CHAPTER - 5

RESULTS AND DISCUSSION

RESULTS

In this chapter the records of thermoluminescence glow curves and the luminescence spectra presented are discussed. The six specimens which were undertaken for the study are 5,7-dihydroxy-4-methyl coumarin and five of its copolymers. The specimens under investigations for thermoluminescence and luminescence are as listed below.

1.	5-7 dihydroxy-4-methyl coumarin	(M)
2.	Copolymer of 5-7 dihydroxy-4-methyl coumarin with Maleic acid	(P1)
3.	Copolymer of 5-7 dihydroxy-4-methyl coumarin with sebacic acid	(P2)
4.	Copolymer of 5-7 dihydroxy-4-methyl coumarin with Phthalic acid	(P3)
5.	Copolymer of 5-7 dihydroxy-4-methyl coumarin with Isophthalic acid	(P4)
6.	Copolymer of 5-7 dihydroxy-4-methyl coumarin with Terephthalic acid.	(P5)

Thermoluminescence and emission spectra have been presented for all the above specimens M, P1, P2, P3, P4, and P5 under various conditions; such as in the as received conditions, after mechanical compression and after the heat treatment. The specimens were exposed to three different doses of β-radiation for recording thermoluminescence spectra. Emission i.e. fluorescence spectra was recorded at the excitation wavelength of 250 nm.

Thermoluminescence spectra for all the specimens in the 'as received' condition are presented in Figures 5.1 to 5.6. Figures 5.7 to 5.12 represent the thermoluminescence spectra for all the annealed and quenched specimens. Figures 5.13 to 5.18 represent the thermoluminescence spectra for mechanically compressed specimens. Fluorescence spectra for as received, annealed and quenched and mechanically compressed specimens are represented in Fig. 5.19 to 5.24.

Figures 5.1 to 5.6 represent the thermoluminescence glow curves for the specimens M, P1, P2, P3, P4 and P5. It is seen from the graph, that thermoluminescence glow peak is observed at 92°C for monomer M. The thermoluminescence glow peak is observed close to 82°C for all the polymer specimens P1 through P5. All the specimens were exposed to radiation for three different durations of 5 minutes, 10 minutes and 15 minutes respectively. From the figures it can be seen that as exposure time increases, the intensity of the thermoluminescence curve also increases.

All the specimens were annealed at temperatures 60, 70 and 80°C for an hour and suddenly cooled to a room temperature. The thermoluminescence spectra presented in Figures 5.7 to 5.12 are for the annealed and quenched specimens M and P1 through P5. The peak has been now around 80°C for all the specimens. A hump or shoulder is observed at 60°C for the specimen P1 when annealed at temperatures 70 and 80°C. It has been observed from the Figures 5.7 to 5.12 that the intensity of thermoluminescence peak is more for the specimens annealed at higher temperature.

The thermoluminescence spectra for mechanically compressed specimens are shown in Figures 5.13 to 5.18, for all the specimens. From the figures, it is observed that for polymers P1 and P2; the TL peak is observed at 85°C while for monomer M and polymer P3, P4 and P5; the thermoluminescence peak is observed at 90°C. In general, it is observed that thermoluminescence intensity is maximum for annealed and quenched specimens and minimum for mechanically deformed specimens.

Figures 5.18 to 5.24 represents the fluorescence spectra for the monomer specimen M and polymer specimens P1 through P5. For the as received specimen M, the emission peak is observed at 430 nm. However, this peak is observed at 410 nm in all the polymer specimens P1 through P5. The intensity of the peak increases in the specimens in the order of M, P2, P1, P3, P4 and P5. The another emission peak occurs at 520 nm as a hump or shoulder in all these specimens. In the same figure, emission spectra for mechanically treated and annealed quenched specimens have also been presented. In case of mechanically compressed specimens, the peaks are observed at 430 nm for monomer M and 410 nm for polymers P1 through P5. The peaks remain at same wavelength as in the 'as received' specimens. The intensity of mechanically compressed specimens is less than that observed in as received specimen. An extra peak at 520 nm is also observed in these specimens. Its intensity has also been observed to be less than that in the as received specimens. Emission spectra for annealed and quenched specimen show the emission peak at 420 nm in specimen M. While, for polymer specimens, the same has been observed at 440nm.

On comparing the emission spectra for annealed and quenched specimens with those, in as received specimens, it can be clearly seen that the emission peak gets shifted to 440 nm from 410 nm for all the polymer specimens P1 through P5.

Comparison between emission spectra of as received, annealed and quenched and mechanically compressed specimens show that the intensity of the peak for annealed and quenched specimen is the highest. The next section provides the discussion of all the above results for the specimens M and P1 through P5.

Figure 5.1 Thermoluminescence spectra for as received specimen M

1) Exposure time - 5 minutes ________
2) Exposure time -10 minutes ---------
3) Exposure time -15 minutes -.-.-.-.-.

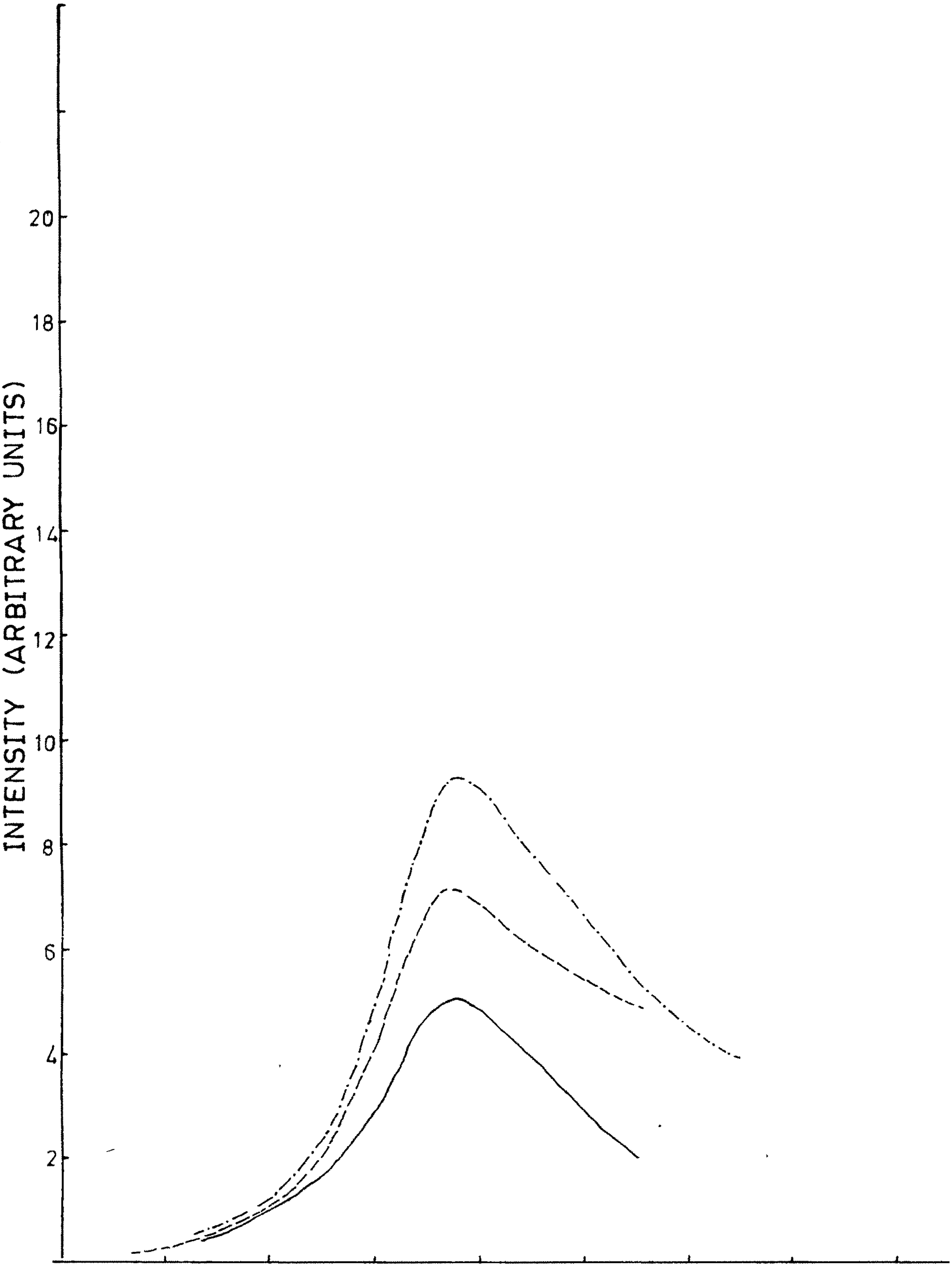


FIGURE 5 1 TEMPERATURE °C

Figure 5.2 Thermoluminescence spectra for as received specimen P_1

1) Exposure time - 5 minutes __________
2) Exposure time -10 minutes ---------
3) Exposure time -15 minutes -.-.-.-.-.

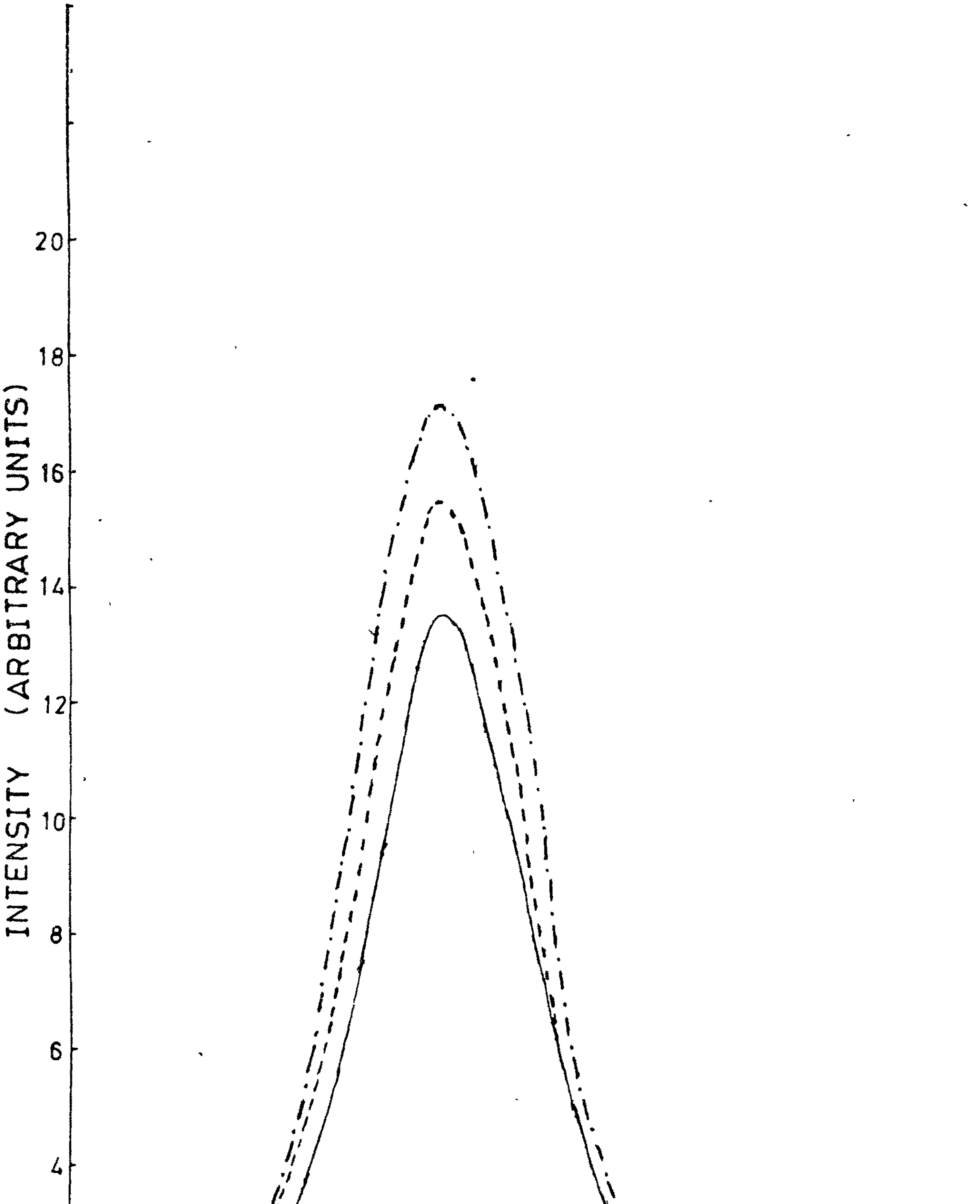

INTENSITY (ARBITRARY UNITS)
20
18
16
14
12
10
8
6
4
2
40
60
80
100
120
TEMPERATURE °C

FIGURE 5·2

Figure 5.3 Thermoluminescence spectra for as received specimen P_2

1) Exposure time - 5 minutes ―――――――
2) Exposure time -10 minutes ---------
3) Exposure time -15 minutes -.-.-.-.-.

