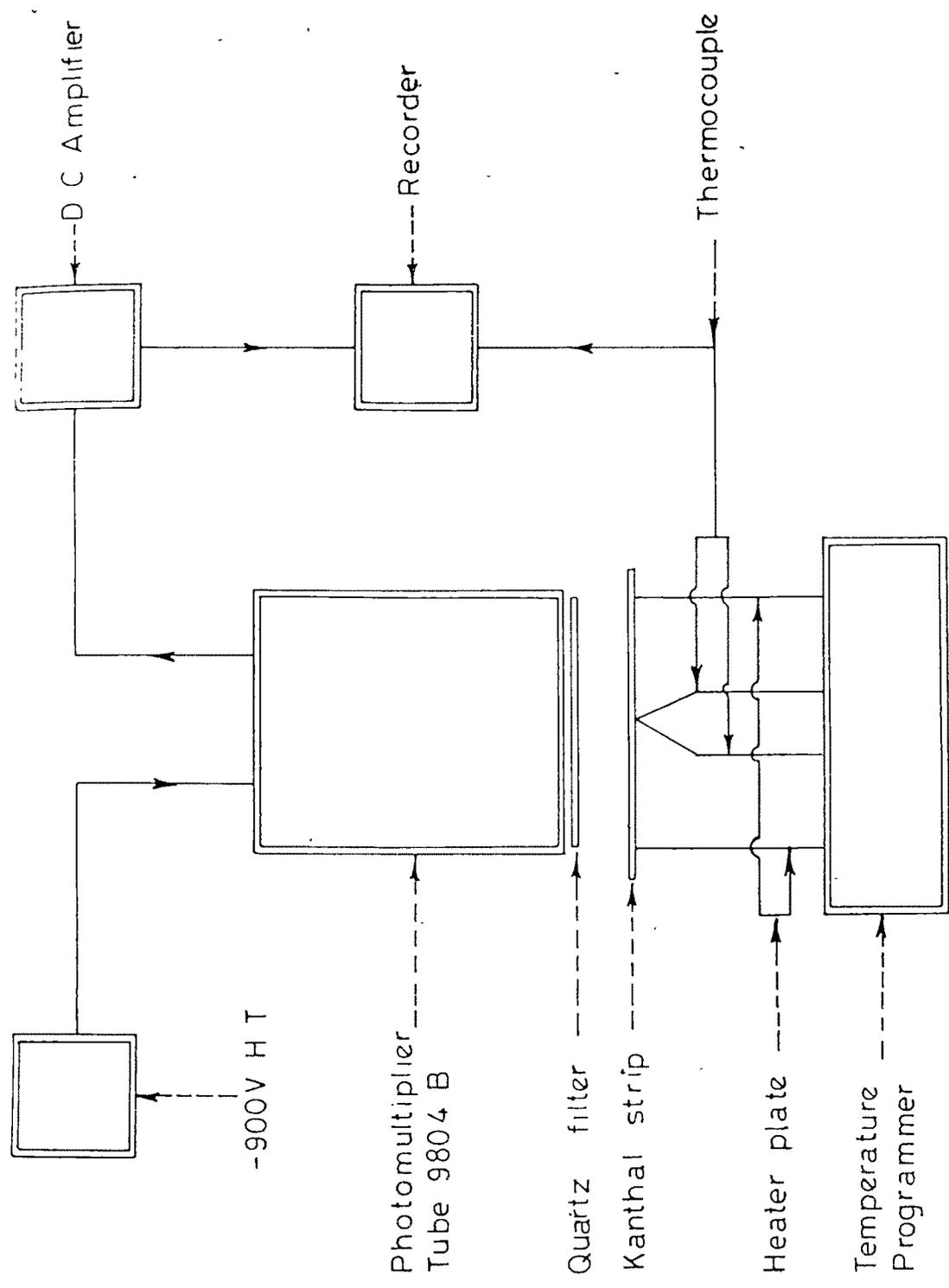
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