CHAPTER - 4

EXPERIMENTAL TECHNIQUES

SYNTHESES OF A MONOMER AND ITS CO-POLYMERS :-

The present section deals with the syntheses of dihydroxy coumarins which are then subjected to the polycondensations.

Maleic acid, Sebacic acid Phathalic acid , Isothapthalic acid and Terephthalic acid used for polymerization were all AR grade. The phloroglucinol required for synthesising the monomer of dihydroxy coumarin was also AR grade. All the chemicals, were claimed to be pure upto 99%, by the manufacturer.

SYNTHESES OF 5,7 - DIHYDROXY - 4 - METHYL COUMARIN [1] :-

An ice -cold mixure of ethylacetoacetate and conc. H_2SO_4 was prepared. The proportionate quantity of phloroglucinol was added slowly to the ice -cold mixture by maintaining the temperature between 0^0 to 5^0C. The reaction mixture was left undisturbed overnight. Next day, it was poured on in the ice-cold water. The solid was separated by filtering and then dried. These solid was then recrystallized by alcohol for purification. Structural formula for the 5,7 - Dihydroxy - 4 - Methyl Coumarin has been shown in figure 4.1.

SYNTHESES OF POLYMERS :-

The syntheses of polymers involve two steps, first being the preparation of acid chloride; and second the polymerization.

PREPARATION OF ACID CHLORIDE [2] :-

Thionyl chloride is used for synthesising acid chloride from acid. The 1:2 proportion of acid and thionyl chloride were refluxed on water for 5 to 6 hours. A drop of pyridine was added as a catalyst in the preparation of acid chloride. Excess of thionyl chloride was then distilled off.

Acid chlorides of maleic acid, sebacic acid, phthalic acid, isophthalic acid and terephthalic acid were prepared by the above method. After the preparation of acid chloride, there are immediately used for the polymerization. The acid chloride have been used instead of the acids, for preparation of polymers because of their higher reactivity. Structural formulae for all these acid chlorides are shown in figure 4.2.

POLYMERIZATION [3] :-

For the synthesising of polymer ; the monomers must be bifunctional. The monomers used for synthesising the polymer here is 5, 7 - dihydroxy - 4 - methyl coumarin and the dibasic acids. Both the monomers satisfy the condition of polymerization, both having the two reactive sites.

Polymers were prepared by condensation of 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 the 5,7 - dihydroxy -4 - methyl coumarin which was dissolved in pyridine, was added to it with continuous stirring. The reaction mixture was stirred continuously by a magnetic stirrer for one and half hours. After this the mixture was kept overnight. Next day,a 1:1 mixture of ice-cold water and Hcl solution is then added to the previous mixture. The white precipitate formed was then separated, filtered and washed with alcohol. This precipitate was then purified by solvent - non solvent method. DMF being used as the solvent while the alcohol as a non solvent.

During the syntheses extreme care was taken with regard to the cleanliness and the purity; while preparing and handling the specimens. All the galsswares used during syntheses were also cleaned by acetone before use. They had been also been dried at 60^0C, on cleaning.

The structural formulae for the monomer (M) and its copolymers P_1,P_2,P_3,P_4 & P_5 have been shown in figure 4.3.

INFRARED SPECTRA :-

The infrared spectra (IR) is principally of use in detecting the functional groups and in disclosing the identity of an unknown compound. In coumarin, IR spectra has revealed the conjugated lectone; 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 observed in the region 3025-3175 cm^{-1} are due to the C-H stretching vibration. The C=C skeletal vibration gives rise to a band at 1613-1639 cm^{-1}. Another band also present at 1410 cm^{-1}, was attributed to tartiary - OH deformation. The different IR frequencies are noted down for coumarin and its copolyesters.

TABLE NO. 1

IR SPECTRA DATA

M	P_1	P_2	P_3	P_4	P_5
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
1160	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 the polymers. This indicates the absence of -OH group, however, 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 polymers specimen proves that no hydroxyl group is present in polymers which can be confirmed by looking at structure.

The IR spectra for the monomer M and polymer specimens P_1,P_2,P_3,P_4 & P_5 are presented in figures 4.4 to 4.9 respectively.

PREPARATION OF SPECIMENS :-

A brief of description of the preparation of the specimens used in the present investigations is given in this section. The specimens are studied in as received condition and in solution forms.

(a) AS RECEIVED MONOMER :-

The syntheses of monomer has already been described earlier. The monomer was crystallized twice from alcohol to insure 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 ' as received ' monomer.

AS RECEIVED POLYMERS :-

All the polymers were accomplished by known method of polycondensation [3,8]. The purification of polymers was carried out by solvent - non solvent 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 purified by solvent -nonsolvent method were dried and powered. The polymers obtained thus are called ' as received polymers' .

(b) PREPARATION OF SOLUTIONS :-

Five solvents having different polarity are selected for studying solvent effect on fluorescence. The selected solvents were Dioxane (DO), Tetrahydrofuran (THF), Dimethyl formamide (DMF), Acetonitrile (ACN) and Dimethyl sulphoxide (DMSO). Different physical properties [9,10,11] of the solvent are listed in table no.2.