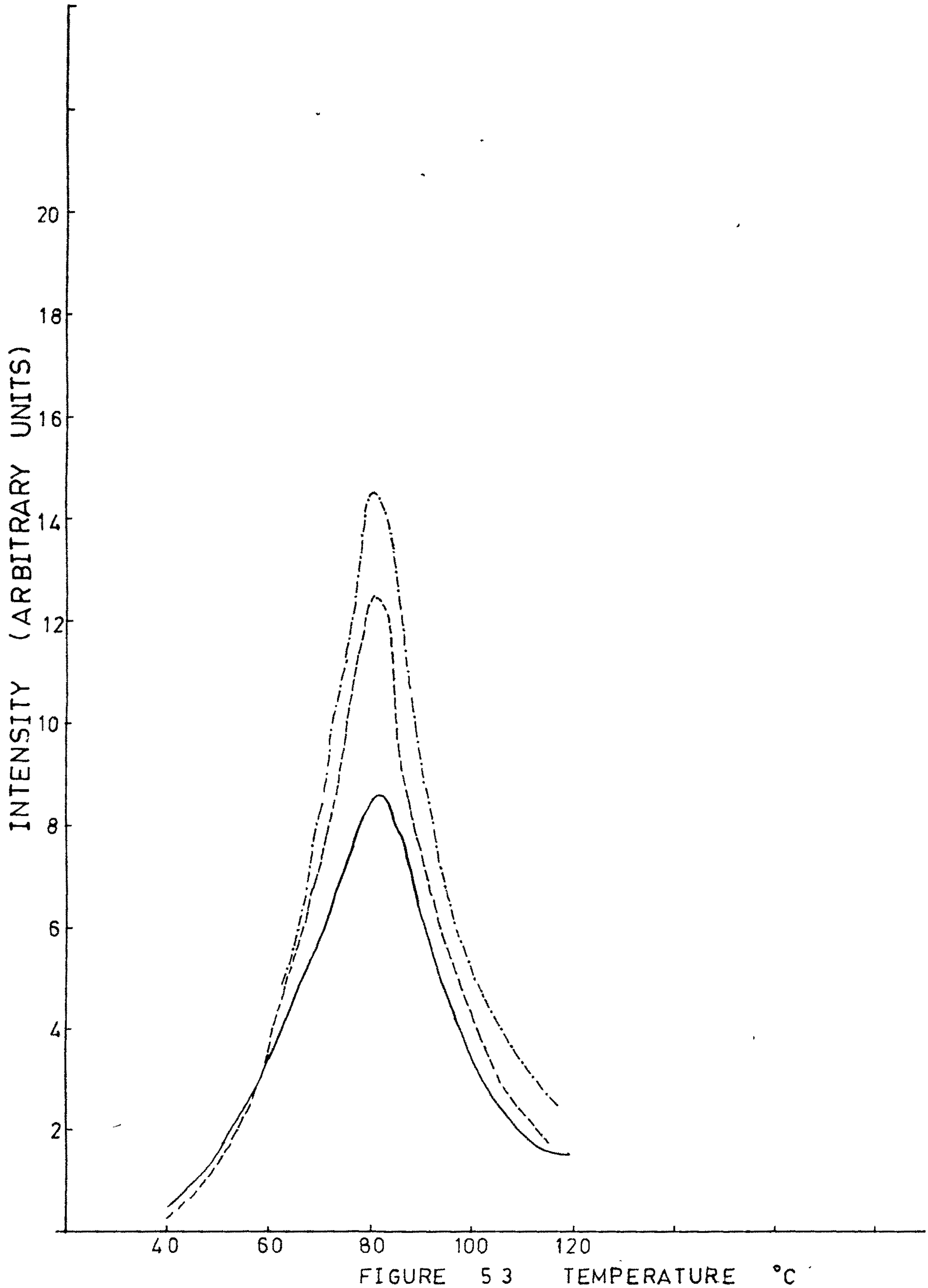

INTENSITY (ARBITRARY UNITS)
20
18
16
14
12
10
8
6
4
2
40
60
80
100
120
TEMPERATURE °C

FIGURE 5 3

Figure 5.4 Thermoluminescence spectra for as received specimen P_3

1) Exposure time - 5 minutes ____________
2) Exposure time -10 minutes ---------
3) Exposure time -15 minutes -.-.-.-.-.

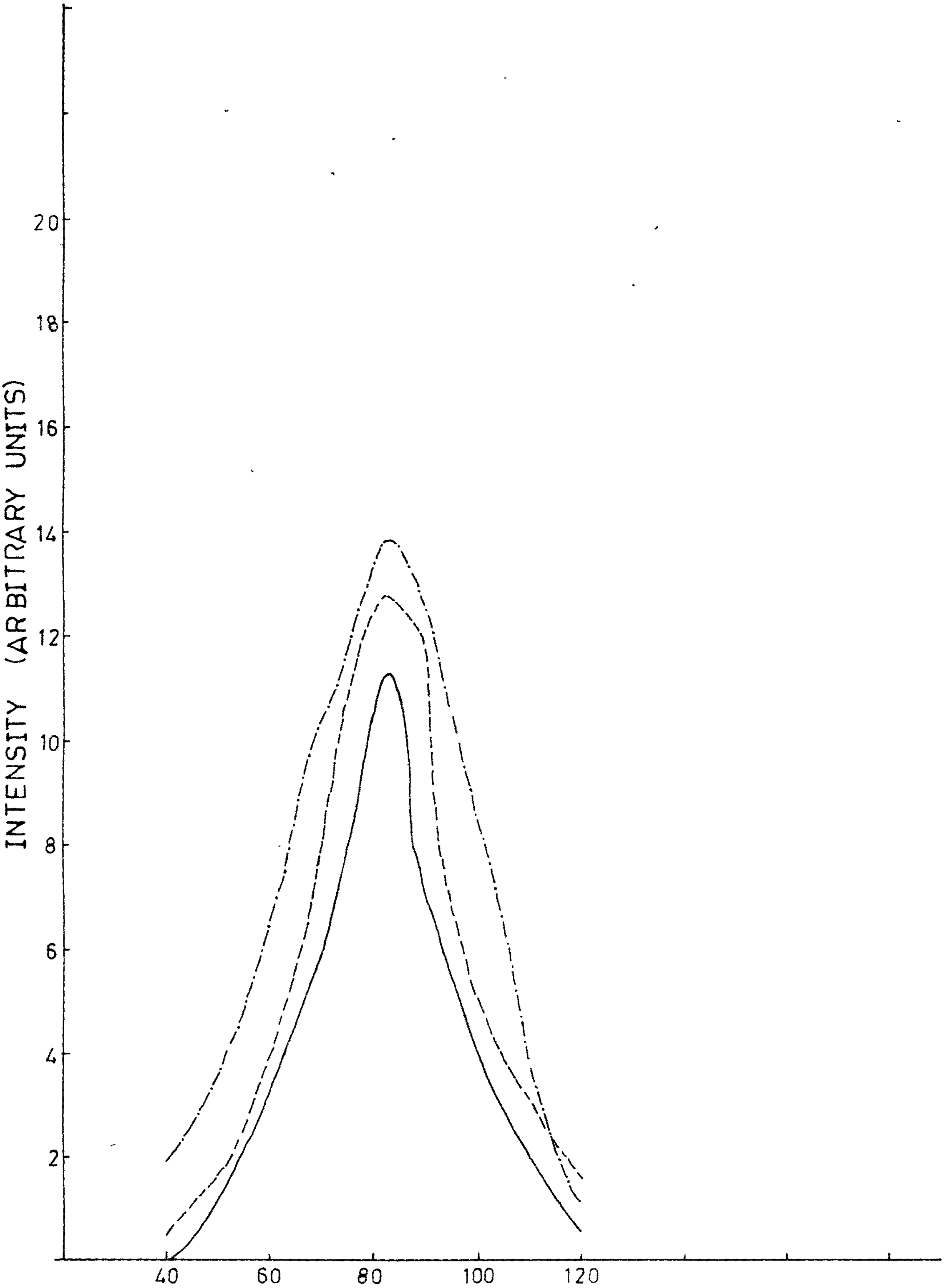


FIGURE 5·4 TEMPERATURE °C

Figure 5.5 Thermoluminescence spectra for as received specimen P_4

1) Exposure time - 5 minutes ——————
2) Exposure time -10 minutes ---------
3) Exposure time -15 minutes -.-.-.-.-.

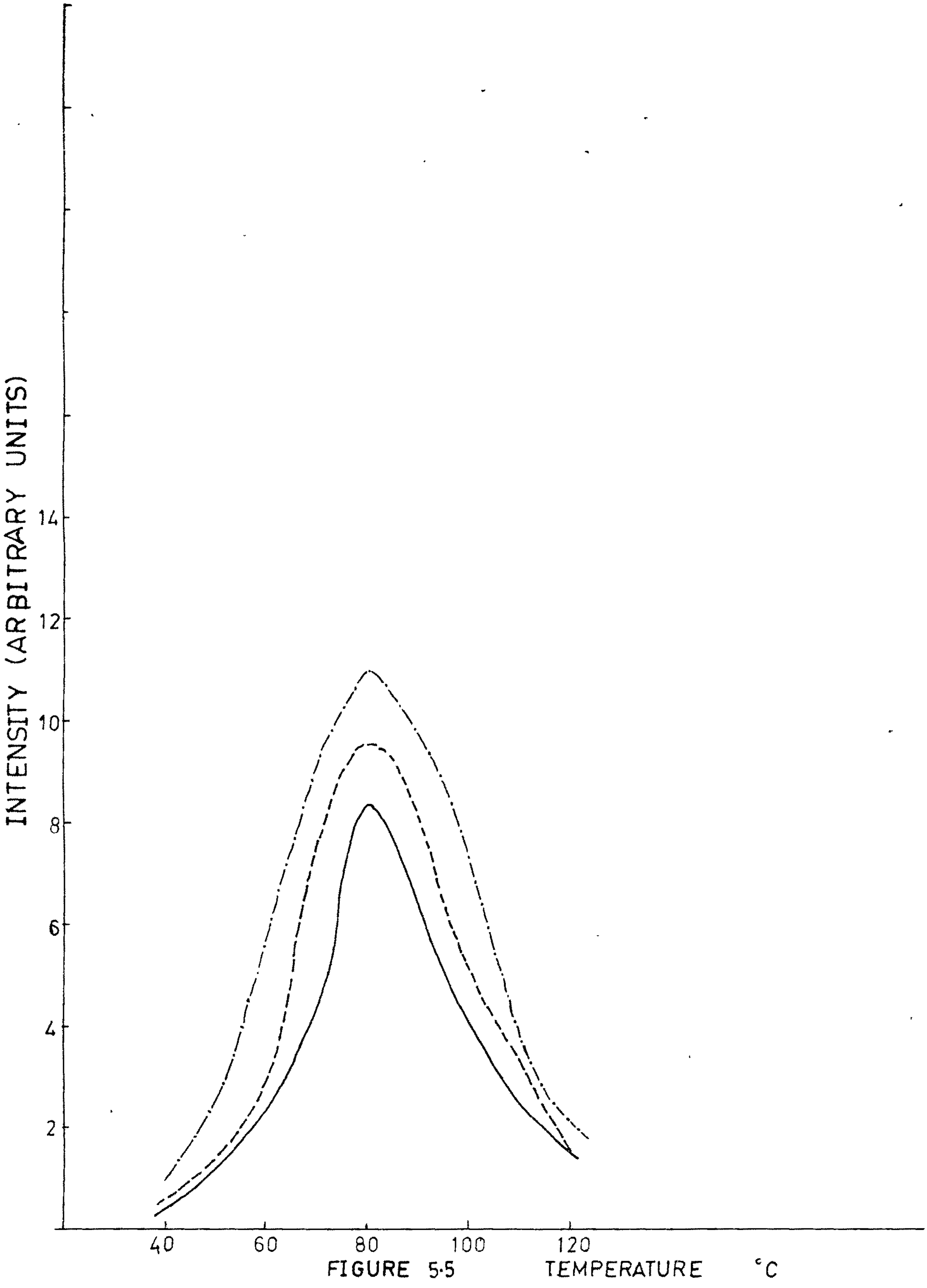

INTENSITY (ARBITRARY UNITS)
14
12
10
8
6
4
2
40
60
80
100
120
TEMPERATURE °C

FIGURE 5·5

Figure 5.6 Thermoluminescence spectra for as received specimen P_5

1) Exposure time - 5 minutes ——————
2) Exposure time -10 minutes ---------
3) Exposure time -15 minutes -.-.-.-.-.

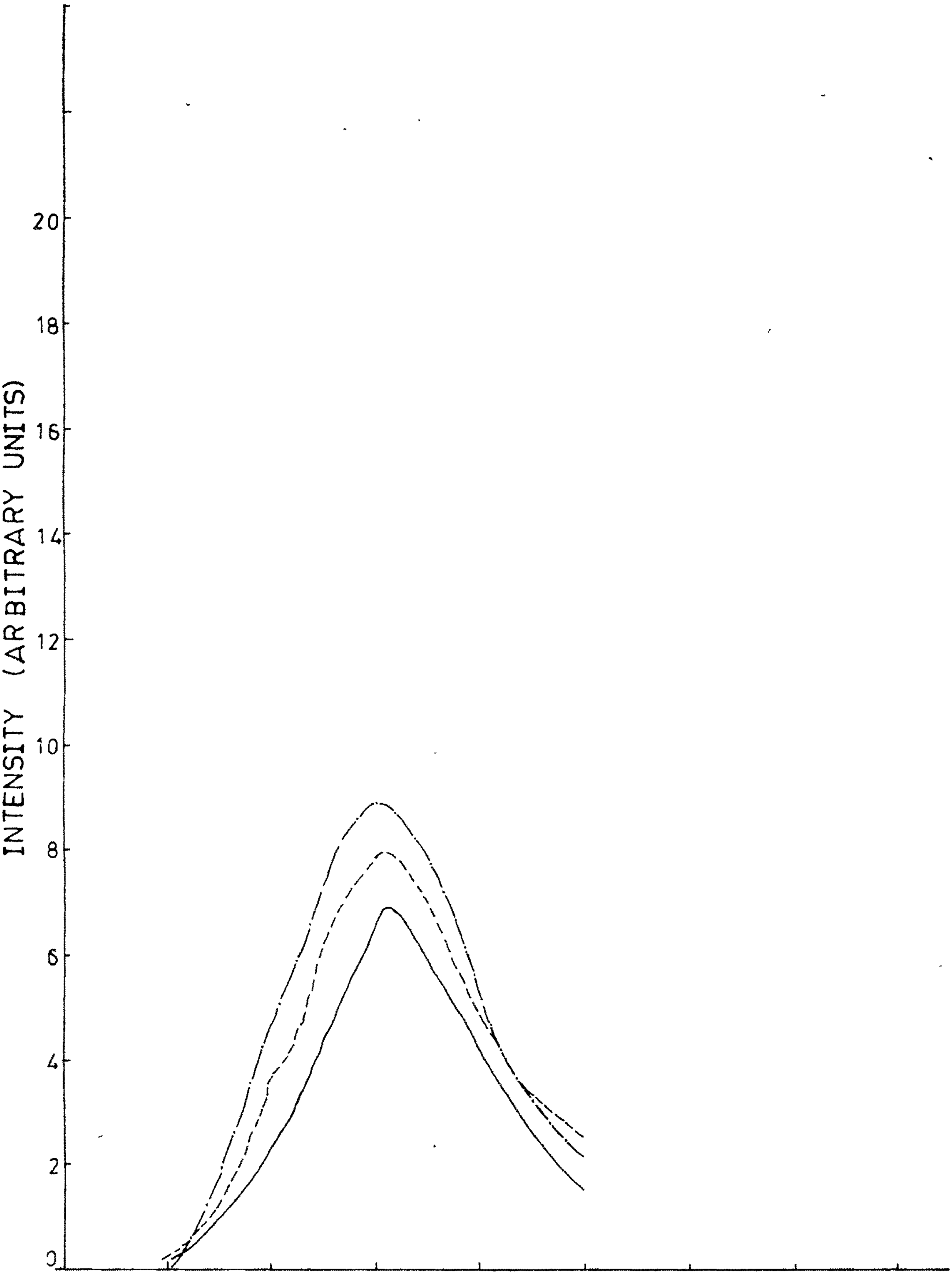

INTENSITY (ARBITRARY UNITS)
20
18
16
14
12
10
8
6
4
2
0
40
60
80
100
120
TEMPERATURE °C

FIGURE 5·6

Figure 5.7 Thermoluminescence spectra for annealed & quenched specimen M

1) Annealing temp. 60°C ―――――――――
2) Annealing temp. 70°C ---------
3) Annealing temp. 80°C -.-.-.-.-.

