CHAPTER V

RESULTS AND DISCUSSION

(A) RESULTS

The excitation and emission spectra of NaCl:Tl powder specimens differing in thallium content were measured at room temperature. The specimens were studied in as-received conditions and after various pretreatments. The results obtained are presented in this section. The preparation of the specimens involved crystallization of 'Specpure' sodium chloride, with varying quantities of thallous chloride, from aqueous solution. Like other alkali halides, sodium chloride does not luminesce strongly in the pure state until the temperature is lowered below 80°K. A weak luminescence in alkali halides at 300°K has been of course, reported earlier[1]. Necessary precautions were therefore taken against the misinterpretation of the experimental data that may be attributed to intrinsic luminescence. The excitation and emission spectra presented in the thesis have been therefore corrected, wherever necessary, by subtracting very low intensity excitation and emission of as-received and pretreated pure NaCl specimens from those of the corresponding thallium-doped specimens. Precautions were also taken to remove the effect of scatter in the instrument by using suitable filters. Luminescence measurements were

carried out for a number of specimens and the typical luminescence spectra are presented for discussion. In all the cases the excitation spectrum of a given specimen was first observed and subsequently its emission spectrum stimulated by the observed excitation was recorded. Each excitation and emission band is designated by the wavelength at which its peak appears. It should however, be mentioned that a band may not appear isolated and may possess satellites to the higher or lower wavelength side. In such a case, changes in the relative intensities of the components within a composite band would lead to an apparent shift in the position of its maximum. In this respect the peak positions indicated can only be regarded as approximate. Wherever necessary, the complex excitation and emission bands have been analyzed by the superposition of bell-shaped curves. The intensities of the excitation and emission bands are given in absolute units.

Overall examination of the excitation and emission spectra obtained in the present measurements indicates that the excitation and the emission bands can be classified into three groups on the basis of the region in which emission occurs. The three groups are :
(i) Excitation bands favouring ultraviolet emission

(ii) Excitation bands favouring near-ultraviolet emission and (iii) Excitation bands favouring visible emission.

(i) Figs. 1 through 14 correspond to various NaCl:Tl phosphors with Tl concentration varying in the range between 10^{-4} to 10^{-1} molar fraction. These figs. exhibit the excitation and emission spectra for specimens, obtained by crystallization from aqueous solution, in as-received condition and after various pretreatments. The data in these figs. concern with the emission of the phosphors in the ultraviolet region.

(Figs. 1 - 4) :

Fig. 1, Curves: 1 and 2 represent the excitation spectra for 320 nm emission of the phosphors with 10^{-4} and 10^{-3} molar fraction Tl. These spectra consist of a single pronounced excitation band at 256 nm. Fig. 2, Curves: 1 and 2 show that the excitation of these phosphors at 256 nm gives emission at 320 nm besides other emission bands in the near-ultraviolet and visible region. It may be mentioned that 256 nm excitation favours 320 nm emission however, this excitation

band is very closely situated to the excitation band (260 nm) responsible for the dominant emission in the near-ultraviolet region (360-390 nm). Fig. 3, Curves: 1 and 2 show the excitation spectra of the phosphors with 10^{-2} and 10^{-1} molar fraction Tl. In both ~~the~~ cases the excitation spectrum resembles the one observed for the phosphor with lower concentration of Tl. It is clearly seen from the figures that the increase of Tl concentration brings about decrease in the strength of 256 nm excitation and the related 320 nm emission band (Fig. 4).

(Figs. 5,6) :

Fig. 5, Curves: 1 and 2 exhibit the excitation spectra for 320 nm emission of two as-received powder specimens (Tl conc. : 10^{-4} and 10^{-3} m.f.) compressed to tablet. In both ~~the~~ cases the excitation spectrum displays band at 256 nm. Fig. 6, Curves: 1 and 2 show that the excitation of the phosphor at 256 nm gives rise to emission at 320 nm alongwith other emission bands.

(Figs. 7 - 10) :

The excitation and emission spectra of the phosphors annealed in evacuated and sealed tubes at 500°C and

subsequently quenched to room temperature, in as-received condition and after compression to tablet, are presented in Figs. 7 to 10. As-received phosphors (Tl conc. : 10^{-4} and 10^{-3} m.f.) exhibit prominent excitation band around 256 nm (Fig. 7, Curves : 1 and 2) for 320 nm emission whereas the emission spectra excited by this band consist of the emission band at 320 nm and other bands in the near-ultraviolet and visible region (Fig. 8, Curves : 1 and 2). It may be noted that 320 nm emission appears more significant relative to other bands in the emission spectrum in the case of specimen having lowest Tl concentration (Fig. 8, Curve : 1).

Compression of the thermally pretreated powder specimen to tablet primarily influences its emission spectrum. The relative strength of 320 nm emission band decreases if the specimen is subjected to compression by stressing (Fig. 10, Curve : 1 and 2). Further, an overall increase in the emission on the long-wavelength side of 320 nm emission is also noticeable.

(Figs. 11 - 14) :

Fig. 11, Curves : 1 and 2 illustrate the excitation spectra of the melt and quenched specimens with 10^{-4} and

10^{-3} molar fraction Tl, measured for emission at 320 nm. Fig. 13 exhibits excitation spectra for the above specimens (for 320 nm emission) after compression to tablets. In all the cases the excitation spectrum displays a single band around 256 nm. The emission spectra for the above specimens, when excited by irradiation into 256 nm band, exhibit 325 nm band and other bands on the long wavelength side. Comparison of the emission spectra of the two specimens one of which is annealed and quenched from 500°C (Fig. 8, Curve : 1) and the other quenched from melt (Fig. 12, Curve : 1), both having same concentration of Tl, clearly indicates that greater thermal shock suppresses 320 nm emission.

(ii) Figs. 15 through 42 represent the luminescence data for near-ultraviolet emission of the phosphors. The specimens, prepared by crystallization from aqueous solution, were examined in as-received condition and after subjecting them to various pretreatments. Thallium content of the phosphors ranged between 10^{-4} to 10^{-1} molar fraction. The results presented in these figures correspond to the near-ultraviolet emission of the phosphor.