TABLE NO. 2

Physical properties of solvent	**DO**	**THF**	**DMF**	**ACN**	**DMSO**
Density	1.0336	0.8892	0.9487	0.7822	1.1014
Viscosity	1.439	0.55	0.924	0.345	1.996
Dieletric constant	2.209	7.58	36.71	37.5	46.68
Refractive index	1.42241	1.4071	1.43047	1.34411	1.4783

All specimens the monomer M and polymers P_1 through P_5 were dissolved in the above solvents at two different concentrations viz. 100 mg of each specimen in 25 ml and 50 ml respectively.

INSTRUMENTATION :-

The instrument mainly used for the study of excitation and emission spectra of polymers is Aminco-Bowman spectrophotofluorometer (SPF)supplied by American Instrument Co. Inc. The SPF consist of an optical unit which includes an electrical panel, xenon lamp with housing and a blower, two monochromators, cell compartment, two slit holders (installed in monochromators) Photomultiplier housing with manually operated slit turret and filter holder with shutter control. The xenon lamp power is supplied from D.C. power supply. The sweep power circuit is energized by a mercury battery contained with the optical unit. The xenon lamp operates on 19.8 Volts D.C. The photomultiplier microphotometer includes an electronics chasis, 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 monochromator (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 gratings are oscillated by motor driven cams to which are coupled the graduated discs for visual observation and also for adjustment of wavelength. provision is also available for the adjustment of wavelength manually. Spring loaded arms follow the continuous cam rotation and oscillate the gratings. The maximum and minimum angular positions of gratings correspond to the high and low points of cams and to the maximum and the 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 motors driven cam moves with uniform speed, the intermediate wavelength value between two extreme readings on the chart could be determined by equally dividing the linear distance between two end points into the number 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 graduated disc.

(B) OPTICAL UNIT :-

The optical unit incorporates two grating monochromators of the basic type first described by Elbert. Properties of this mounting are discussed fully in two articles by W.G. Fastie. The schematic diagram of the optical system is shown in the figure 4.10 which illustrates the following

1) The excitation monochromator selects light of monochromatic wavelength from the xenon arc lamp and focuses it on the sample holder. The light emitted from the sample is received by emission monochromator and directed onto the photomultiplier tube.

2) Monochromators are optically identical except for a difference in 'blaze ' wavelength between the two gratings. The excitation grating is blazed at 300 nm (first order) to strengthen the out put from the xenon lamp which decreases below 400 nm. The emission grating is blazed at 500 nm (first order) to improve the response to the emission at wavelength from 400-600 nm.

3) The xenon arc lamp , located at the focus of the spherical near, MR-1 (vide figure 4.10), 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 mirror 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 long and 3.5 mm high). Emitted light from the sample is similarly 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 the trial and error. This arrangement remains unchanged throughout 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 wavelength 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 300 nm , 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 the excitation as well as 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.

4) 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 condition of high humiity. The solid sample is fixed on the sample holder with the help non fluorescent grease, and placed diagonally in the sample compartment such that sample faces both 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 way that it gives the maximum emission. Solvent under study was filled up in rectangular cuvette. Cuvette filled with solvent was kept in the sample compartment, such that the two faces of cuvette faces both excitation and emission monochromator.

(C) PHOTOMULTIPLIER MICROPHOTOMER UNIT :-

This assembly essentially consists of a light sensitive photomultiplier tube with associated circuitary and an amplifier which responds to a small current produced by photomultiplier tube and registers the amplified current on a microphotometer. The photometer sensitivity is controlled by the metermultiplier switch reduces the meter reading in the steps of 1,3,10,30,100, 300 and 1000. The 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 function of the wavelength of the exciting source Whereas, emission spectra are records of the spectral distribution 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 of 20 nm at the completion of each emission scan until a maximum is indicated on the photometer.

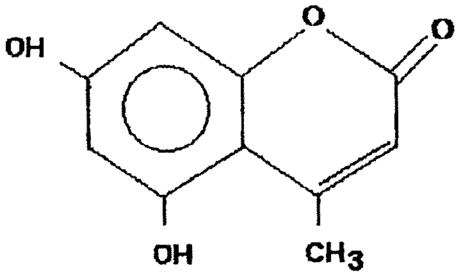
(d) When excitation wavelength was located, the emission scan was stopped and the emission wavelength was adjusted for maximum emission indicated on the meter.

(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 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 above an 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 P_1 to P_5 in as received conditions. Rectangular cuvette having 1 cm x 1 cm base was used for recording fluorescence of the specimens in solution forms.