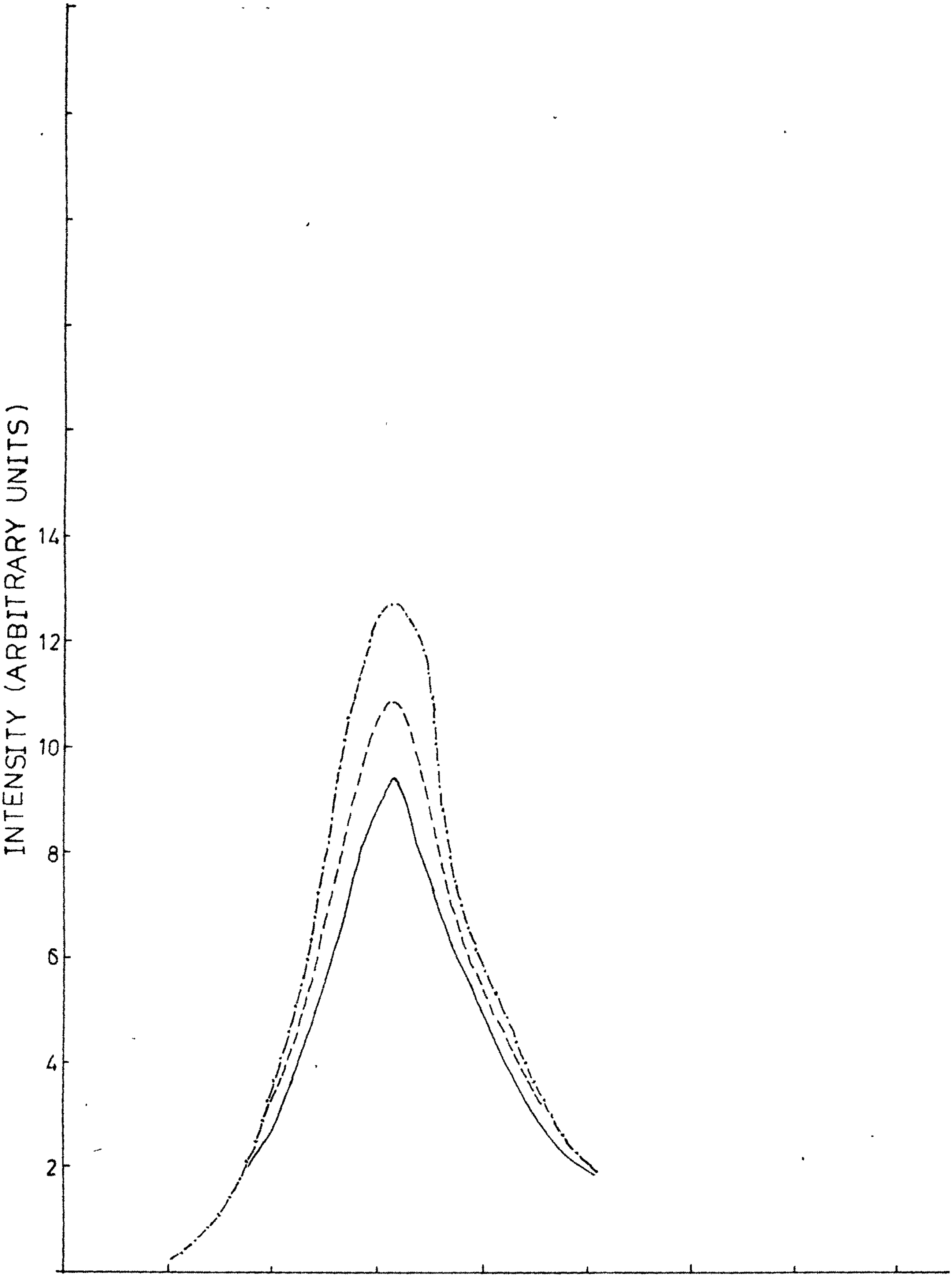

INTENSITY (ARBITRARY UNITS)
14
12
10
8
6
4
2
40
60
80
100
120
TEMPERATURE °C

FIGURE 5·7

Figure 5.8 Thermoluminescence spectra for annealed & quenched specimen P_1

1) Annealing temp. 60°C ___________
2) Annealing temp. 70°C ---------
3) Annealing temp. 80°C -.-.-.-.-.

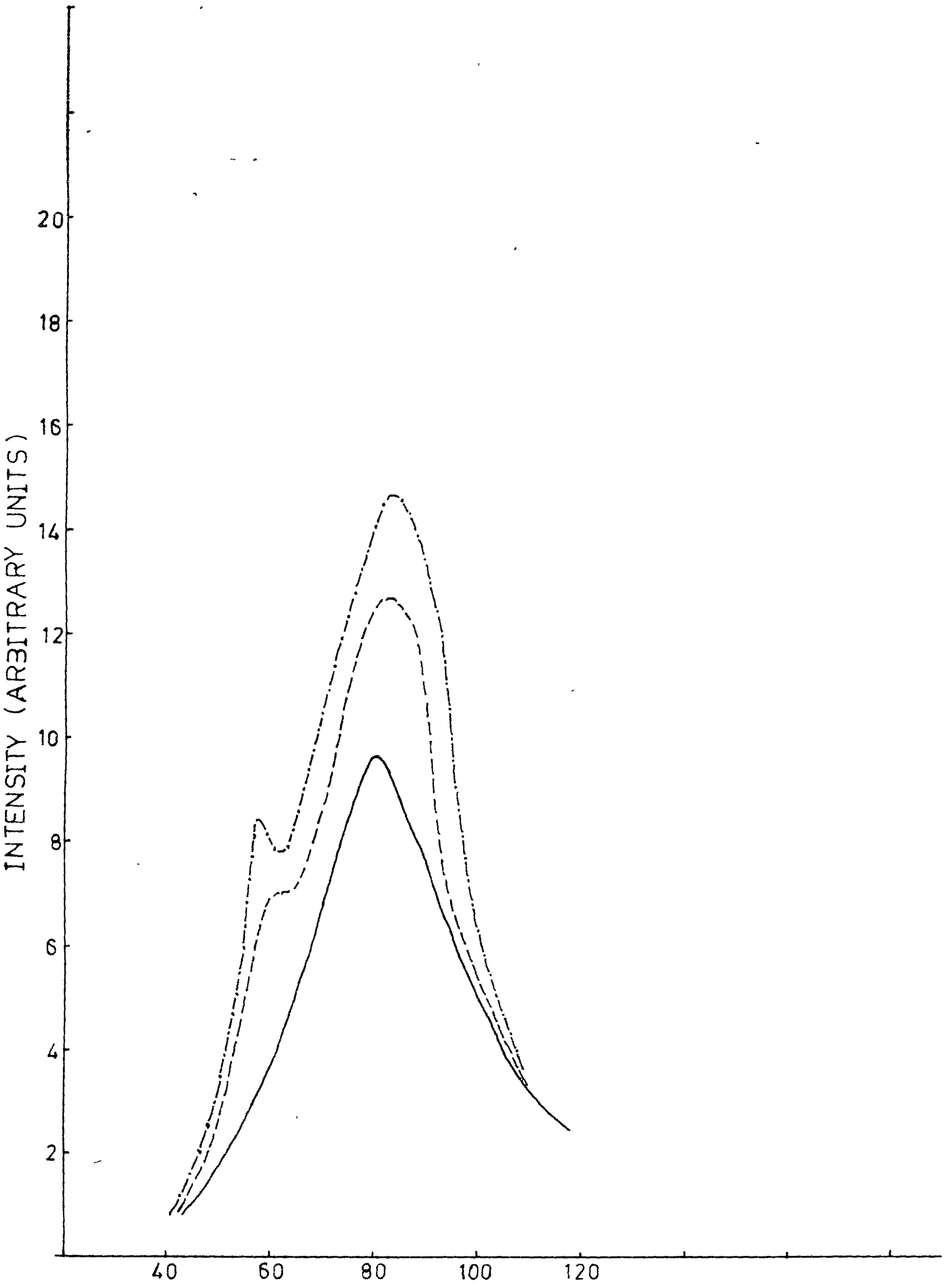

INTENSITY (ARBITRARY UNITS)
20
18
16
14
12
10
8
6
4
2
40
60
80
100
120
TEMPERATURE °C

FIGURE 5·8

Figure 5.9 Thermoluminescence spectra for annealed & quenched specimen P_2

1) Annealing temp. 60°C ————
2) Annealing temp. 70°C ---------
3) Annealing temp. 80°C -.-.-.-.-.

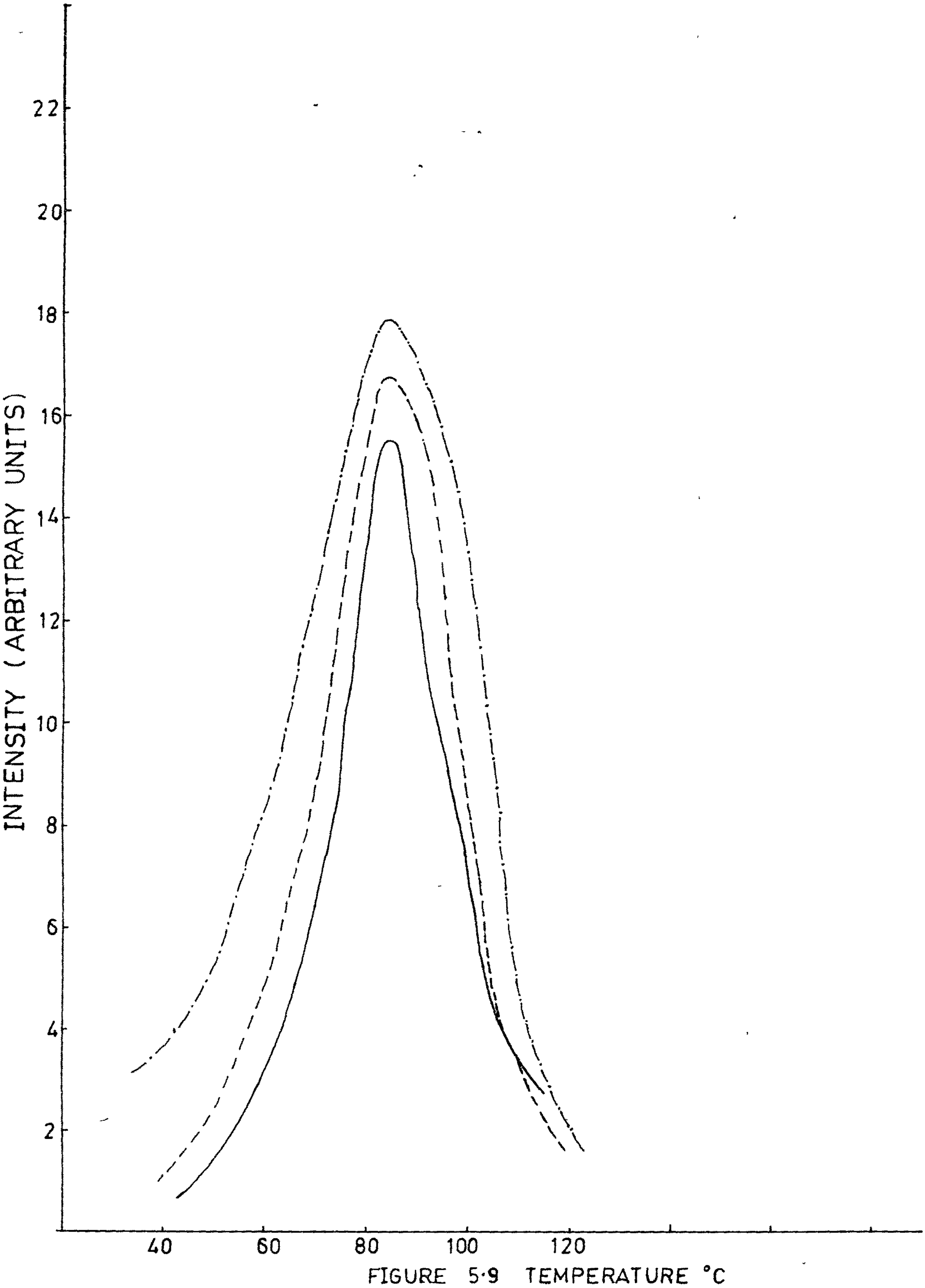


FIGURE 5·9 TEMPERATURE °C

Figure 5.10 Thermoluminescence spectra for annealed & quenched specimen P_3

1) Annealing temp. 60°C ――――――
2) Annealing temp. 70°C ---------
3) Annealing temp. 80°C -.-.-.-.-.