(Figs. 15 - 22) :

The excitation spectra of as-received specimens, differing in Tl concentration, are presented in the Figs.15, 17, 19 and 21. The excitation spectra for these specimens in general, exhibit a principal band between 260 nm and 265 nm and a subsidiary band between 225 and 230 nm. The emission spectra excited by these bands are shown in Figs.16, 18, 20 and 22. Excitation of the phosphor by absorption of light at 230 nm gives rise to emission spectrum somewhat similar to the one excited by 265 nm band. The difference in the intensities of the bands in the emission spectra excited by 230 and 265 nm band is clearly observable. Further, the 320 nm emission band is conspicuous by its absence in the emission spectrum excited by 230 nm band. At lowest Tl concentration (10^{-4} m.f.) the emission spectra for both 230 and 265 nm excitation consist of a pronounced band at 360 nm and other bands in the ultraviolet and visible region. With the increase in Tl concentration the peak position at 360 nm shifts to the long wavelength side indicating that 360 nm band is composite in nature. This presumption is substantiated by the clear appearance of a double maximum (at 360 and 390 nm) in the emission spectrum (Fig. 22, Curves : 1 and 2) for highest Tl

concentration (10^{-1} m.f.). It may also be noted that in the emission spectra excited by 265 nm band, the bands in the visible region become more conspicuous in the case of specimen with highest Tl concentration (Fig. 22, Curve : 2). On the other hand, at highest Tl concentration, there is a marked decrease in the strength of the emission band around 390 nm excited by either 230 nm or 265 nm band.

(Figs. 23 - 30) :

The excitation and emission spectra of the specimens deformed by compression to tablets are presented in Figs. 23-30. Excitation spectra of these specimens, though differing in Tl concentration, display in common a primary band around 265 nm and a secondary band around 230 nm (Figs. 23, 25, 27 and 29). The emission spectra excited by absorption of light into 230 nm and 265 nm band in general, consist of a prominent band at 390 nm, bands of lesser intensity in the region between 360-380 nm and other bands of still lesser intensity at 450, 480 and 520 nm. Comparison of the emission spectra for the specimens in the form of powder (Figs. 16, 18, 20 and 22) and in the form of tablet (Figs. 24, 26, 28 and 30), having same Tl concentration,

clearly indicate the suppression of 320 nm band in the spectra for the tabletted specimens. Further, deformation-induced enhancement in the intensities of the emission bands in the 360-390 nm region as well as in the visible region is also observable.

(Figs. 31 - 38) :

Figs. 31-38 represent the excitation and the emission spectra of the specimens, annealed in evacuated and sealed tubes at 500°C and then quenched to room temperature, in as-received condition and after compression to tablet. The excitation spectra of these specimens also exhibit two bands, one around 230 nm and other around 268 nm. Excitation of the specimens either at 230 nm or 268 nm gives rise to dominant emission in the 360-390 region. It may also be noted that the deformation induces enhancement in the intensities of the visible emission bands (compare Curve : 2 in Fig. 32 with that in Fig. 36 and Curve : 2 in Fig. 34 with that in Fig. 38).

(Figs. 39 - 42) :

The excitation and emission spectra of melt and quenched specimens in as-obtained condition and after

deformation by stressing were also recorded. Figs. 39 and 41 demonstrate the excitation data for the specimens before and after compression to tablet. It is seen that in both the cases the excitation spectrum consists of a dominant band at 267 nm. In the excitation spectrum of one of the tabletted specimens, an excitation band at 280 nm is also discernible (Fig. 41, Curve : 1). It is noteworthy that the 230 nm excitation band appearing alongwith 265 nm excitation band, in the spectra of the specimens examined so far, is surprisingly absent in the excitation spectra of melt and quenched specimens. Excitation into 267 nm band results in the emission principally in the near-ultraviolet region with subsidiary emission in the visible region.

Results described above for NaCl:Tl phosphors, as-received from solution, with four different Tl concentrations are summarized in Table 1. Table 2 incorporates the data obtained for variously pretreated NaCl:Tl phosphors. In these tables and the others following, the number in the bracket refers to Fig. No. and the abbreviation given above the peak wavelength indicates the relative strength of the band. The following abbreviations are used:

S - Strong; M - Medium; W - Weak; V.W. - Very Weak.

TABLE 1

Excitation and Emission Bands Displayed by As-received NaCl:Tl Phosphors Differing in Tl Concentration (Wavelengths in nm)

Sr. No.	Specimen	Tl Conc. in m.f.	Excitation band	Emission	
				Band/ Bands favoured	Other bands
1.	NaCl:Tl Powder phosphor prepared from aqueous solution	10^{-4}	S 256 (1)	S 320 (2)	S 360 W 450
2.	" "	"	M 225 (15)	S 360 (16)	W 480 W 520
3.	" "	"	S 260 (15)	S 360 (16)	S 320 M 450 W 480
4.	" "	10^{-3}	S 256 (1)	M 320 (2)	S 370 W 430 W 480
5.	" "	"	M 228 (17)	S 370 (18)	M 450 W 520
6.	" "	"	S 263 (17)	S 370 (18)	M 320 M 450 W 480

contd.....

TABLE 1

Sr. No.	Specimen	Tl Conc. in m.f.	Excitation band	Emission			
				Band/ Bands favoured	Other bands		
7.	NaCl:Tl Powder phosphor prepared from aqueous solution	10^{-2}	S 256 (3)	M 320 (4)	M 360	S 378	W 430
					W 480		
8.	" "	"	M 228 (19)	S 378 (20)	M 360	M 450	W 520
9.	" "	"	S 263 (19)	S 378 (20)	W 325	M 360	W 450
10.	" "	10^{-1}	S 256 (3)	M 320 (4)	M 360	S 384	W 450
					W 480		
11.	" "	"	M 230 (21)	S 384 (22)	M 360	M 450	W 520
12.	" "	"	S 262 (21)	S 384 (22)	M 325	M 360	M 450
					W 480		

TABLE 2

Excitation and Emission Bands Exhibited by Pretreated NaCl:Tl Phosphors (Wavelengths in nm)

Sr. No.	Specimen	Tl Conc. in m.f.	Excitation band	Emission			
				Band/ Bands favoured	Other bands		
1.	As-received NaCl:Tl powder phosphor compressed to tablet	10^{-4}	256 (5)	M 320 (6)	M 360	S 385	M 450
					M 480		
2.	" "	"	W 228 (23)	S 390 (24)	S 375	W 480	W 520
3.	" "	"	S 267 (23)	S 390 (24)	W 320	S 380	M 450
					M 480		
4.	" "	10^{-3}	S 256 (5)	M 320 (6)	M 360	S 385	M 450
					W 480		
5.	" "	"	M 227 (25)	S 390 (26)	M 360	S 375	W 520
6.	" "	"	S 264 (25)	S 390 (26)	W 320	S 375	M 450
					M 480		

contd....