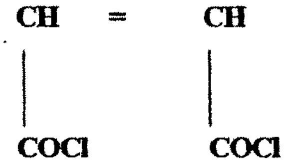
MONOMER M

FIGURE 4. 1

1. **SEBACYL CHLORIDE**

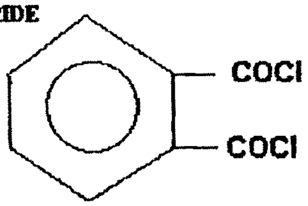
$ClOC-(CH_2)_8-COCl$

2. **MALEIC ACID DI CHLORIDE**

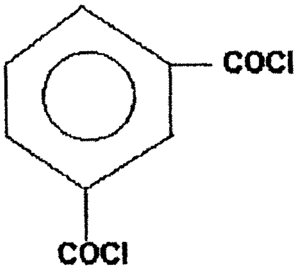


$$\begin{array}{ccc} CH & = & CH \\ | & & | \\ COCl & & COCl \end{array}$$

3. **PHTHALOYL CHLORIDE**



4. **ISOPHTHALOYL CHLORIDE**



5. **TEREPHTHALOYL CHLORIDE**

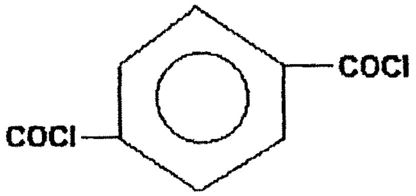
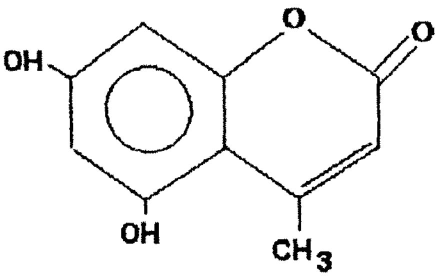
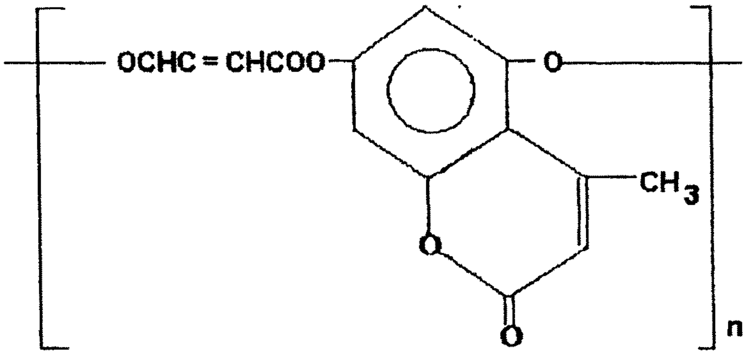