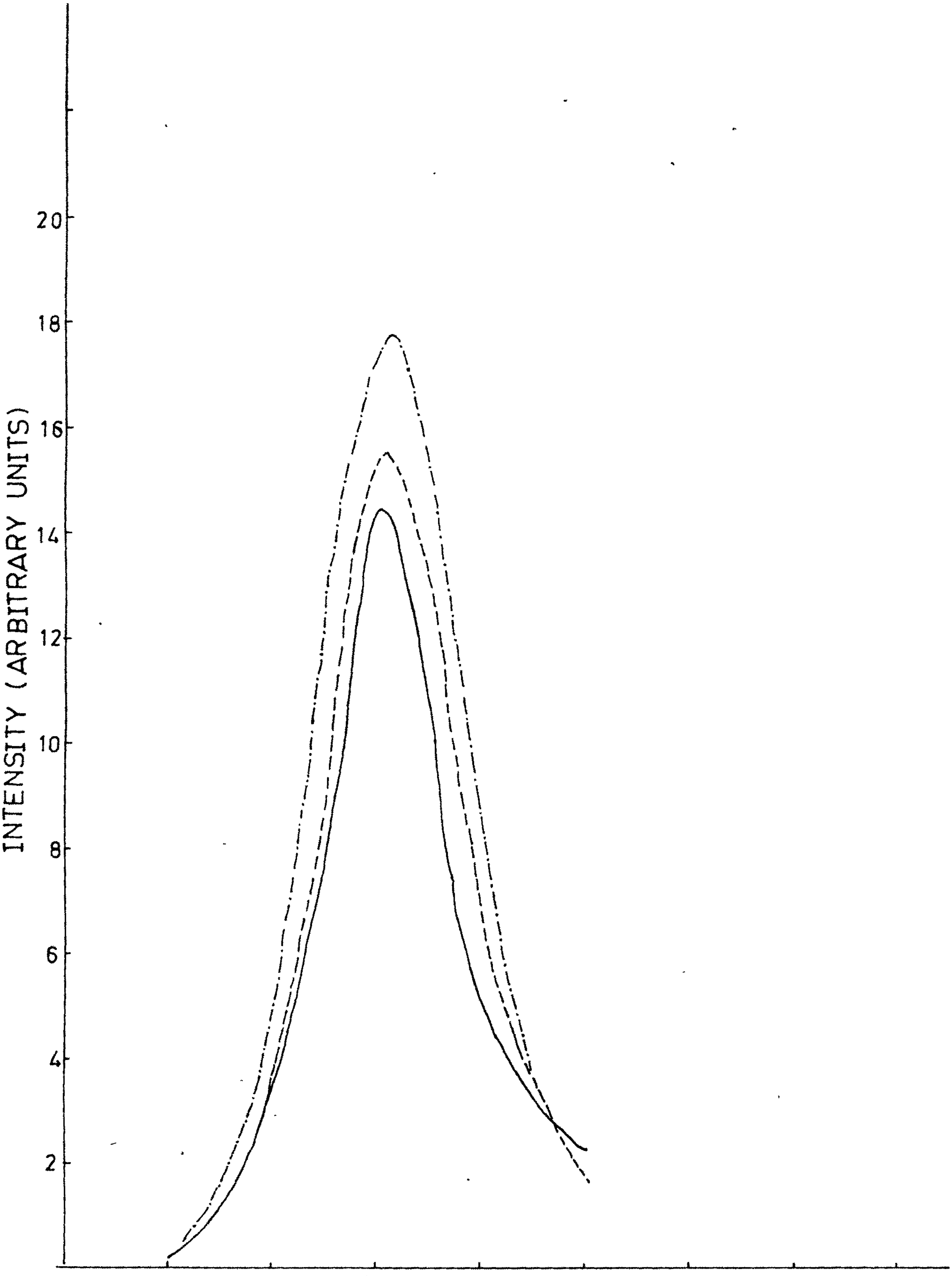
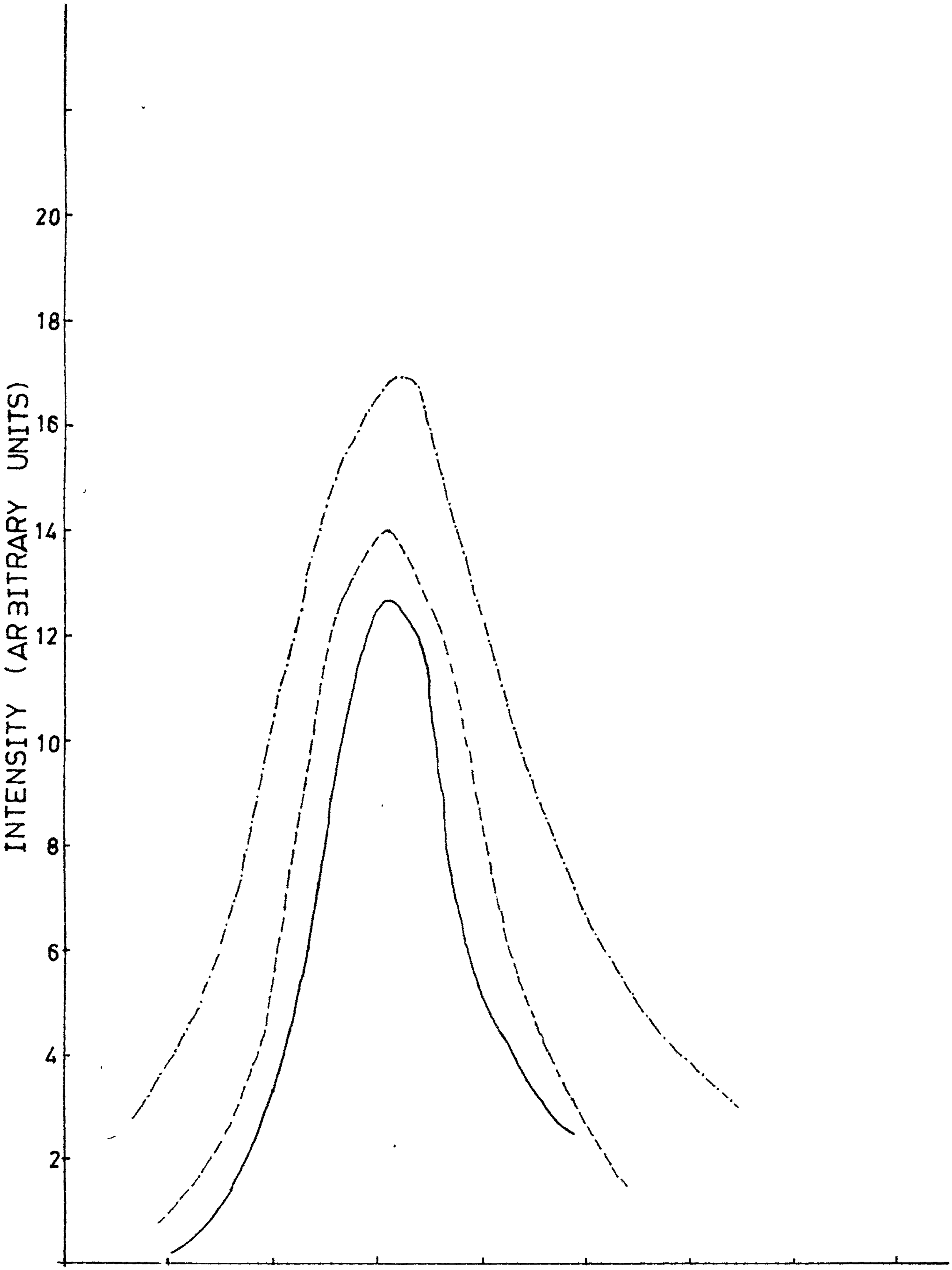

INTENSITY (ARBITRARY UNITS)
20
18
16
14
12
10
8
6
4
2
40
60
80
100
120
TEMPERATURE °C

FIGURE 5·10

Figure 5.11 Thermoluminescence spectra for annealed & quenched specimen P_4

1) Annealing temp. 60°C ——————
2) Annealing temp. 70°C ---------
3) Annealing temp. 80°C -.-.-.-.-.



INTENSITY (ARBITRARY UNITS)
20
18
16
14
12
10
8
6
4
2
40
60
80
100
120
140
160
TEMPERATURE °C

FIGURE 5·11

Figure 5.12 Thermoluminescence spectra for annealed & quenched specimen P_5

1) Annealing temp. 60°C ___________
2) Annealing temp. 70°C ----------
3) Annealing temp. 80°C -.-.-.-.-.