TABLE 2

Sr. No.	Specimen	Tl Conc. in m.f.	Excitation band	Emission	
				Band/ Bands favoured	Other bands
7.	As-received NaCl:Tl powder phosphor compressed to tablet	10^{-2}	M 235 (27)	S 392 (28)	M 360 M 450 W 520
8.	" "	"	S 265 (27)	S 392 (28)	W 320 M 365 M 450 M 480 W 520
9.	" "	10^{-1}	M 228 (29)	S 395 (30)	S 370 M 520
10.	" "	"	S 265 (29)	S 395 (30)	M 480

contd.....

TABLE 2

Sr. No.	Specimen	Tl Conc. in m.f.	Excitation band	Emission	
				Band/ Bands favoured	Other bands
11.	NaCl:Tl powder phosphor annealed and quenched from 500°C	10^{-4}	S 258 (7)	S 320 (8)	S 360
12.	" "	10^{-3}	S 259 (7)	S 320 (8)	S 362
13.	" "	10^{-2}	M 233 (31)	S 364 (32)	W 450
14.	" "	"	S 266 (31)	S 364 (32)	M 450 M 480
15.	" "	10^{-1}	M 228 (33)	S 372 (34)	W 450 W 480
16.	" "	"	S 267 (33)	S 372 (34)	M 450 M 480

contd....

TABLE 2

Sr. No.	Specimen	Tl Conc. in m.f.	Excitation band	Emission	
				Band/ Bands favoured	Other bands
17.	NaCl:Tl powder phosphor annealed and quenched from 500°C and then pressed to tablet	10^{-4}	S 257 (9)	S 320 (10)	S 360, M 480, S 385, M 450
18.	" "	10^{-3}	S 259 (9)	M 320 (10)	S 360, M 450, S 375, W 480, S 390
19.	" "	10^{-2}	M 233 (35)	S 364 (36)	S 385, W 450
20.	" "	"	S 267 (35)	S 375 (36)	M 320, M 450, M 480
21.	" "	10^{-1}	M 235 (37)	S 382 (38)	M 450, M 480
22.	" "	"	S 267 (37)	S 388 (38)	M 450, M 480

contd.....

TABLE 2

Sr. No.	Specimen	Tl Conc. in m.f.	Excitation band	Emission			
				Band/ Bands favoured	Other bands		
23.	NaCl:Tl melt and quenched powder phosphor	10^{-4}	S 260 (11)	M 325 (12)	S 360	W 450	
24.	" "	10^{-3}	S 256 (11)	S 325 (12)	S 362	W 450	W 480
25.	" "	10^{-2}	S 267 (39)	S 375 (40)	M 325	M 450	W 480
26.	" "	10^{-1}	S 267 (39)	S 375 (40)	W 320	M 450	W 480

contd.....

TABLE 2

Sr. No.	Specimen	Tl Conc. in m.f.	Excitation band	Emission	
				Band/ Bands favoured	Other bands
27.	NaCl:Tl melt and quenched powder pressed to tablet	10^{-4}	S 259 (13)	M 320 (14)	S 360 W 450
28.	" "	10^{-3}	S 260 (13)	S 325 (14)	S 370 W 480
29.	" "	10^{-2}	S 267 (41)	S 390 (42)	V.W. 320 M 450 W 480 W 520
30.	" "	10^{-1}	S 267 (41)	S 390 (42)	V.W. 320 M 450 M 480 W 520

(Figs. 43 - 50) :

Preliminary experiments indicated that the emission of the phosphor in the visible region is favoured by excitation into wavelengths between 265 and 280 nm. Measurements were made therefore to investigate in detail the excitation spectra for visible emission of as-received (from solution) and pre-treated NaCl:Tl phosphors. The results obtained are presented in Figs. 43 through 50. For most of the specimens examined, the excitation spectra were recorded for three emission bands noted in the visible region, namely 450, 480 and 520 nm. It is seen that instead of 230 nm excitation band, observed alongwith 265 nm excitation band for near-ultraviolet emission of the specimens, there now appears an excitation band around 240 nm for visible emission of the specimens. Since the excitation band (260 nm region) for strong near-ultraviolet emission has an extensive overlap with the excitation band (265-280 nm region) for weaker visible emission, the emission spectrum obtained by excitation into 265-280 nm region band nearly coincides with the one excited by 265 nm band.

(Figs. 51 - 54) :

Present measurements also included the studies of the excitation and emission spectra of as-received TlCl

powder and its tabletted specimen. Figs. 51 and 53 respectively demonstrate the excitation spectra for as-received and mechanically deformed specimens. In both the cases the excitation spectrum consists of a broader and flatter band, stretching roughly from 210 to 270 nm. The emission spectrum for any of the specimens is nearly independent of the wavelength of the exciting light. While the excitation spectrum of TlCl does not exhibit well defined maxima, its emission spectra display two emission bands namely, at 360 and 385 nm. In the powder specimen one observes principal emission band at 385 nm and a subsidiary band at 360 nm (Fig. 52). On the other hand, in a tabletted specimen, the 360 nm becomes much more pronounced and overshadows the 385 nm band. It is interesting to note that in untreated or pretreated TlCl the emission is only in the 360-385 nm region.

(Figs. 55 - 63) :

In yet another series of experiments excitation and emission spectra of (i) aqueous solution of TlCl and (ii) TlCl in saturated aqueous solution of NaCl were examined. The results obtained are presented in Figs. 55 through 63. The saturated solution of TlCl exhibits an excitation band

around 255 nm (Fig. 55, Curve : 1). A broad emission band peaking at 390 nm is observed by excitation at this wavelength (Fig. 56, Curve : 1). It is seen from the excitation and emission curves for TlCl-solution that the intensity of the excitation as well as the emission band increases with the decrease in the concentration of the solution. The enhancement in the intensity of these bands continues till the solution is diluted to 1:50 (Fig. 59, Curve : 1 and Fig. 60, Curve : 1). With further dilution of the solution, the intensity of the excitation and the emission band begins to drop. It is of interest to note that with the decrease in the concentration of TlCl-solution there is a shift in the position of the excitation and the emission maximum to the short-wavelength side i.e. from 390 nm to 360 nm. In addition, a new excitation band appears around 206 nm for TlCl-solution with 1:20 dilution (Fig. 57, Curve : 2). This excitation band grows in intensity as the concentration of the solution decreases and simultaneously a shift in the position of the band to the long-wavelength side is observed till it stabilizes around 214 nm (Fig. 59).