FIGURE 4.2 STRUCTURAL FORMULAE FOR ACID CHLORIDES

MONOMER M

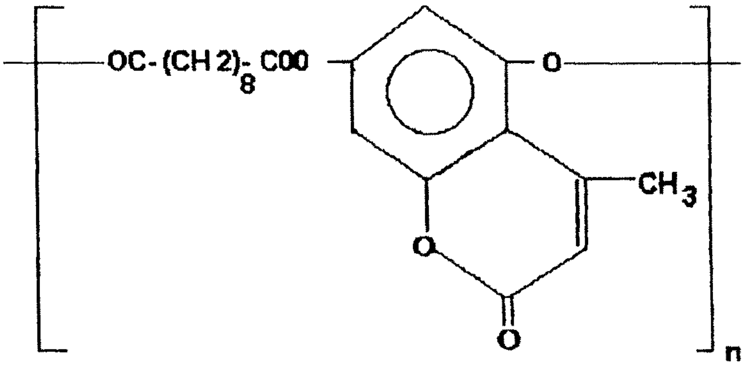


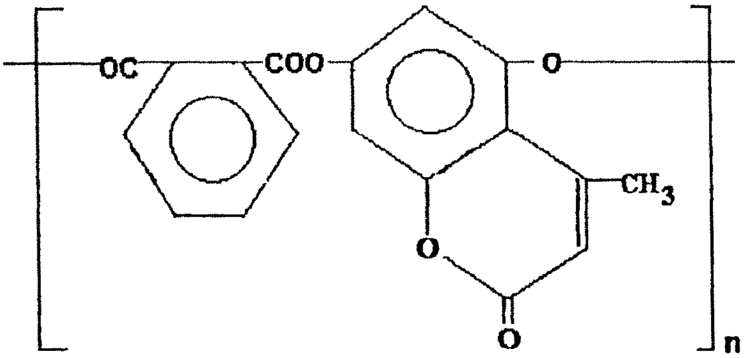


POLYMER SPECIMEN P1

FIGURE 4. 3

POLYMER SPECIMEN P2