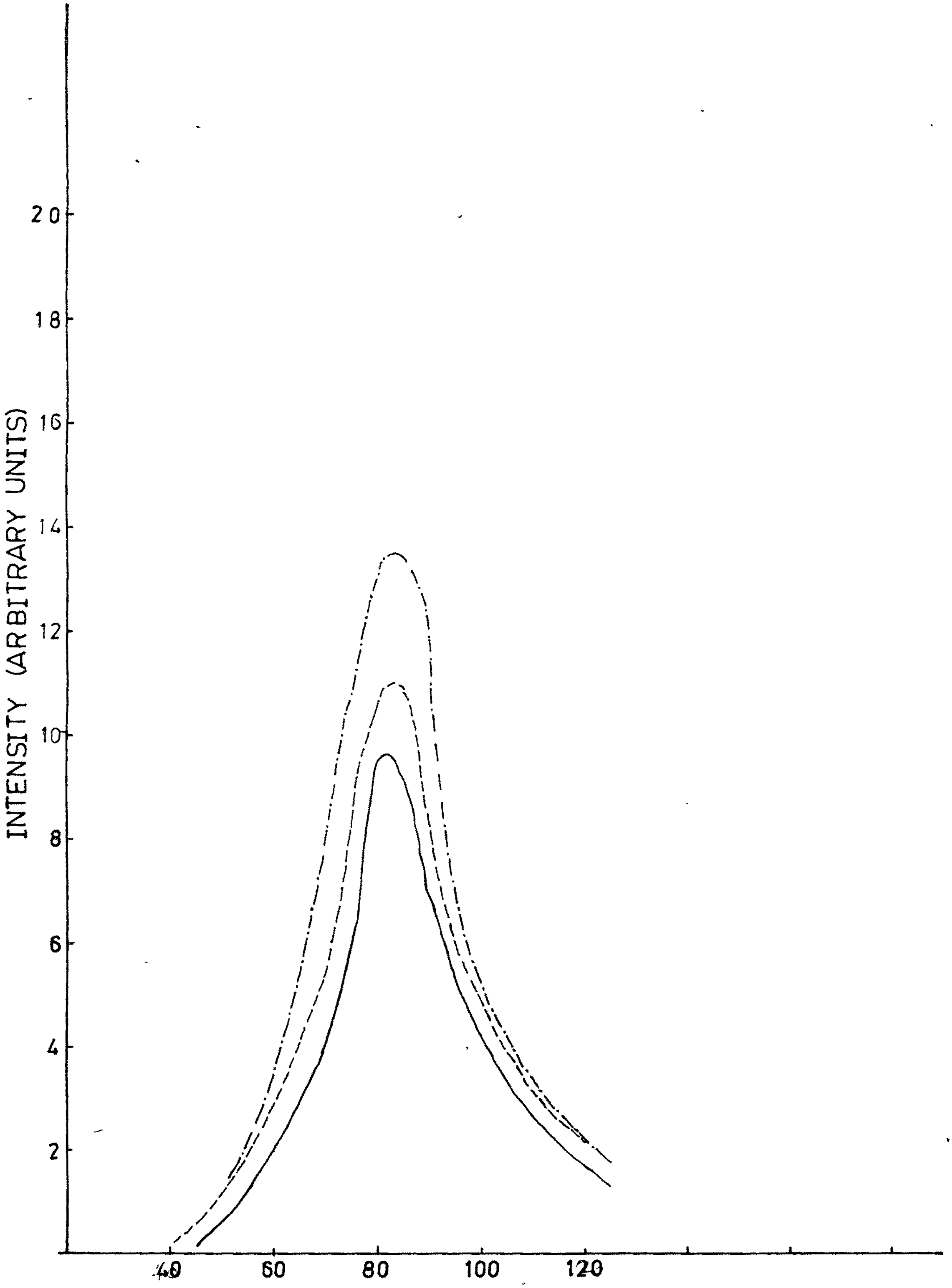

INTENSITY (ARBITRARY UNITS)
20
18
16
14
12
10
8
6
4
2
40
60
80
100
120
TEMPERATURE °C

FIGURE 512

Figure 5.13 Thermoluminescence spectra for Mechanically Deformed speciman M

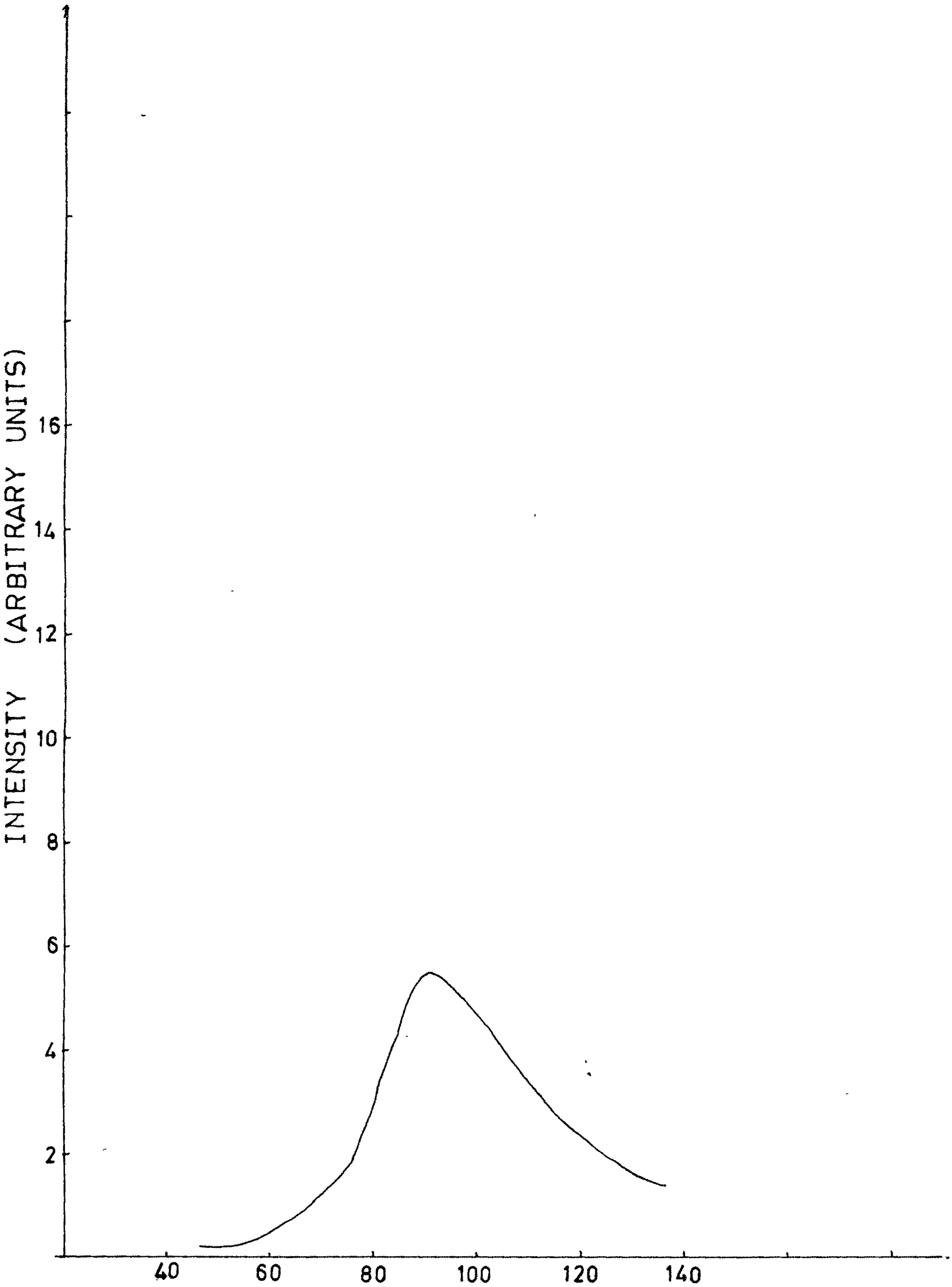

INTENSITY (ARBITRARY UNITS)
16
14
12
10
8
6
4
2
40
60
80
100
120
140
TEMPERATURE °C

FIGURE 5·13

Figure 5.14 Thermoluminescence spectra for Mechanically Deformed speciman P_1

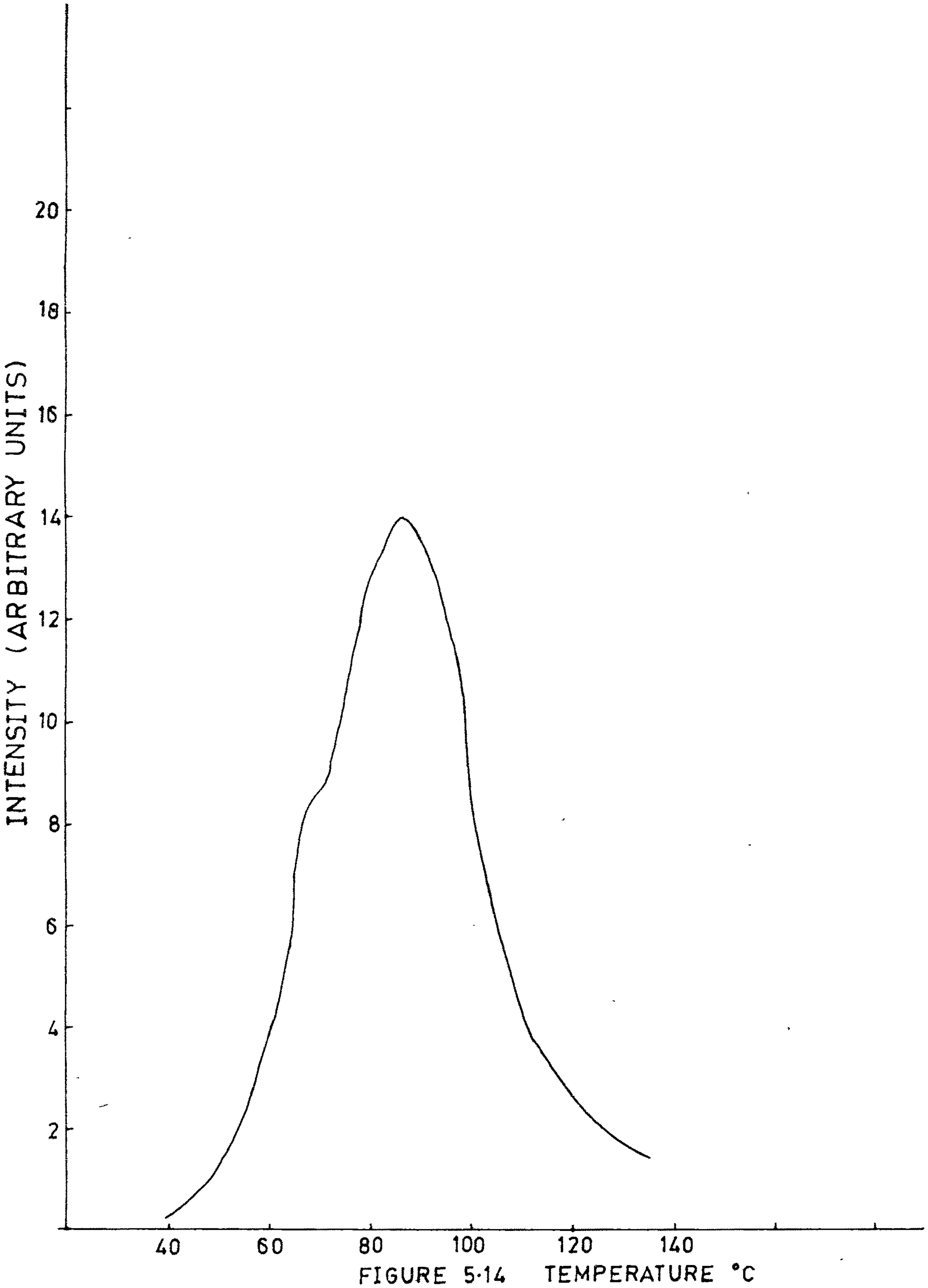


FIGURE 5·14 TEMPERATURE °C