Figs. 61, 62 and 63 demonstrate the excitation and emission spectra obtained for TlCl in aqueous saturated

solution of NaCl. The excitation spectra for this solution consist of a band at 258 nm when 1 mg TlCl is added to 20 c.c. of saturated NaCl solution (Fig. 61, Curve : 1). The band maximum shifts to long-wavelength side as TlCl concentration is increased. The position of the maximum moves to 272 nm when 10 mg TlCl is added to saturated NaCl solution (Fig. 61, Curve : 6). The emission spectra excited by 260-275 nm region band and 230 nm band are presented in Figs. 62 and 63 respectively. In both the cases there is a strong emission band at 425 nm. The emission spectra obtained by excitation into 260-275 nm region however, shows other emission bands of lower intensities at 450, 480 and 520 nm (Fig. 62).

Fig. 1 : Excitation spectra of NaCl:Tl powder specimens for 320 nm emission.
As-received specimens (i.e. as obtained by crystallization from aqueous solution).

Curve : 1 - For Tl concentration $\sim 10^{-4}$ m.f.

Curve : 2 - " " $\sim 10^{-3}$ m.f.

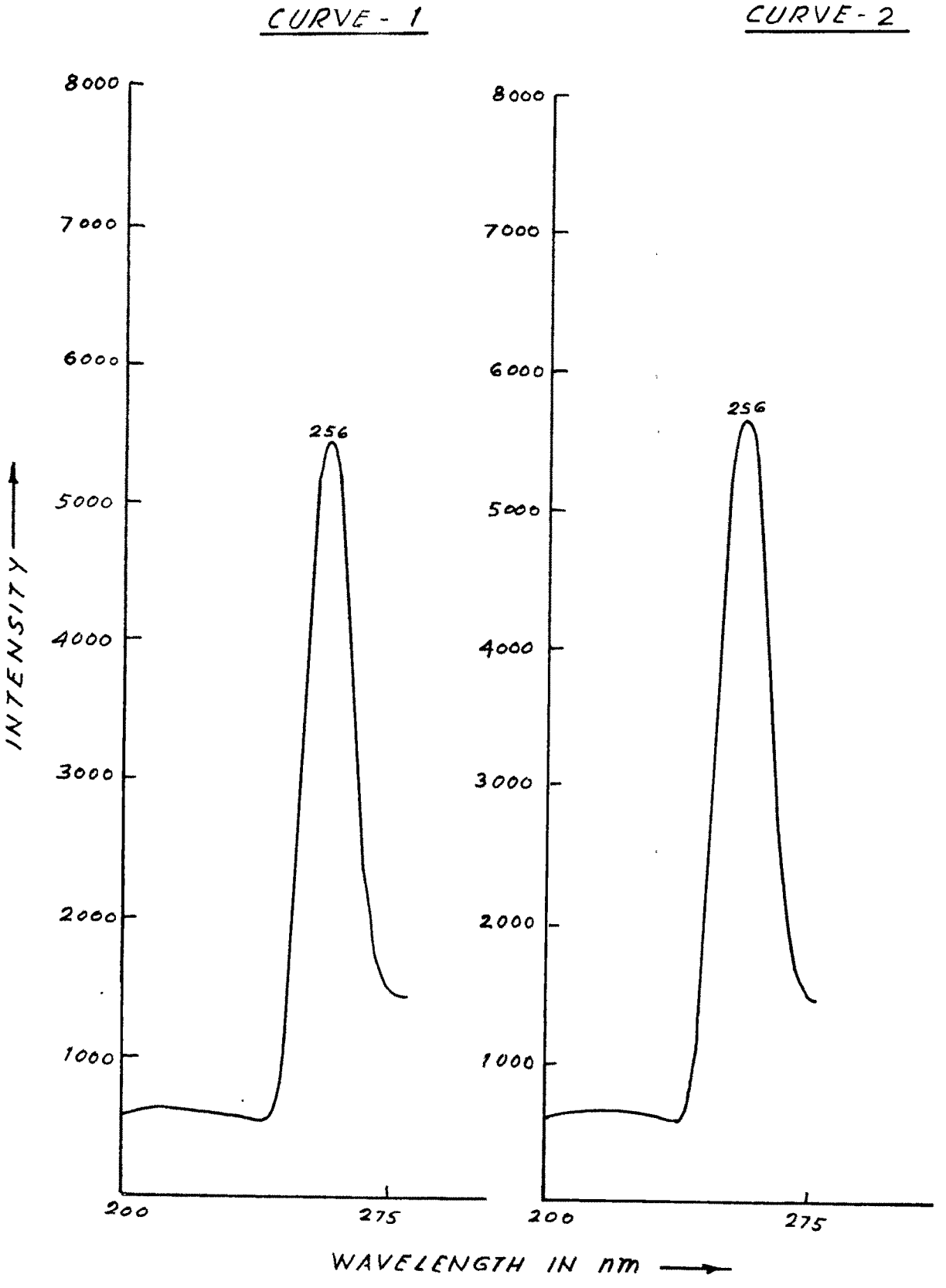
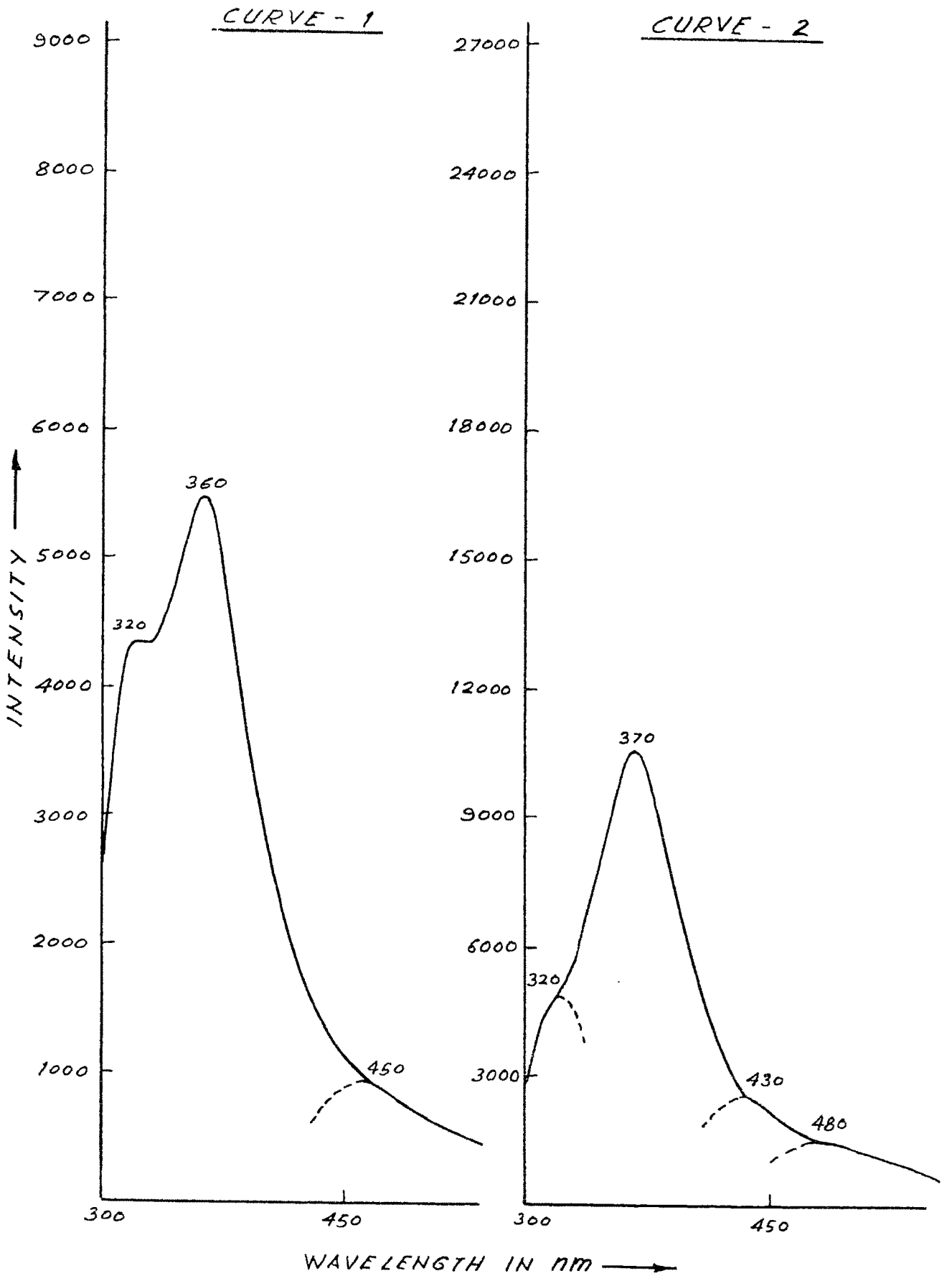