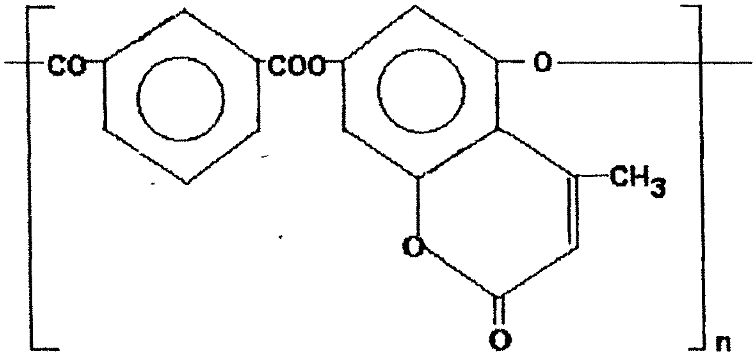


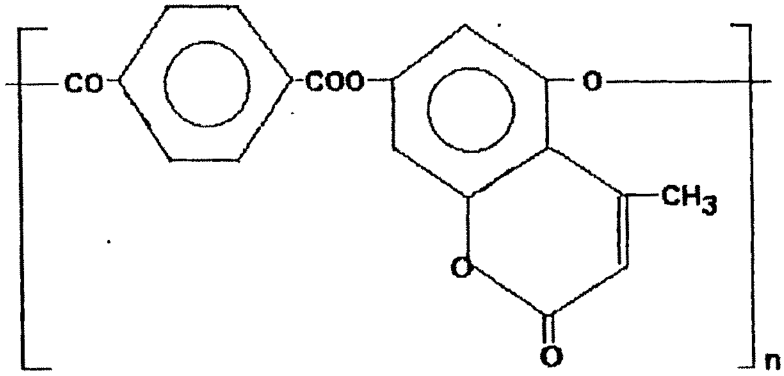


POLYMER SPECIMEN P3

FIGURE 4. 3

POLYMER SPECIMEN P4





POLYMER SPECIMEN P5

FIGURE 4.3

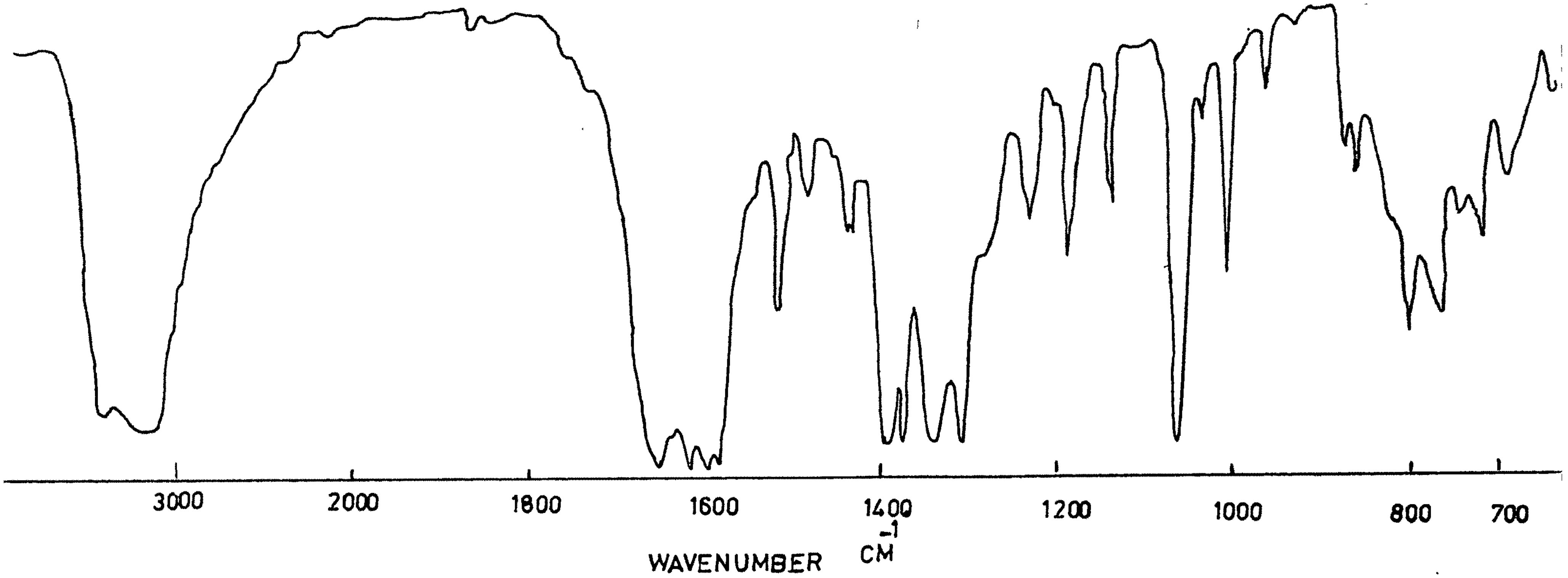