Figure 5.15 Thermoluminescence spectra for Mechanically Deformed speciman P_2

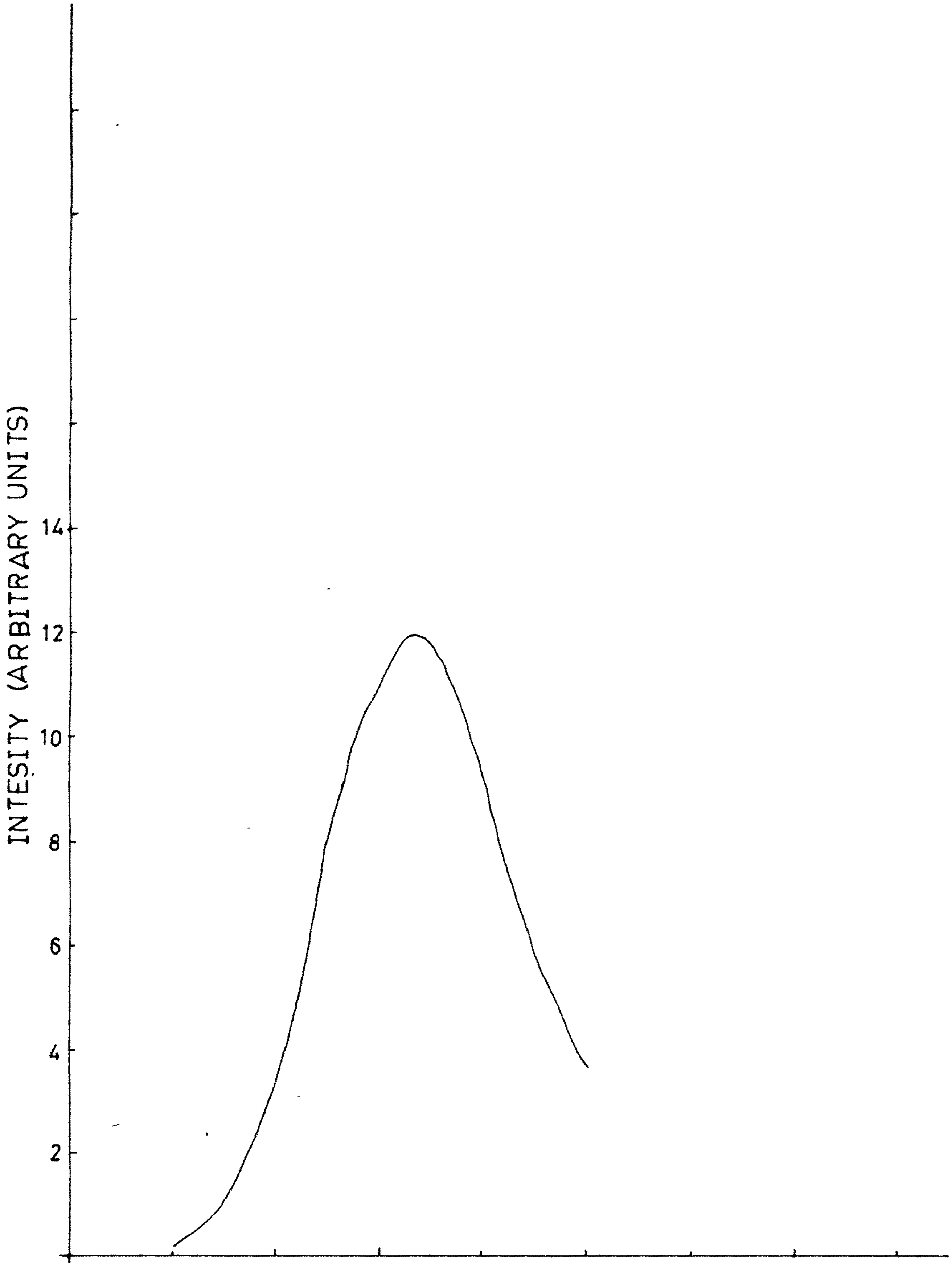

INTESITY (ARBITRARY UNITS)
14
12
10
8
6
4
2
40
60
80
100
120
TEMPERATURE °C

FIGURE 5·15

Figure 5.16 Thermoluminescence spectra for Mechanically Deformed speciman P_3

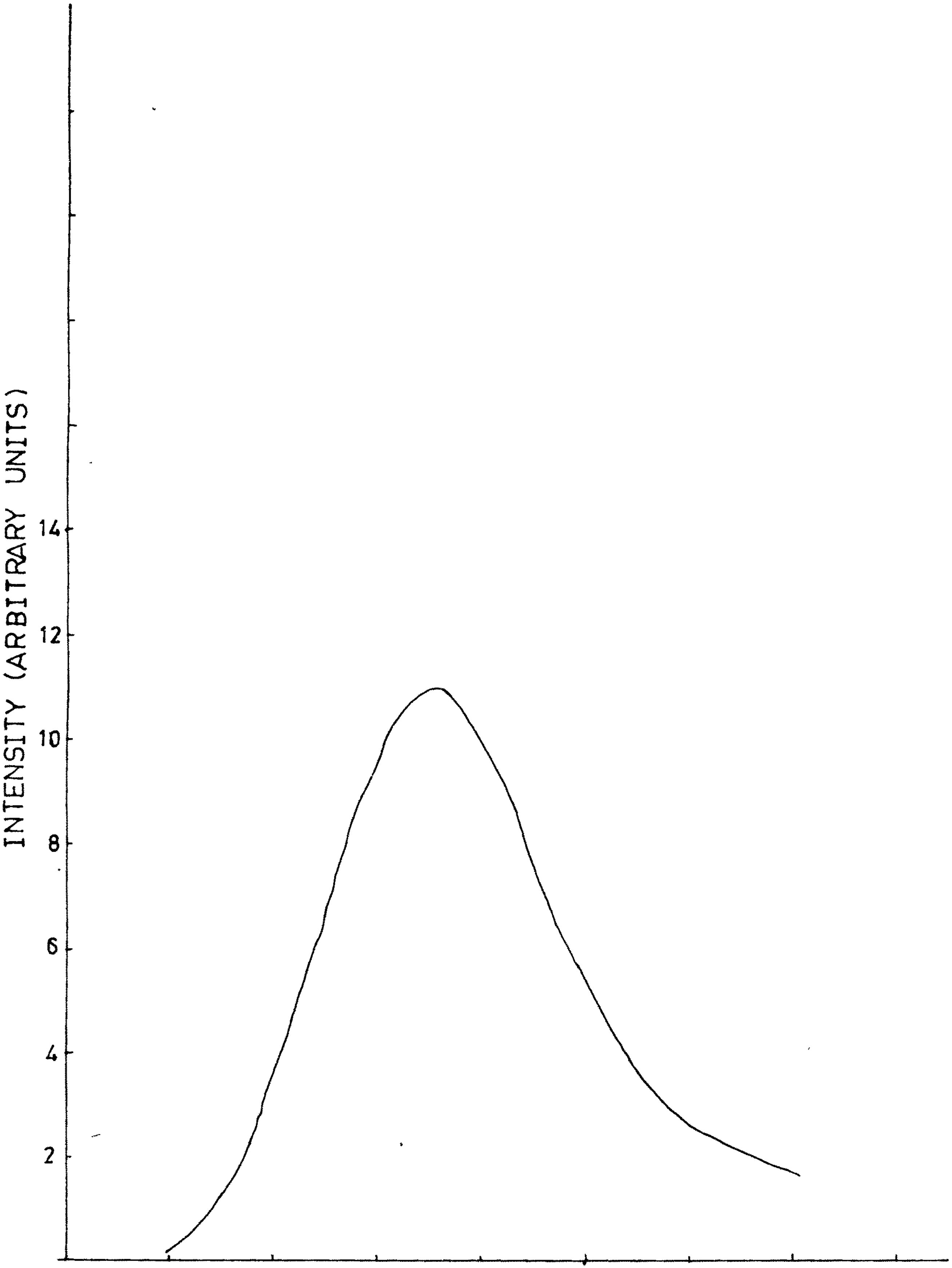


FIGURE 5·16 TEMPERATURE °C

Figure 5.17 Thermoluminescence spectra for Mechanically Deformed speciman P_4

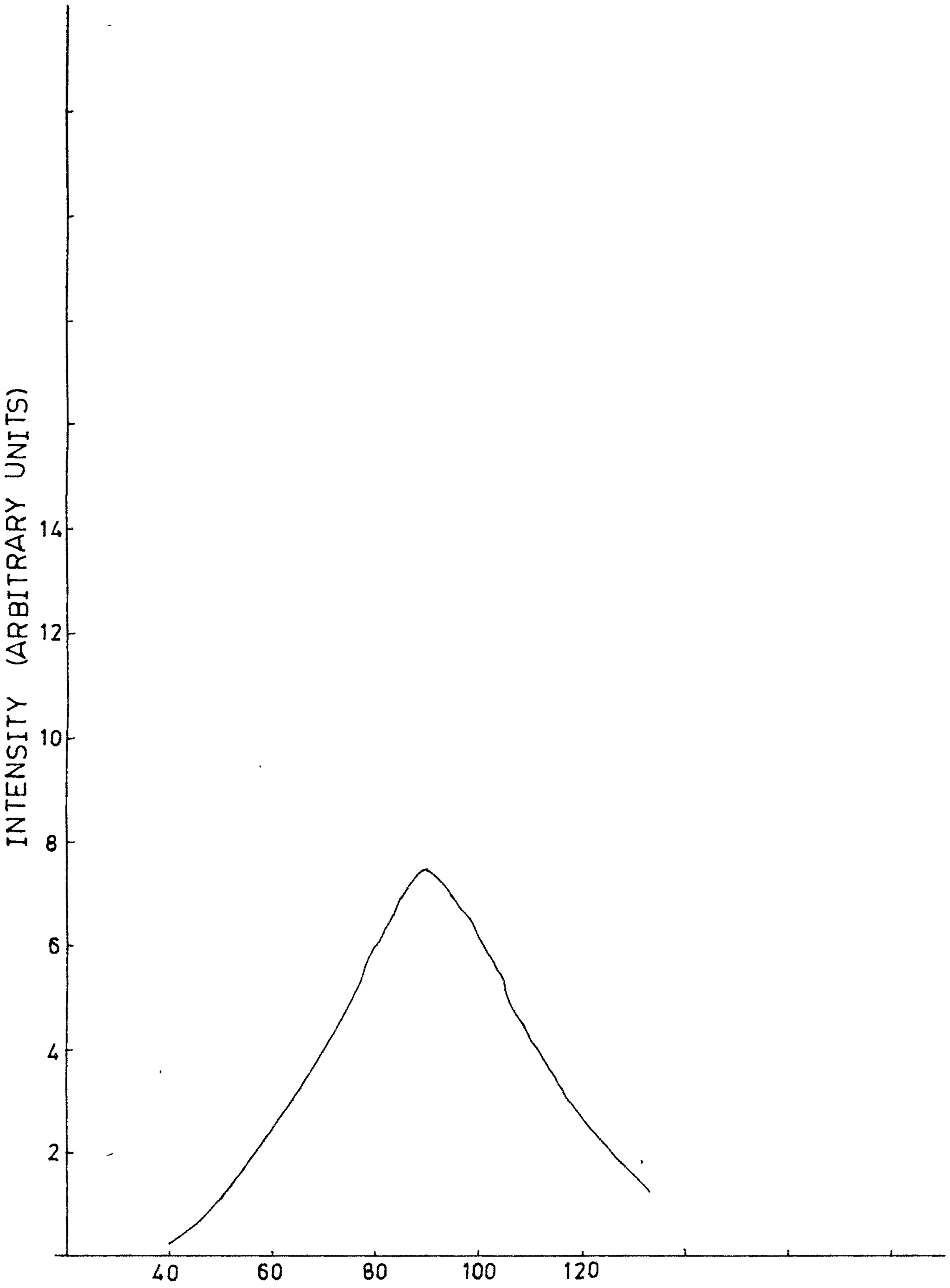
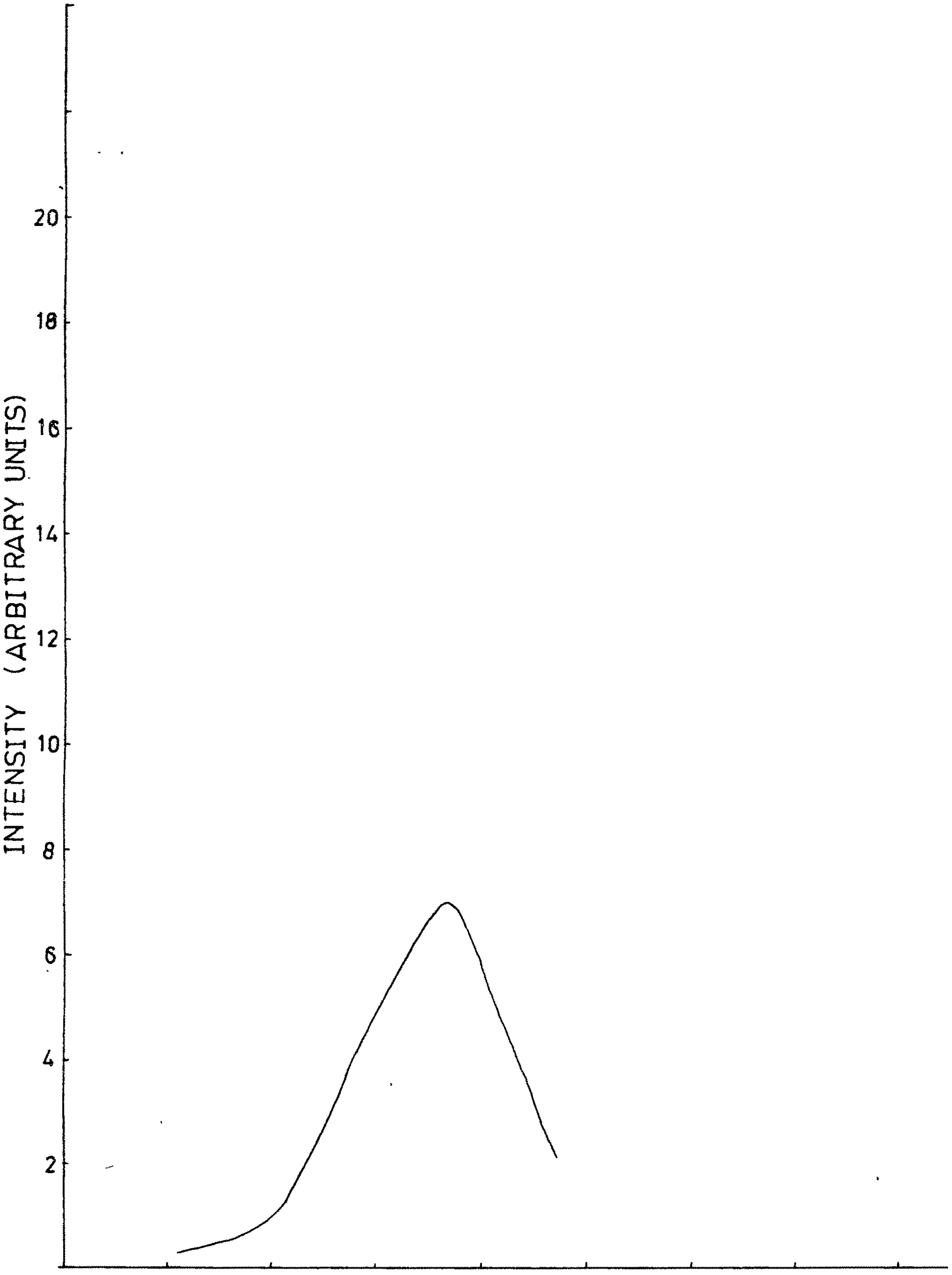