CURVE - 1
CURVE - 2
8000
7000
6000
5000
4000
3000
2000
1000
256
INTENSITY
200
275
WAVELENGTH IN nm

FIG. 1

Fig. 2 : Emission spectra of NaCl:Tl powder specimens upon excitation at 256 nm. As-received specimens (i.e. as obtained by crystallization from aqueous solution).

Curve : 1 - For Tl concentraion $\sim 10^{-4}$ m.f.

Curve : 2 - " " $\sim 10^{-3}$ m.f.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CURVE - 2
9000
8000
7000
6000
5000
4000
3000
2000
1000
27000
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
360
320
450
370
320
430
480
300
450
300
450
WAVELENGTH IN nm

FIG. 2

Fig. 2 : Excitation spectra of NaCl:Tl powder specimens for 320 nm emission. As-received specimens (i.e. as obtained by crystallization from aqueous solution).

Curve : 1 - For Tl concentration $\sim 10^{-2}$ m.f.
Curve : 2 - " " $\sim 10^{-1}$ m.f.

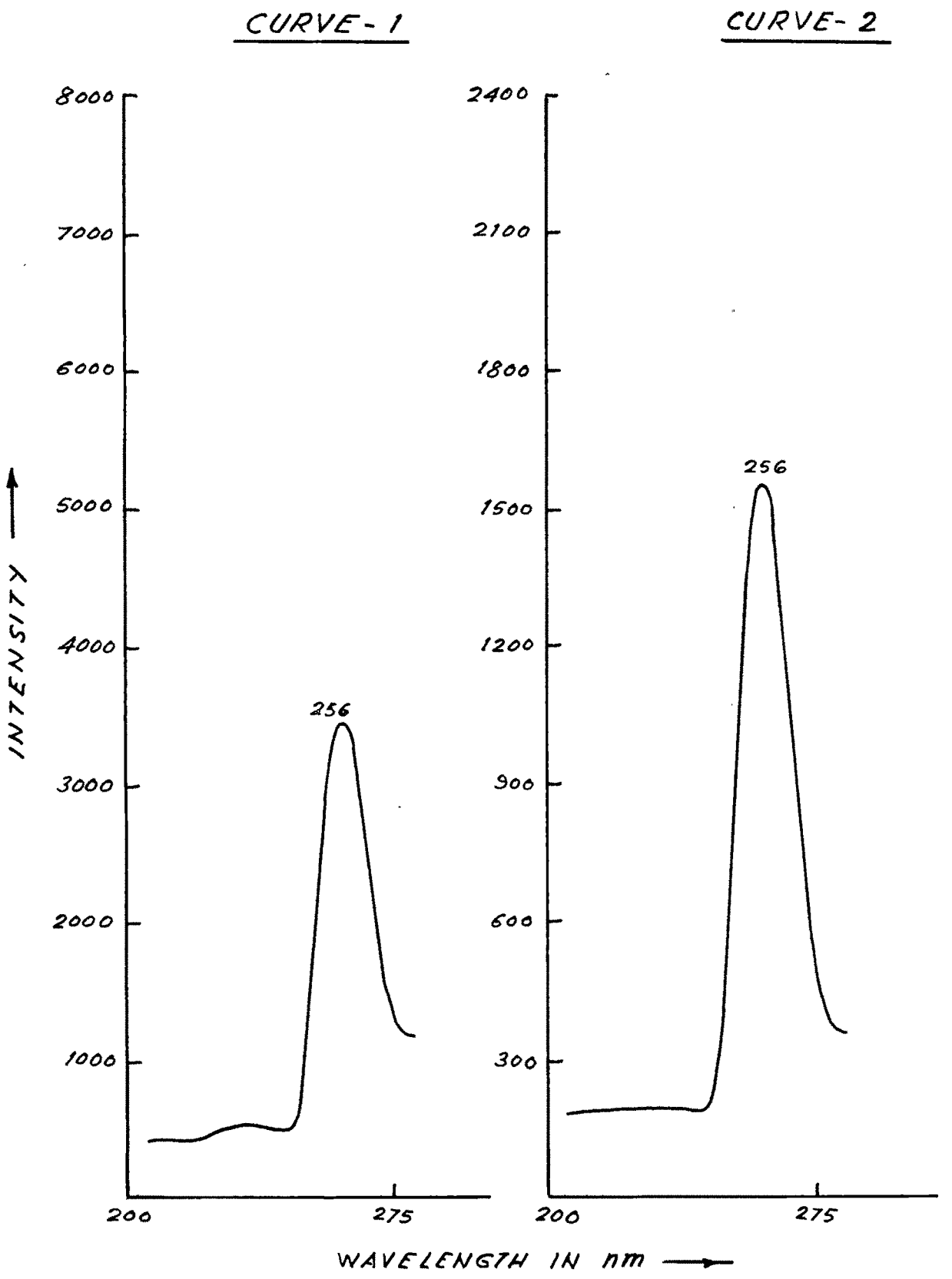

CURVE-1
CURVE-2
8000
7000
6000
5000
4000
3000
2000
1000
2400
2100
1800
1500
1200
900
600
300
256
256
INTENSITY
200
275
200
275
WAVELENGTH IN nm

FIG. 3

Fig. 4 : Emission spectra of NaCl:Tl powder specimens upon excitation at 256 nm. As-received specimens (i.e. as obtained by crystallization from aqueous solution).

Curve : 1 - For Tl concentration $\sim 10^{-2}$ m.f.
Curve : 2 - " " $\sim 10^{-1}$ m.f.

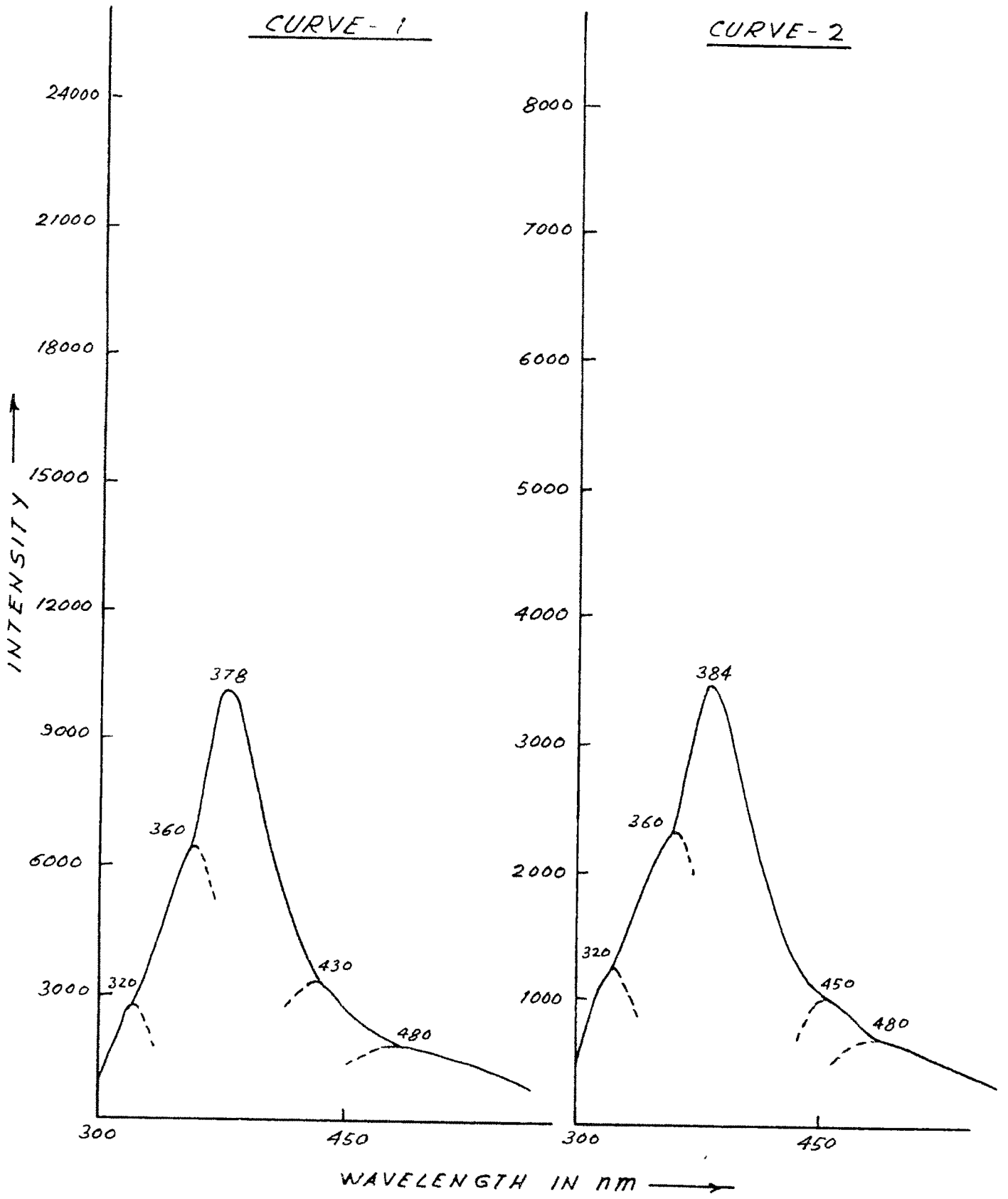

CURVE - 1
CURVE - 2
INTENSITY
24000
21000
18000
15000
12000
9000
6000
3000
8000
7000
6000
5000
4000
3000
2000
1000
378
360
320
430
480
384
360
320
450
480
300
450
300
450
WAVELENGTH IN nm

FIG 4

Fig. 5 : Excitation spectra of NaCl:Tl
as-received specimens, compressed to
tablet for 320 nm emission.

Curve : 1 - For Tl concentration $\sim 10^{-4}$ m.f.
Curve : 2 - " " $\sim 10^{-3}$ m.f.