FIGURE 4-4 IR SPECTRA FOR SPECIMEN M-

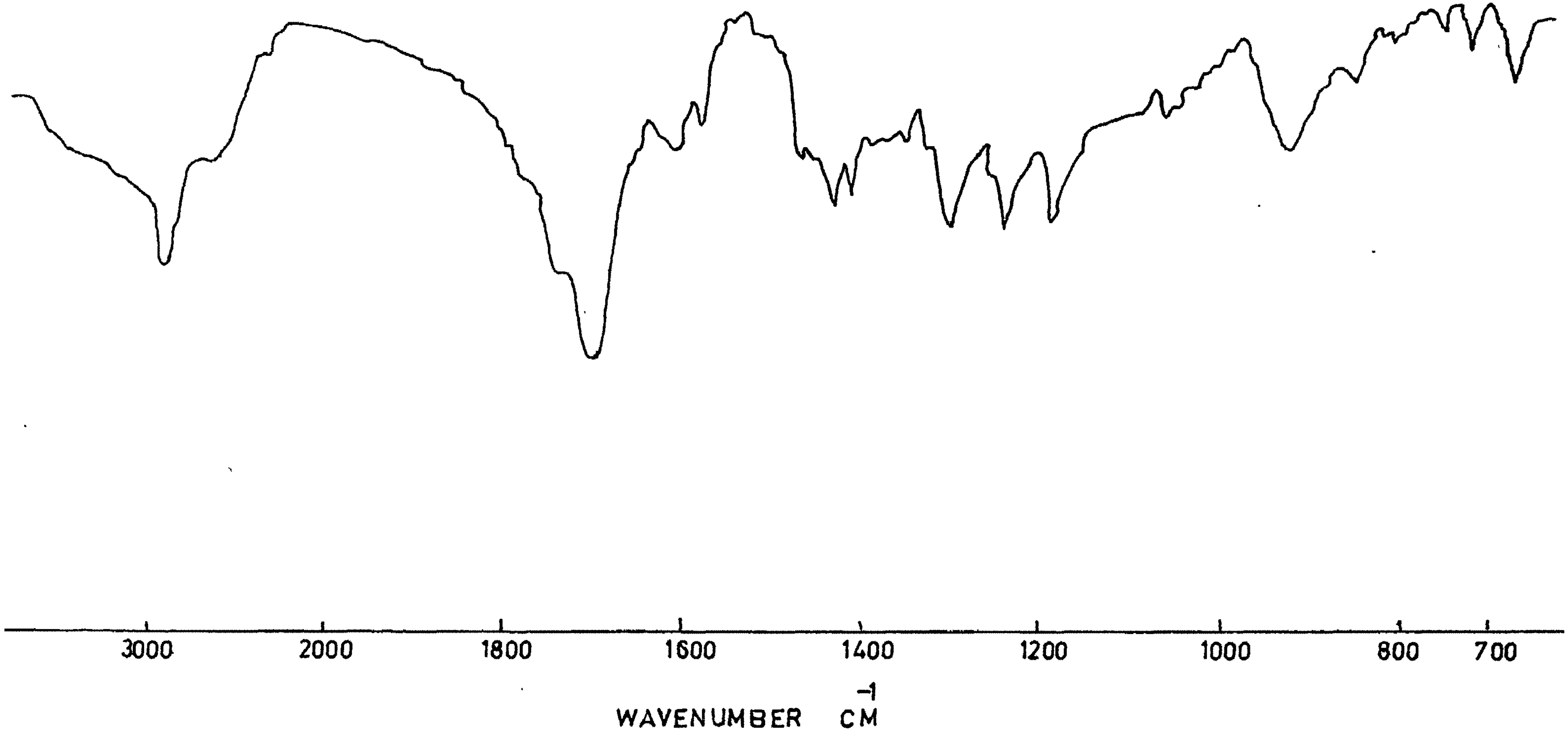


FIGURE-4·5 IR SPECTRA FOR SPECIMEN P1

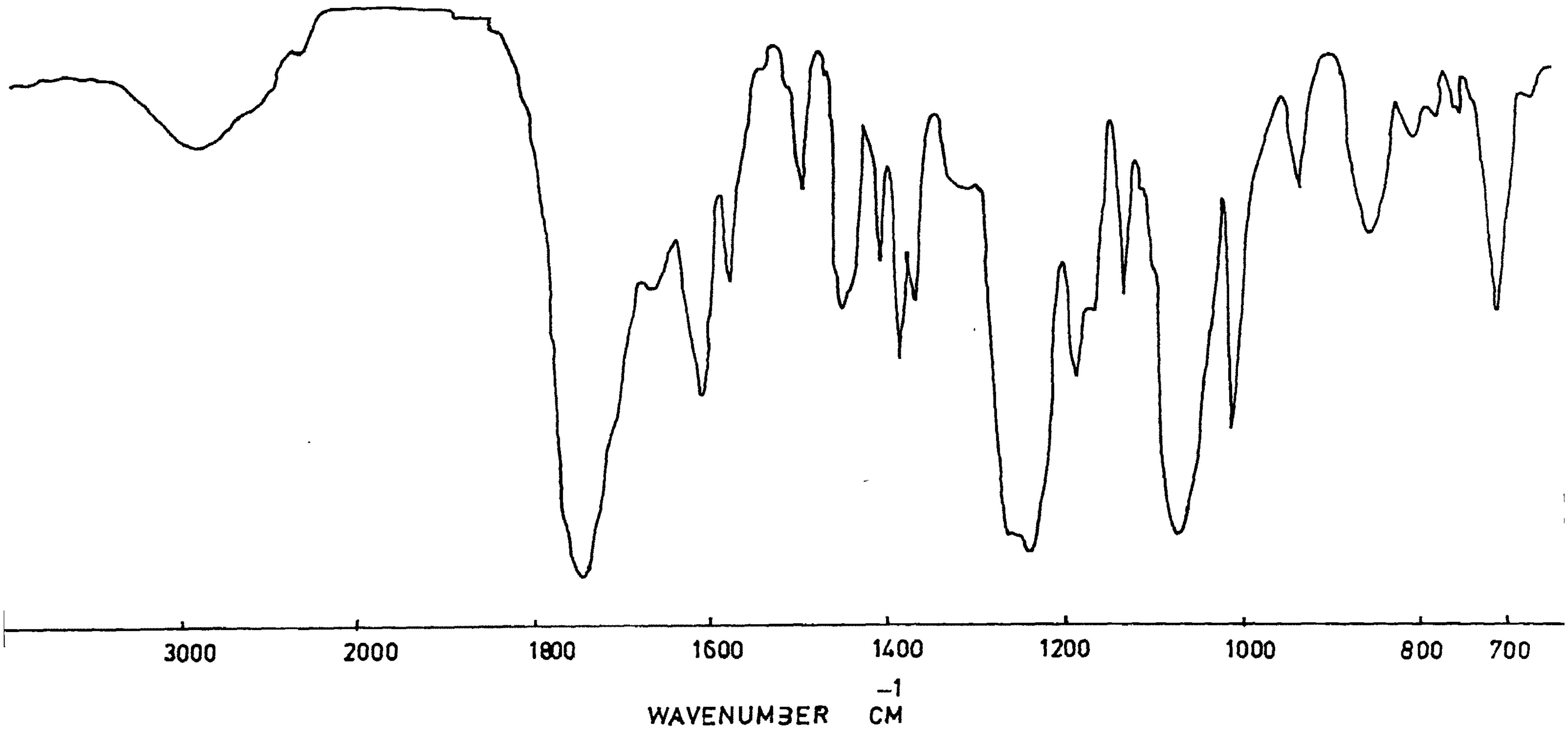


FIGURE-4-6 IR SPECTRA FOR SPECIMEN P_2

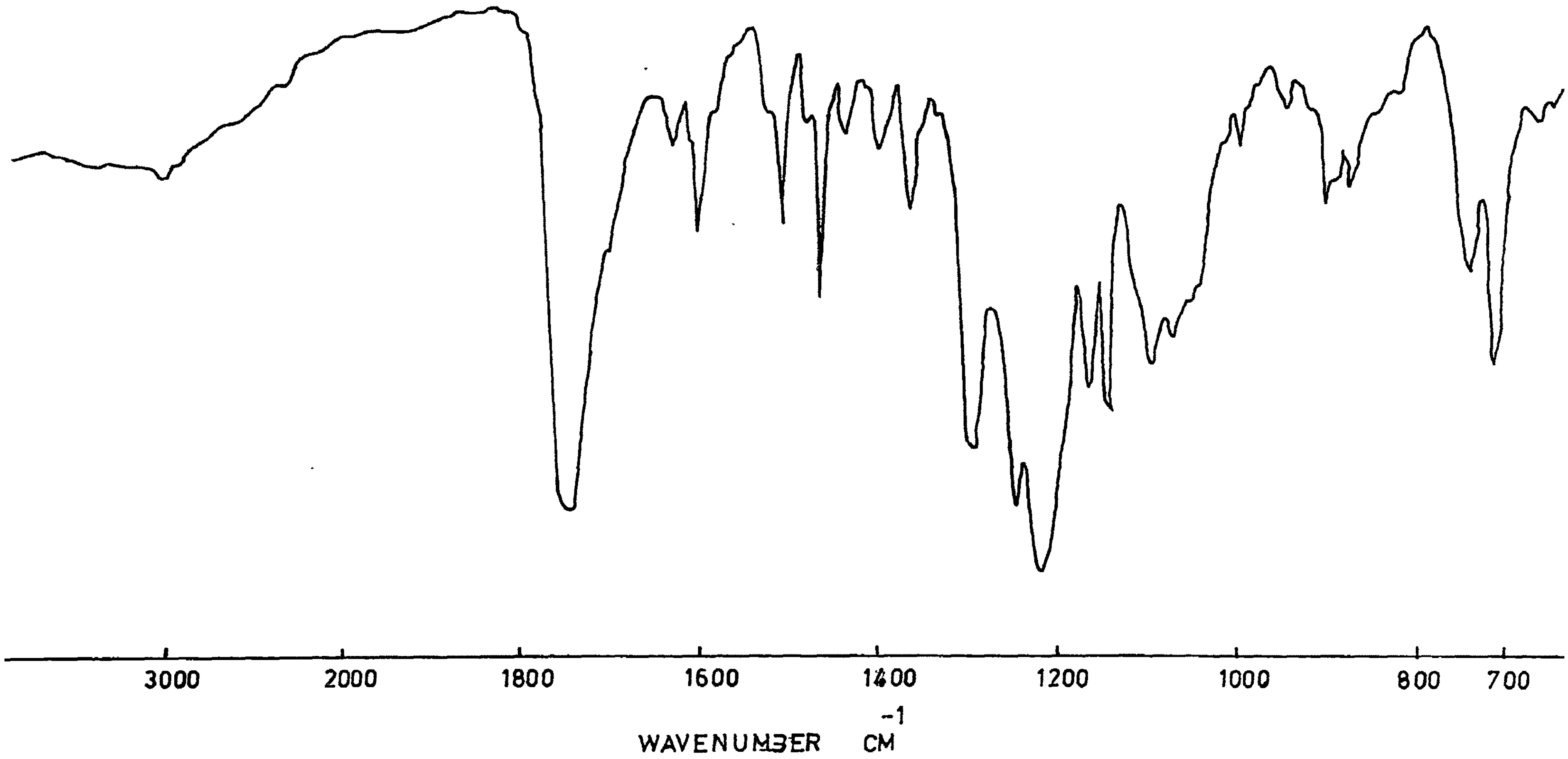