FIGURE 5·17 TEMPERATURE °C

Figure 5.18 Thermoluminescence spectra for Mechanically Deformed speciman P_5



INTENSITY (ARBITRARY UNITS)
20
18
16
14
12
10
8
6
4
2
40
60
80
100
120
TEMPERATURE °C

FIGURE 5·18

Figure 5.19 Fluorescence Spectra for Specimen M

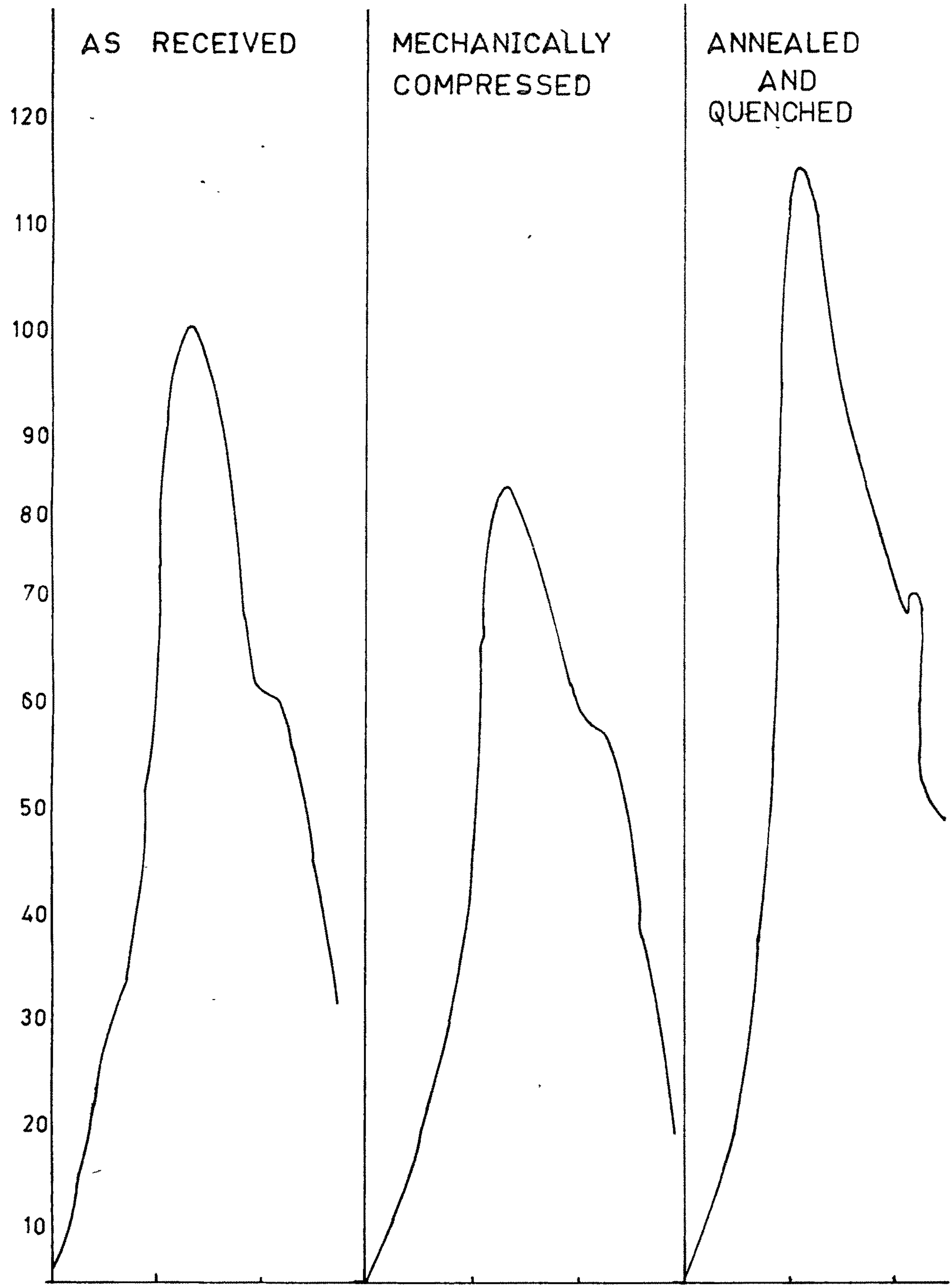


FIGURE 5·19 WAVELENGTH nm

Figure 5.20 Fluorescence Spectra for Specimen P_1

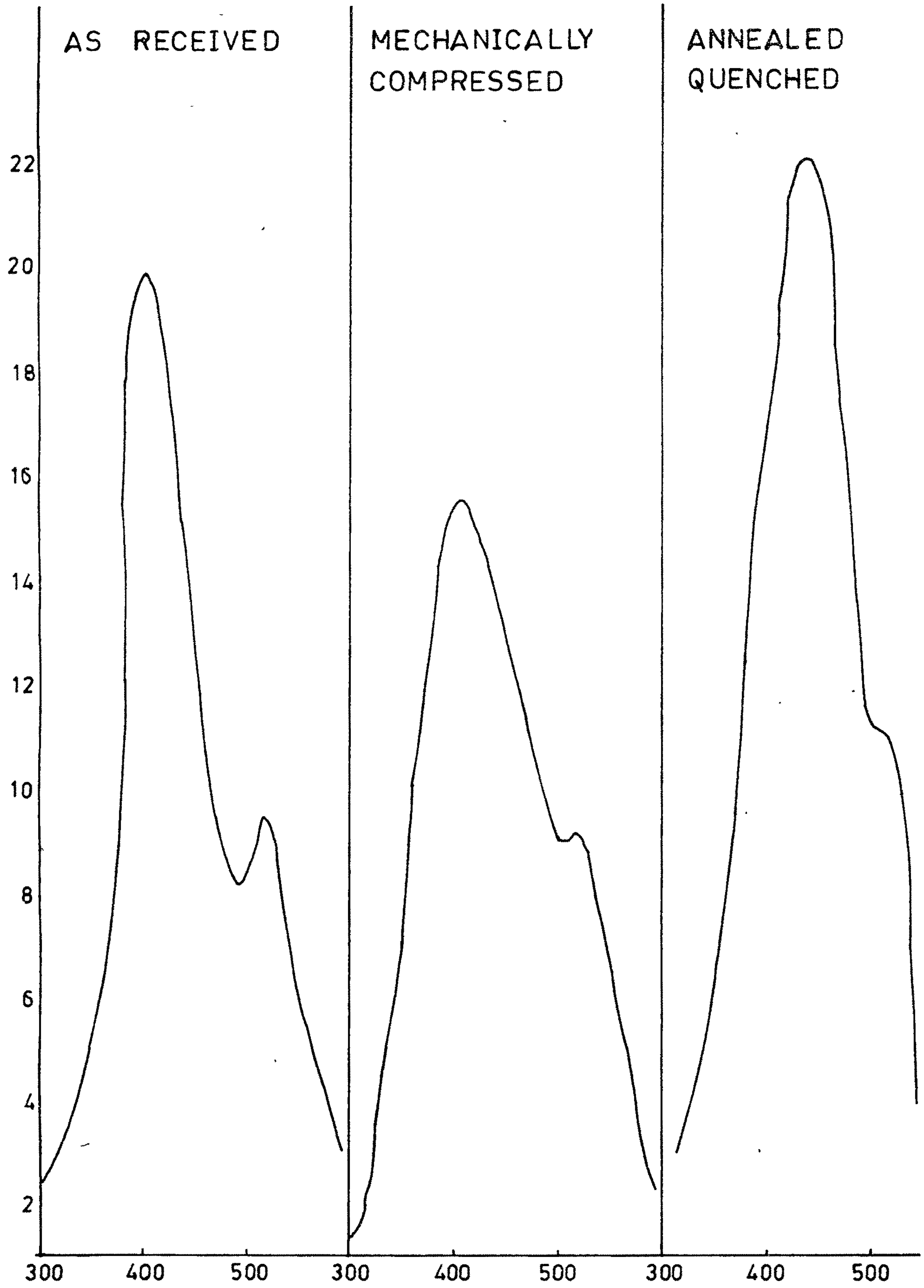


FIGURE 5·20 WAVELENGTH nm

Figure 5.21 Fluorescence Spectra for Specimen P_2

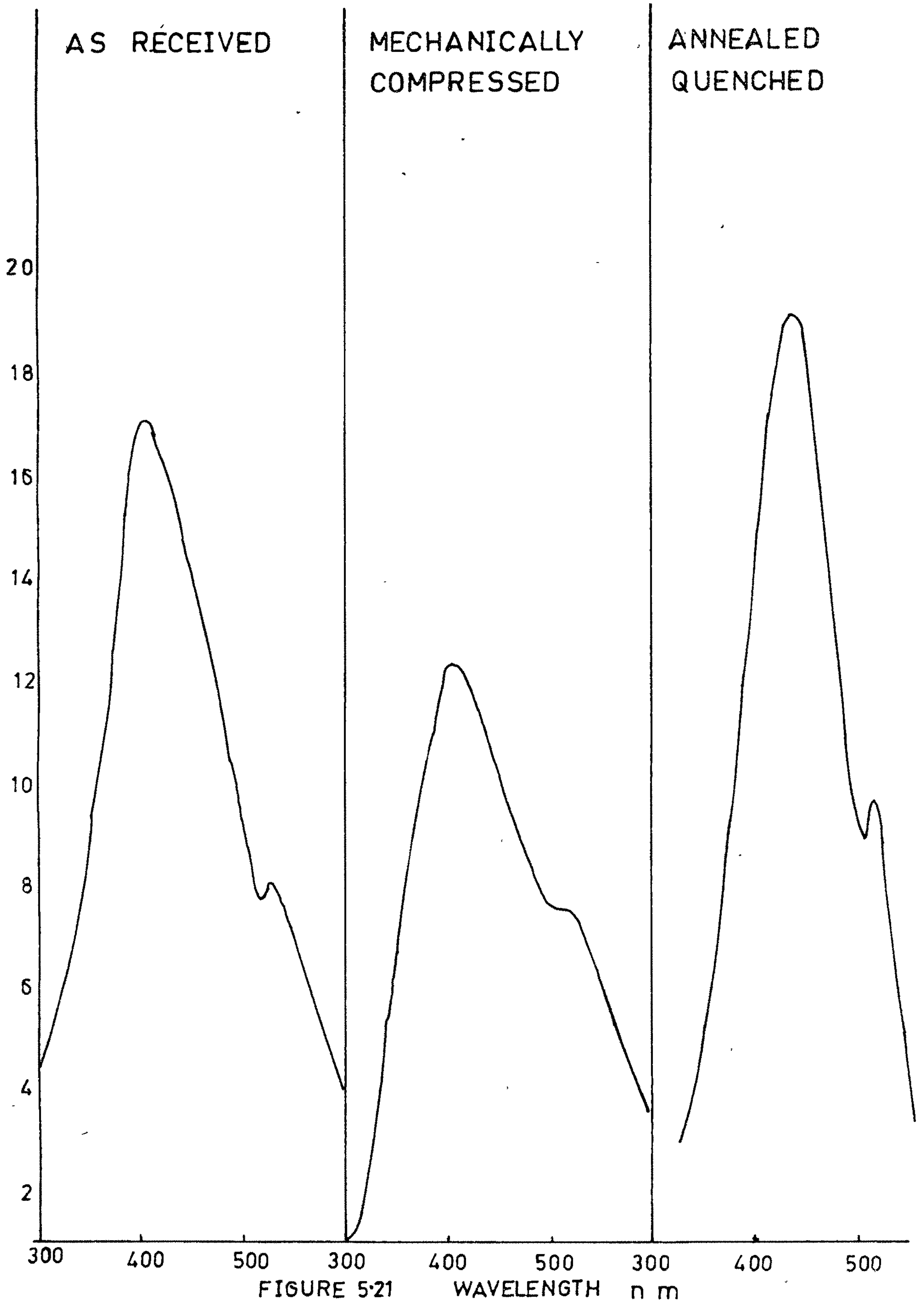


FIGURE 5·21 WAVELENGTH n m

Figure 5.22 Fluorescence Spectra for Specimen P_3

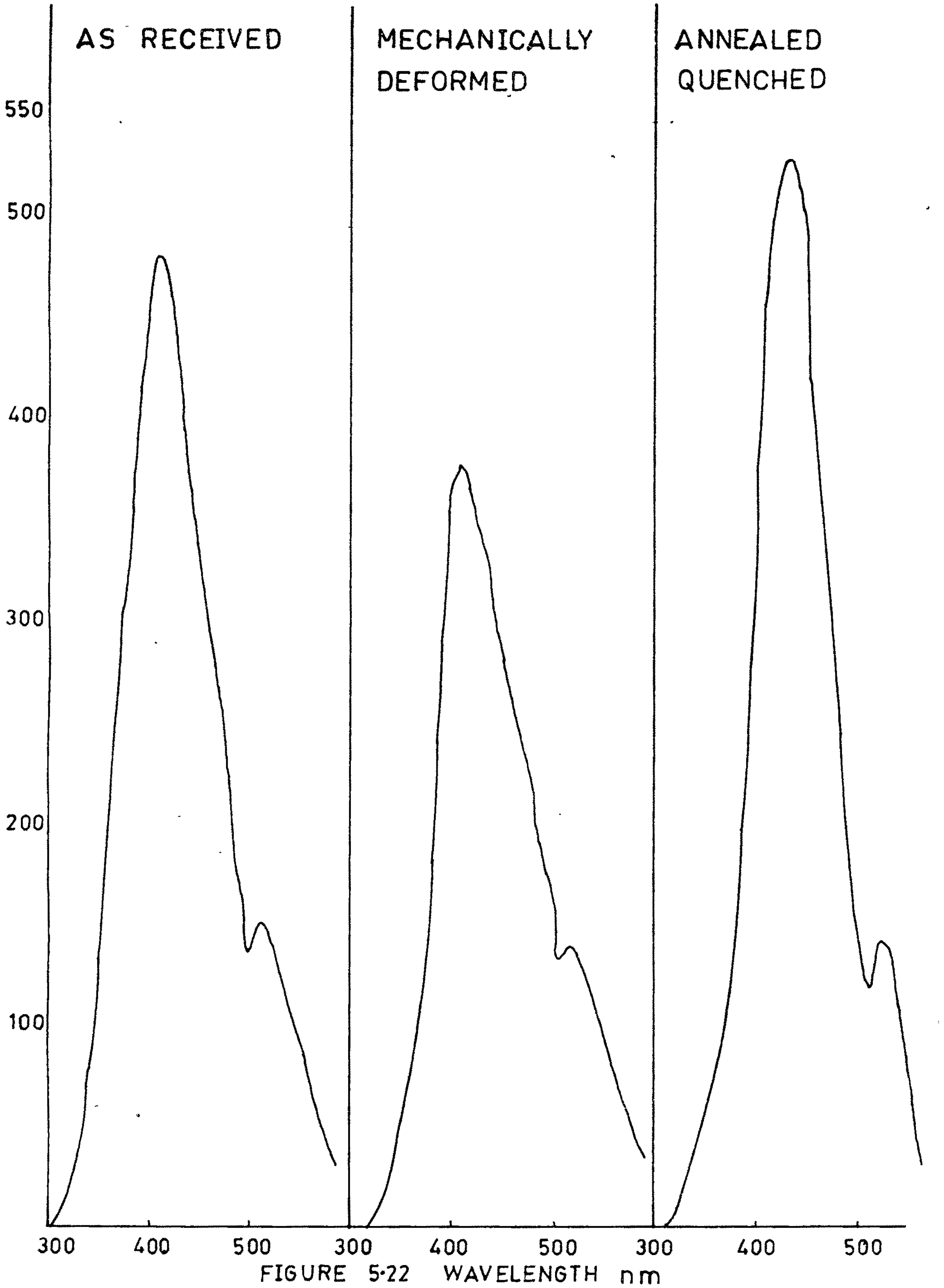
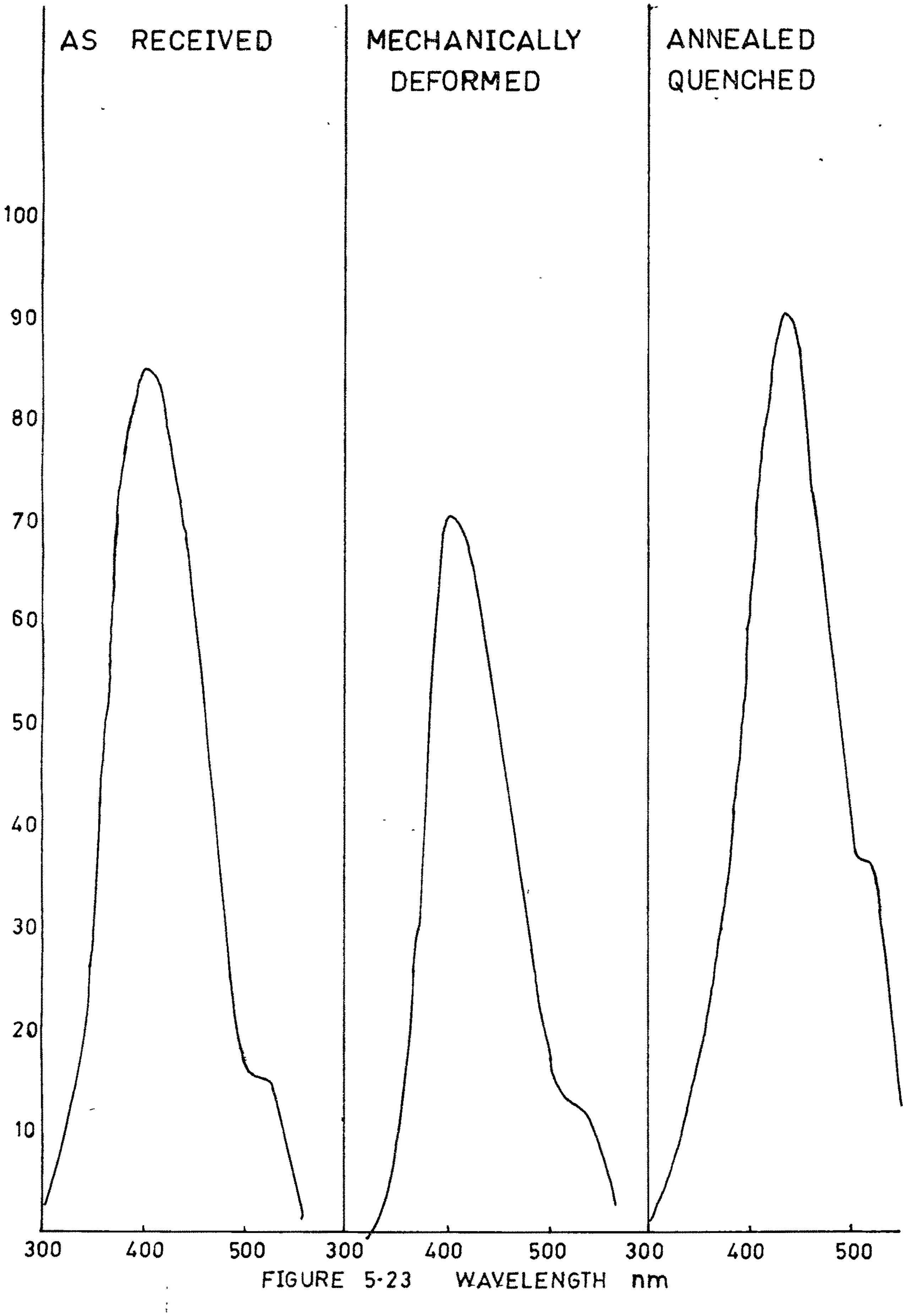

AS RECEIVED
MECHANICALLY DEFORMED
ANNEALED QUENCHED
550
500
400
300
200
100
300
400
500
300
400
500
300
400
500
WAVELENGTH nm

FIGURE 5·22

Figure 5.23 Fluorescence Spectra for Specimen P_4



AS RECEIVED
MECHANICALLY DEFORMED
ANNEALED QUENCHED
100
90
80
70
60
50
40
30
20
10
300
400
500
300
400
500
300
400
500
WAVELENGTH nm