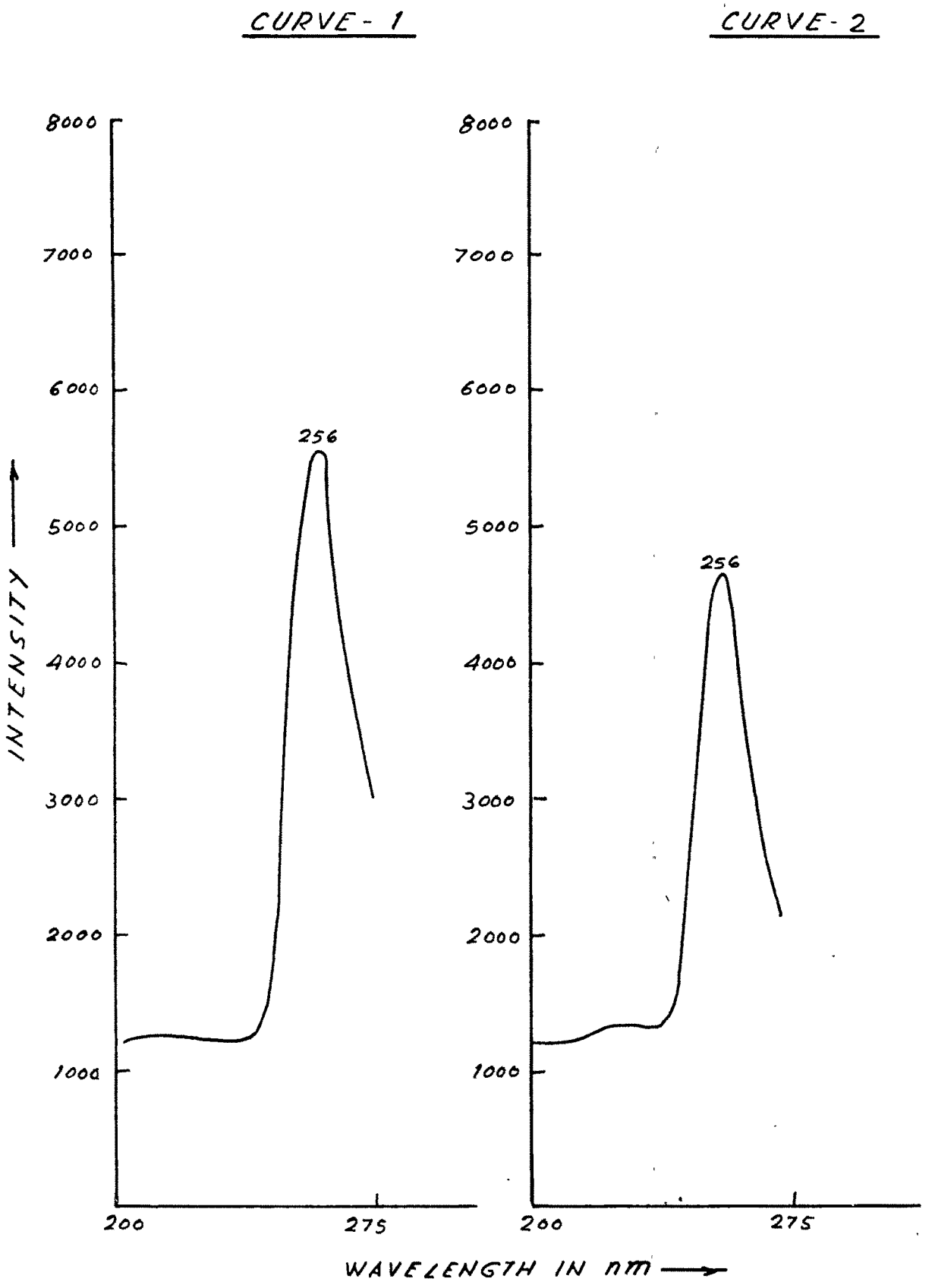
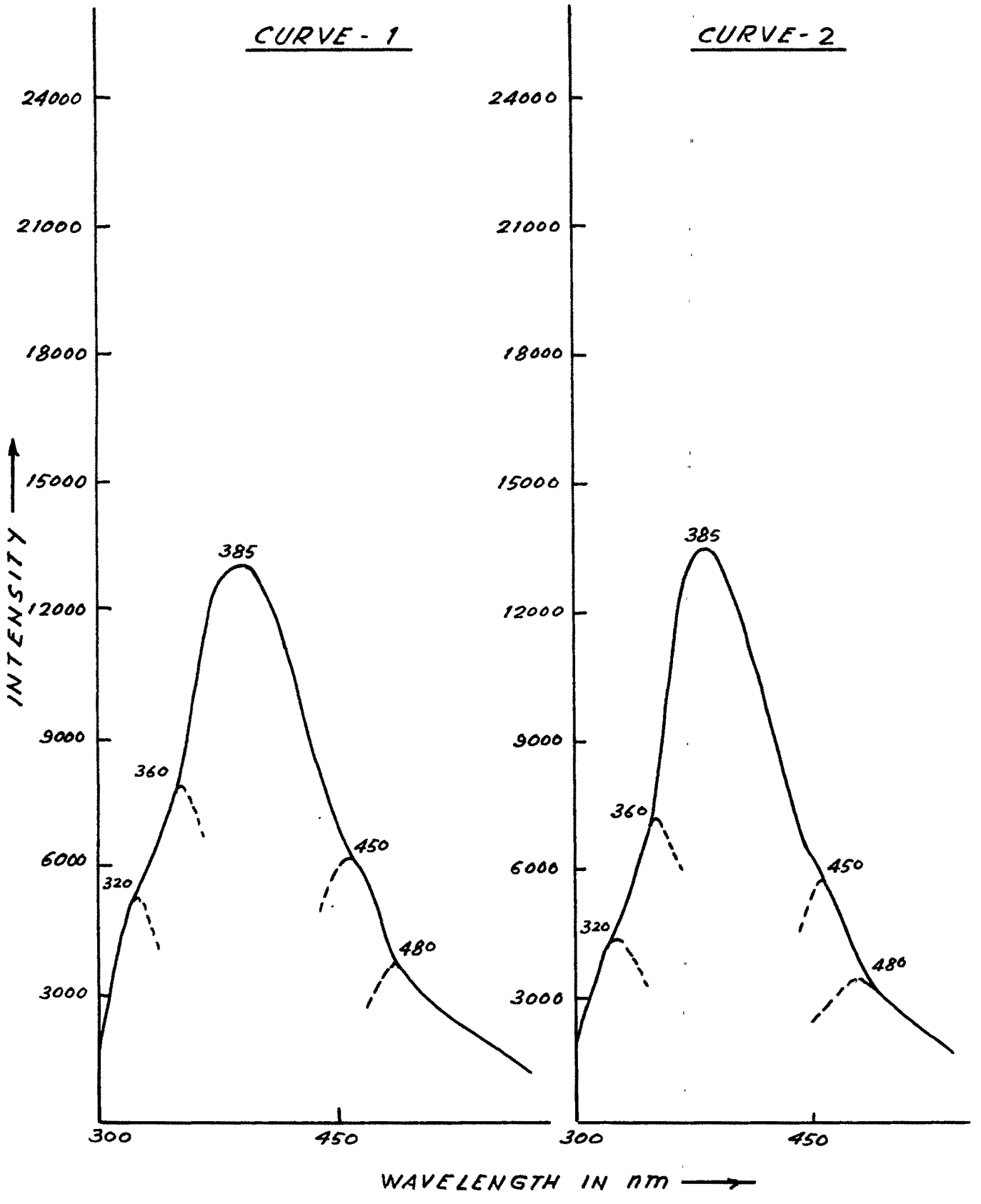