FIGURE-4·7 IR SPECTRA FOR SPECIMEN P_3

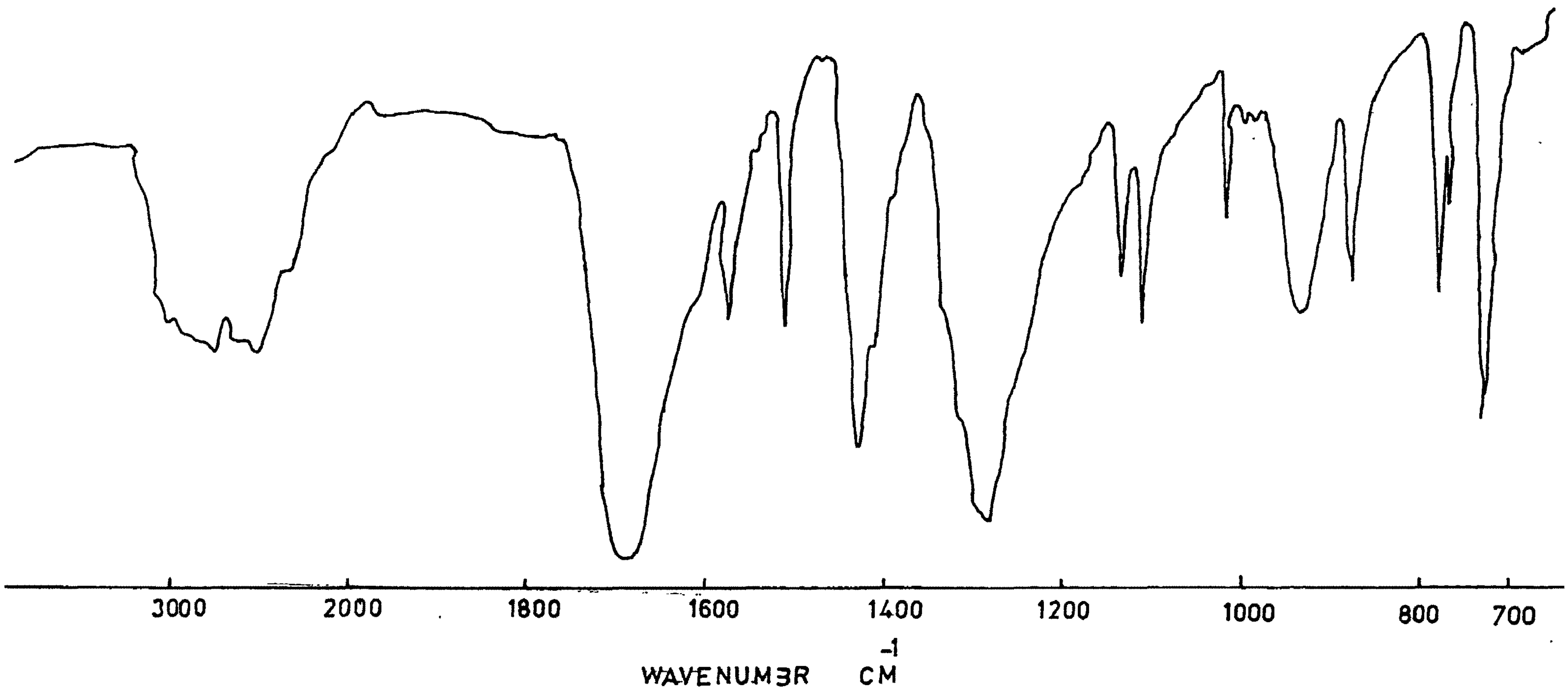


FIGURE-4.8 IR SPECTRA FOR SPECIMEN P_4

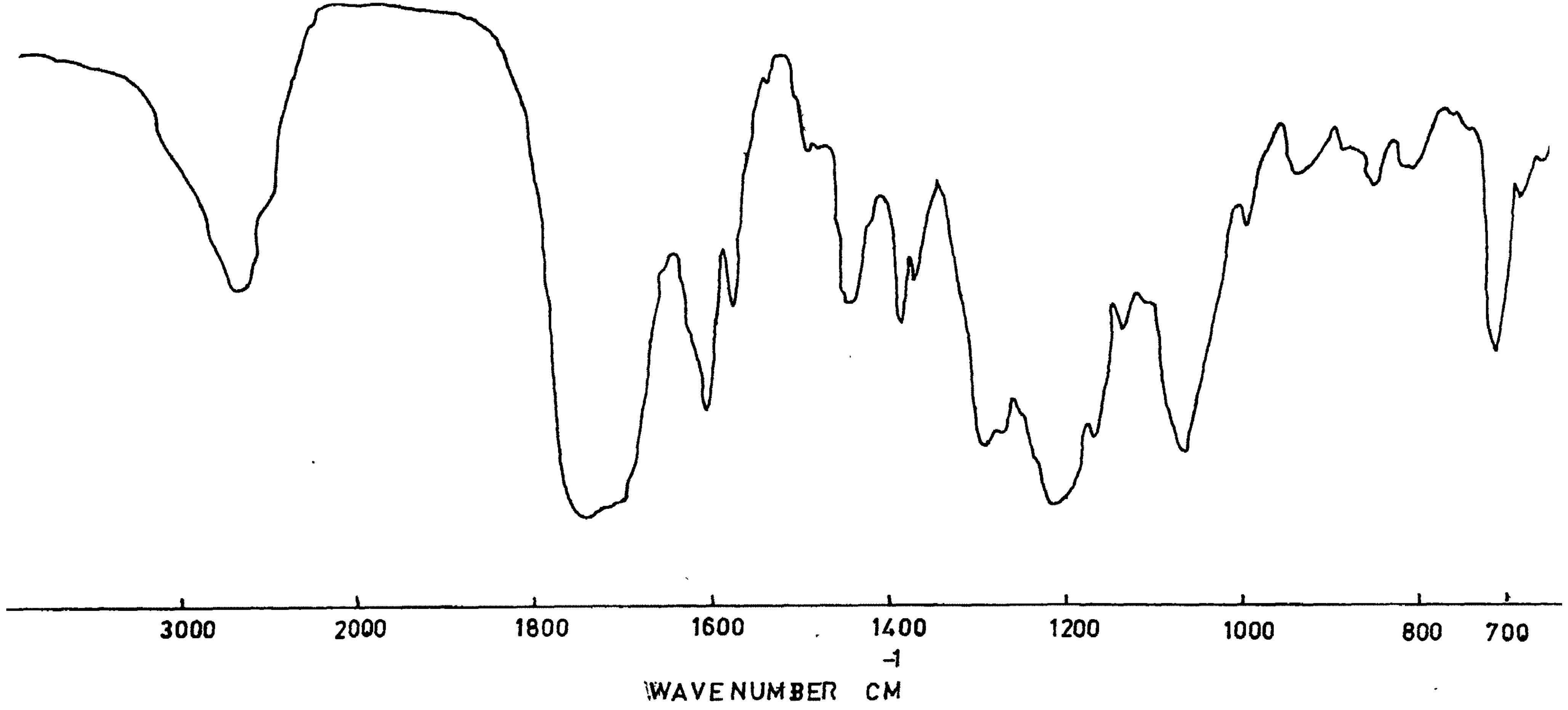


FIGURE-4·9 IR SPECTRA FOR SPECIMEN P_5