FIGURE 5·23

Figure 5.24 Fluorescence Spectra for Specimen P_5

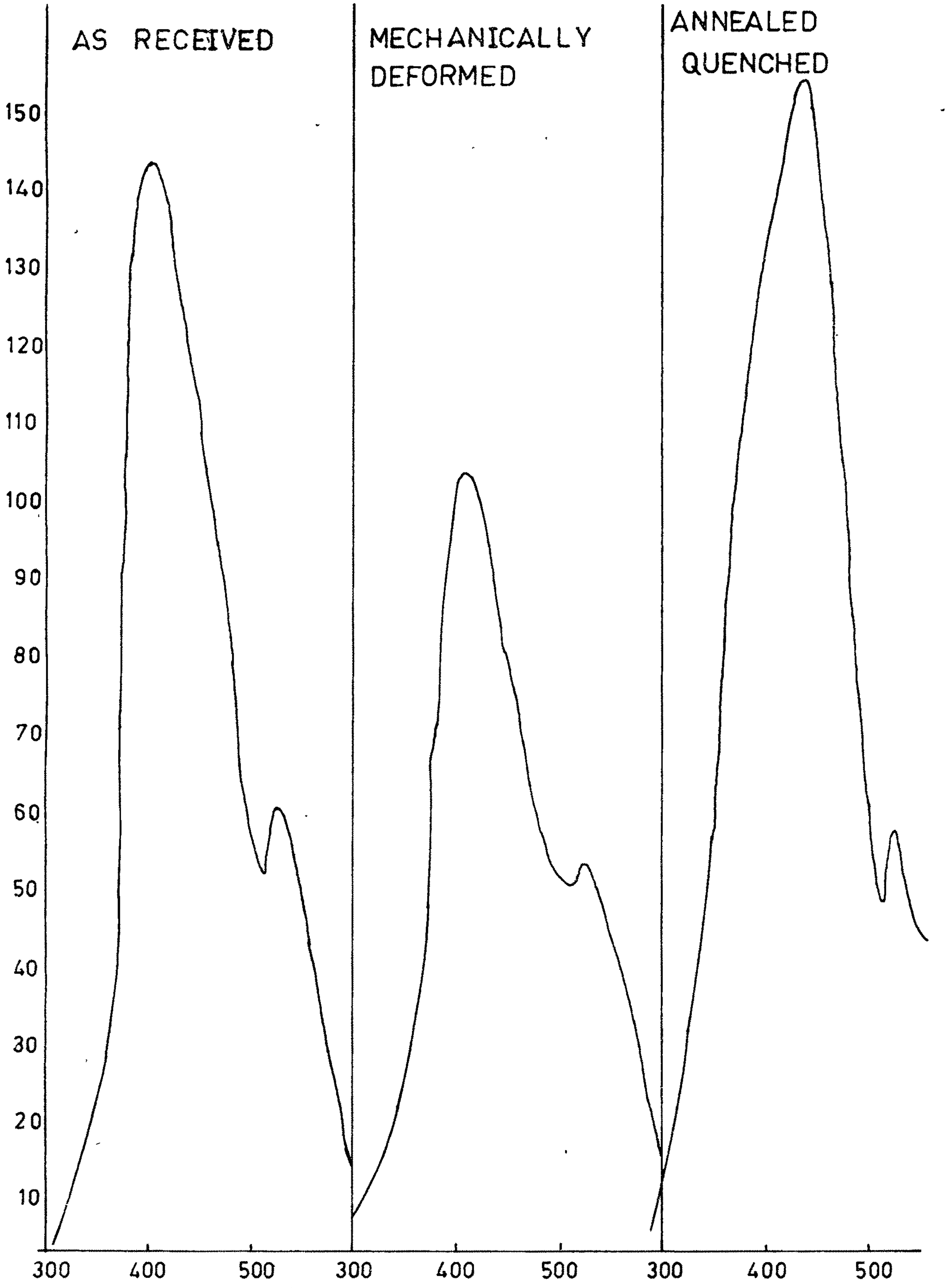

AS RECEIVED
MECHANICALLY DEFORMED
ANNEALED QUENCHED
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
300
400
500
300
400
500
300
400
500
WAVELENGTH nm

FIGURE 5·24

DISCUSSION

Thermoluminescence spectra and fluorescence spectra are recorded for the monomer specimen M and polymer specimens P1, P2, P3, P4 and P5.

The thermoluminescence in polymers has been studied by some workers (1-3). It is known from these studies, that there are two models proposed to explain the thermoluminescence of the polymers viz.

1. Radical-Radical recombination model (4)
2. Electron-ion recombination model (5,6,7)

Among them, the electron-ion recombination model has been widely accepted.

When a specimen is irradiated, ionisiation takes place. The freed electrons then are trapped at various sites; leaving the positive ion (8) behind. The majority of electrons will be trapped close to their parent ions. On heating the specimen, electrons in the trap get enough energy to escape from the trap. After the escape, the electrons can recombine with positive ions. This electron-ion recombination gives rise to the luminescence. This model (5-7) has been employed to explain the phenomenon of electroluminescence (8).

Anoter model which explains thermoluminescence is the radical-radical recombination model (4). It is assumed that when a polymer specimen is subjected to an irradiation, radicals get formed, some radicals then are trapped. On heating the specimen, radicals in the traps get enough energy to escape. After which, these escaped radicals will recombine with those untrapped ones. This recombination gives rise to luminescence.

Radical-Radical recombination model has not been accepted as widely as the other one, because of the formation of the radicals will be possible only under the high dose of radiation. At high doses, the intensity of the thermoluminescence is low due to the destruction of the luminescent centre and untrapping of some of the trapped electrons due to radiation (9) may take place. This makes the validity of this model doubtful.

The electron ion recombination model has been accepted by many workers (5,10), because the probability of formation of ions due to the exposure of material to radiations.

For the specimens, under the present investigations, it is suggested that the electron-ion recombination model is more acceptable for explaining the thermoluminescence. 5,7 dihydroxy-4-methyl coumarin and its polymers are easily ionised when they are subjected to radiations from the structural formula of coumarin, it can be seen that a loan pair of electrons is present on the oxygen at C1 and C3 positions in all the above specimens. However, in polymers, an additional loan pair of electron is also present on the oxygen in the ester group present in the backbone of chain.

Hence, when a monomer and polymers are exposed to radiations, ionisation takes place and the released electrons may get trapped. On supplying the heat energy, they may be detrapped and recombine with the ions, thereby giving luminescenece. Thus, thermoluminescence occuring in the specimens under investigations can be explained on the basis of the electron-ion recombination model.

Patridge (9) suggested four different types of traps, for the polymers.

Cavity traps suggested by Nikolskii (11) and Thomas et al (12). The voids of irregular shape, defined by the local spatial configuration of local chain are the cavity traps. These traps can be broken by the motion of pendant groups or of the backbone segments.

Second type of traps suggested are neutral molecules with positive electron affinity. These types of traps were suggested to be present in polyethylene (13) and paraffins (14).

Third types of the traps suggested are of free radicals which can capture the electrons. This type of traps are also reported by few workers(15).

The fourth type of traps are due to the molecules or molecular groups which have the electron affinity. This molecule may capture electrons by distorting polymer structure in its vicinity. Thermoluminescence emission from polytetrafluoroethylene (16) and polytetrafluoroethylene oxide (16) were explained on the assumption of the presence of this type of traps.

Specimens under the present investiation do not get into free radicals (17) on irradiation. Further, they do not contain neither any attached molecule or molecular group having positive electron affinity (17) nor the molecules themsleves possess positive electron affinity (17). This can easily confirmed by observing the structural formulae of specimens M and P1 through P5. Therefore, traps present in the above

The specimen subjected to preheat treatment show a thermoluminescnce peak shifts slightly on the lower side of 82°C observed in the 'as received' specimen.

The annealing of the polymer specimen at an elevated temperature will result in the onset of microbrownian and macrobrownian motions (23,24) for the chain.

The quenching produces different spatial configurations of the chain, compared to the original one, on freezing of the chain motion. Different spatial configurations due to freezing of the chain motion will create the cavity traps of slightly lower energy, resulting into the shift of thermoluminesnce peak towards lower temperature.

It is also seen from the thermoluminescence glow curves that for higher annealing temperature, the intensity of thermoluminescence peak is higher. When a specimen is annealed at higher temperature, more number of electrons get the thermal energy, resulting in the trapping of more number of electrons. Therefore, more number of electrons get released from traps at the peak temperature. This explains why intensity of thermoluminescence peak increases with an increase in annealing temperatures.

It is also observed from the thermoluminescence spectra of polymers annealed at 70 & 80°C, that a hump or shoulder is present at 60°C. However, this shoulder is missing in the specimens annealed at 60°C. The shoulder observed here is due to the formation of new traps having lower energy. At the elevated temperatures, the chains are set in motion may be a microbrownian or macrobrownian form of motion (23). The polymer chains, then may break and the sites at the end of breaked chains, where electrons are losely bound result in the formation of new traps. Alternately, it is possible that the pyrone ring may open up wherein the losely bound electrons will form new traps. The possibility of later mechanism is ruled out on knowing that, energy needed for the opening of the pyrone is larger than the energy required to break the chain in midway. Therefore it is possible that during the annealing, the chain might get broken and this broken chain may give rise to the formation of new traps which is responsible for the shoulder arising at 60°C.

From thermoluminescence spectra of mecahnically compressed specimens, it can be observed that thermoluminescence peak is present at 85°C for P1 and P2 slighty on the lower side compared to those in 'as received' specimens. However, for the polymer specimens P3, P4 and P5 the peak shift to 90°C, on the higher side of temp.

When polymer specimens are compressed, the distance between different chains decrease. The molecules may go out of plane, tilt, rotate, thus occupying lesser space(24). Thus change in the geometrical placement of a chain can take place. Now, the spatial configurations of chains will be definately different from the spatial configurations of the chains before the treatment.

Different spatial configurations of chain will create the cavity traps of different energies. In case of P1 and P2, cavity traps of lower energy might be formed, resulting into the shift of thermoluminescence glow peak slightly on the lower temperature side. However, for polymer specimens P3, P4 and P5, thermoluminesnce peak is observed to be on the higher temperature side to 90°C, suggesting that the cavity traps with higher energy are formed in the new spatial configuration of the chain.

specimens may be cavity traps. The presence of cavity traps is confirmed from the structure of polymers. Cavity traps are the voids with an irregular shape of a local chain. Careful observation of the structure of polymer indicates that the pyrone ring in the 5,7 dihydroxy-4-methyl coumarin, looks like a pendant group in the chain of polymer.

A void (Cavity) is formed due to the pendant goups, when a number of polymer chains are placed closed to each other. Therefore, it has been suggested that traps present in the specimens under investigations, are mainly the cavity type.

The thermoluminescence intensity measures the number of trapped electrons in any material capable of producing thermoluminescence. Generally, it has been observed that TL intensity decreases (9,18) as the dose increases. This suggests that increased dose can either destruct the luminescent centre or untrap the charges trapped within. This type of decerease of intensity, with the increase in dose, has been observed in polyethylene (19). However, few workers (20) have also reported the increase in intensity with the increased dose. This increase of intensity suggests that more charges may be trapped due to the increased radiation dose in addition to those already present inside the traps. This clearly explains the increase in intensity of a TL peak with the increase in dose in all the specimens investigated in the present work.

However, the increase in intensity was reported to vary with the dose of radiation (21,22). After a certain maximum, a drop in intensity is observed (10). This corresponds to the destruction of luminescent centres, the destruction of traps and also the formation of radicals.

The emission bands observed are at 430 nm in specimen M and at 410 nm in all the polymer specimens. This bond is attributed to the benzene ring attached to the pyrone ring. The emission for the coumarin is observed at 351 nm. Substitution (25) of the hydroxyl and methyl groups at C-5, C-7, and C-4 positions create bathochromatic shift of emission spectra to 430 nm. This has also been supported by other authors (26, 27). The hydrogen bond is present between the hydroxyl group in monomer M, however, such hydrogen bond is not present in polymers. The absence of hydrogen bond (28, 29, 30) in polymer shifts the emission hypsochromically to 410 nm.

The intensity of emission at 410 nm increases in specimens P1 to P5 compared to specimen M. An appreciable increase in number of molecules forming the chains in specimens P1 to P5 causes the intensity of this emission to increase. In polymers P1 and P2, 5-7 dihydroxy-4-methyl coumarins are connected by aliphatic acid units. The intensity in specimen P2 is much higher than that in P2. This is due to the difference in repeating units of polymers P1 and P2. In polymer P1, repeating unit consists of the aliphatic part -CH=CH while in polymer P2, repeating unit consists of the aliphatic part $-(CH8)_3-$. The double bond in aliphatic part of P1 contributes to the increased polarizability of the molecule of P1. This increased polarizability of P1 contributes to the increased intensity of fluorescence.

The comparision of the intensity for specimen P1 and P2 with the intensity of specimens P3 to P5 show that later specimens exhibit more intensity. This can also be explained on the basis of the polarizability. Polarizability is larger in the specimens P3 to P5 because repeating units of the same consist of aromatic parts instead of the aliphatic ones. The Π-bond character of the aromatic nucleus will enhance the polarizability of polymer molecules P3 to P5. The enhanced polarizability is reflected in the increased intensity of the above band. It can be seen that intensity of emission band in the polymer specimen P5 is more than in P4 than in P3. The steric factors (31, 32, 33) play an important role in deciding the intensity. The steric hindrance (Crowding of group) decreases the intensity of fluorescence viz. The cyanine dyes show less intensity due to steric hindrance. The steric hindrance in P5 is less than P4 less than in P3. The comparison of the structure of repeating units of P5 with P4 and P3 show that repeating units of later have higher steric hindrance due to 1,3 and 1-2 substitution on the benzene ring of acid. The steric interaction will be maximum in the specimen P3 due to the presence of phthalate group in repeating units. Therefore, the intensity of fluorescence in P3 is minimum among the polymers P3, P4 and P5. The steric hindrace is least in P5 due to the presence of terephthalate group in repeating units. This in turn results in the higher intensity in specimen P5.

EFFECT OF MECHANICAL DEFORMATION

All the specimens are mechanically compressed and their luminescence spectra are reorded. Mechanically compressed specimens show the emission at the identical position but with reduced intensity compared to 'as received' specimen. The specimens are compressed together wherein there is a possibility of the polymer going out of plane and getting a tilt so that it occupies lesser (24) space. The effect is the observed less intensity compared to that in 'as received' form.

EFFECT OF THERMAL TREATMENT

The annealing of the polymer specimens at an elevated temperatures will make the atoms disperse from each other due to the absorption of thermal energy which may onset microbrownian and macro brownian motions (23) of the chain. On slow cooling, it is expected that polymer chains should occupy the same position. However, sudden cooling of these annealed specimen to room temperature produces the configuration of chains in polymer specimens other than the original one. It may be possible that polymeric chains might have broken into smaller chains. This change in the configuration due to sudden cooling shifts the emission from 410 nm to 440 nm. Sudden cooling New geometrical configuration may be responsible for this shift. However, the quenching of monomer specimen M does not change its geometrical configuration. Therefore, the emission peak remains at 430 nm. The relative intensity can be explained on the basis polarizability and steric hindrance similar to that in as received specimens.

The second peak which is observed in the emission spectra at 520 nm may be attributed to the presence of heteroatom, also the oxygen at position C-2 in the pyrole ring of coumarin. The non-bonding electron present on the oxygen can be held mainly responsible for this peak. It is observed that position of emission peak in the monomer M and polymer specimens P1 to P5 are same. This is expected, since structure of pyrole ring remains in same the monomer specimen M and polymer specimens P1 to P5, not as observed in the benzene ring which is conjugated to pyrole ring 5,7 position of monomer is substituted by the hydroxyl group while this position now is occupied by the ester group in polymers. Therefore, no shift in the ground state energy level to expected . This is expected to be the reason for the peak not getting shifted in polymers.

This tries to explain the various peak positions alongwith the intensity in all the specimens chosen for investigations.

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