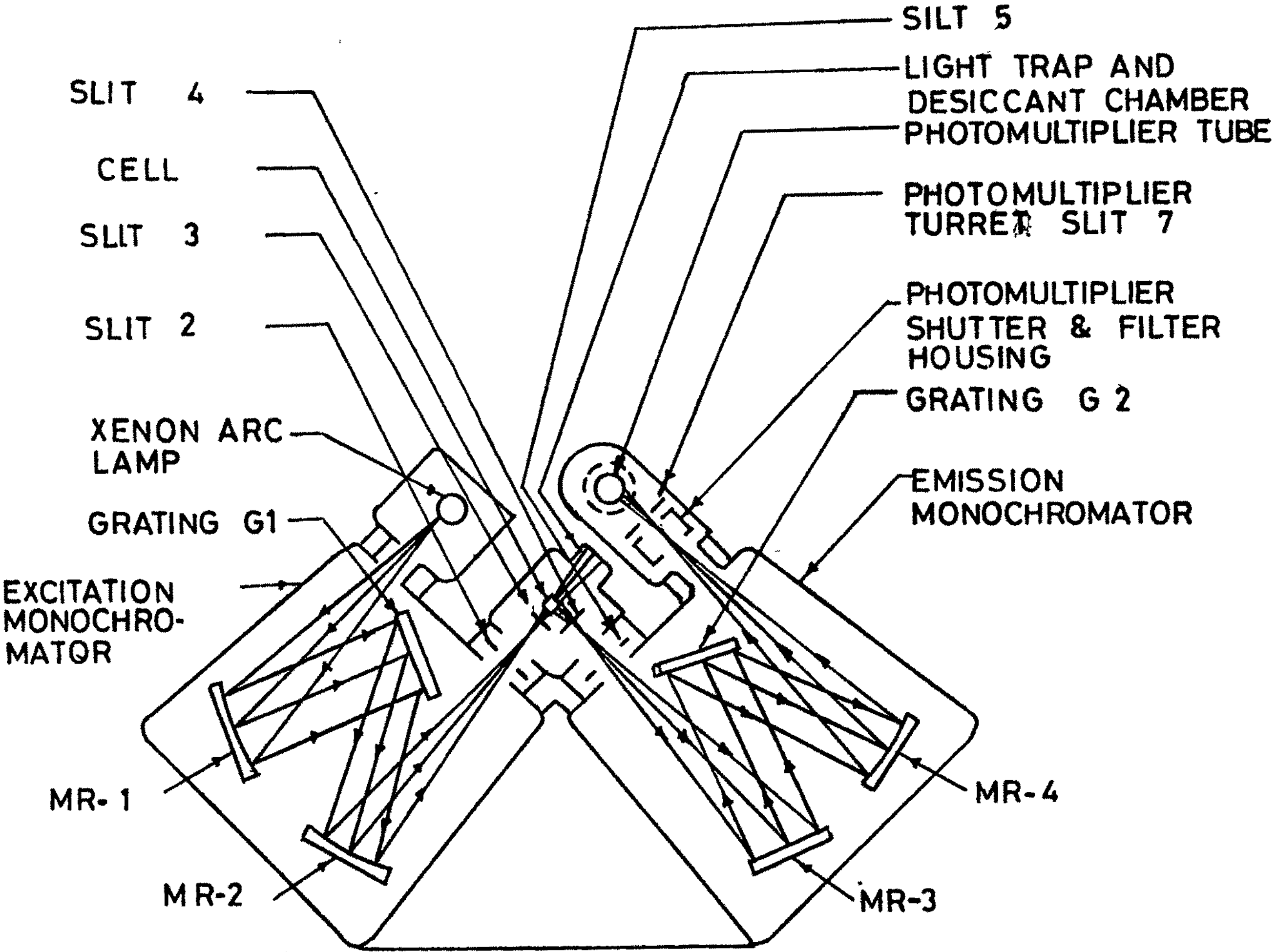


FIG.4-10 OPTICAL UNIT SHOWING POSITION OF SLITS

REFERENCE

1)	Kaufman K.D. & Kelly R.C.	1965	J.Het. Chem., 2,91.
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