CURVE - 1
CURVE - 2
8000
7000
6000
5000
4000
3000
2000
1000
INTENSITY
256
256
200
275
200
275
WAVELENGTH IN nm

FIG. 5

Fig. 6 : Emission spectra of NaCl:Tl
as-received specimens compressed to
tablet upon excitation at 256 nm.

Curve : 1 - For Tl concentration $\sim 10^{-4}$ m.f.
Curve : 2 - " " $\sim 10^{-3}$ m.f.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CURVE - 2
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
385
360
320
450
480
300
450
WAVELENGTH IN nm

FIG. 6

Fig. 7 : Excitation spectra of NaCl:Tl powder specimens for 320 nm emission. Specimens annealed at 500°C for 24 hours in evacuated and sealed tube and quenched rapidly to room temperature.

Curve : 1 - For Tl concentration $\sim 10^{-4}$ m.f.

Curve : 2 - " " $\sim 10^{-3}$ m.f.

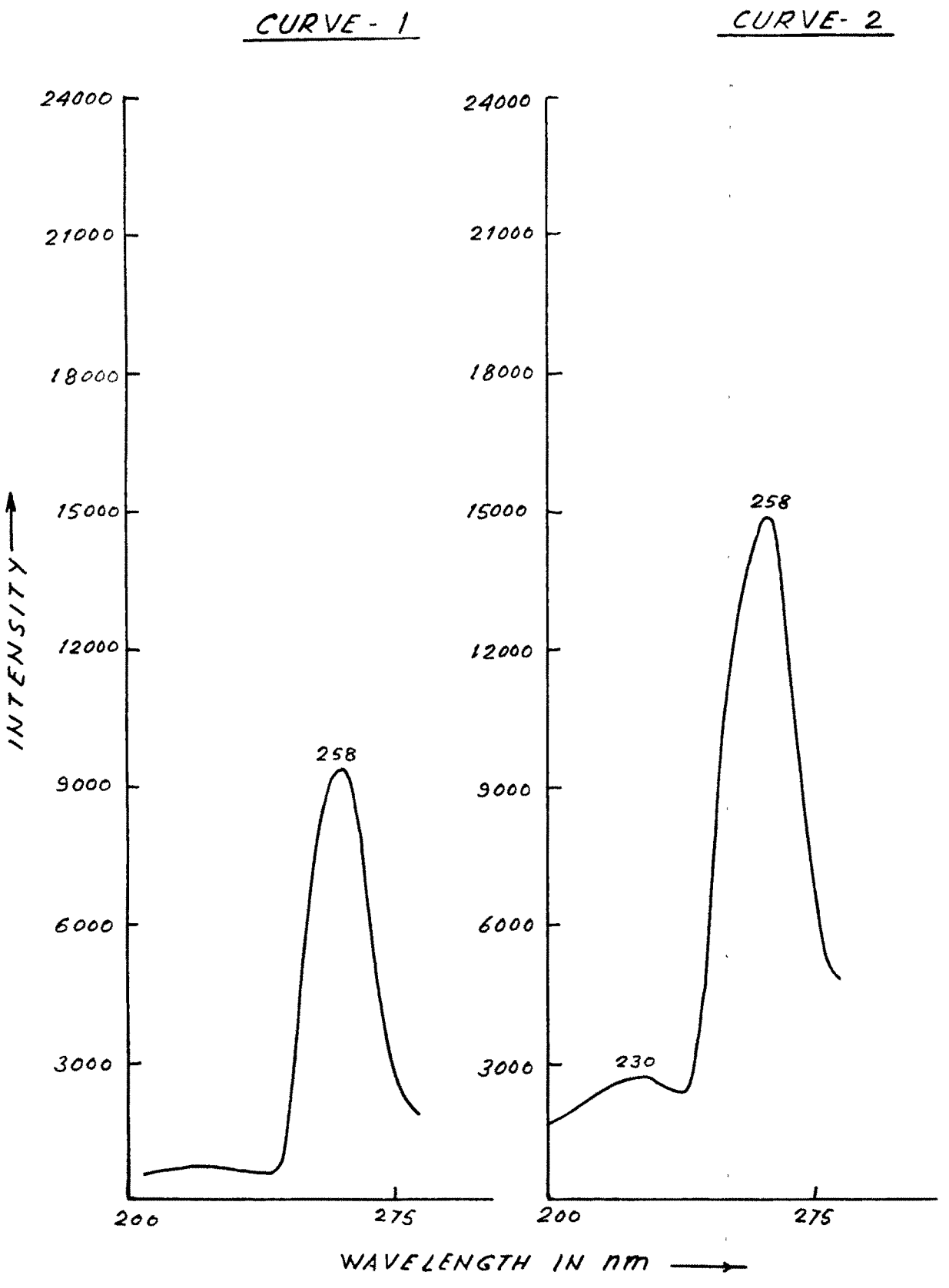

CURVE - 1
CURVE - 2
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
258
230
200
275
WAVELENGTH IN nm

FIG. 7

Fig. 8 : Emission spectra of NaCl:Tl powder specimens upon excitation at 258 nm. Specimens annealed at 500°C for 24 hours in evacuated and sealed tube and quenched rapidly to room temperature.

Curve : 1 - For Tl concentration $\sim 10^{-4}$ m.f.

Curve : 2 - " " $\sim 10^{-3}$ m.f.

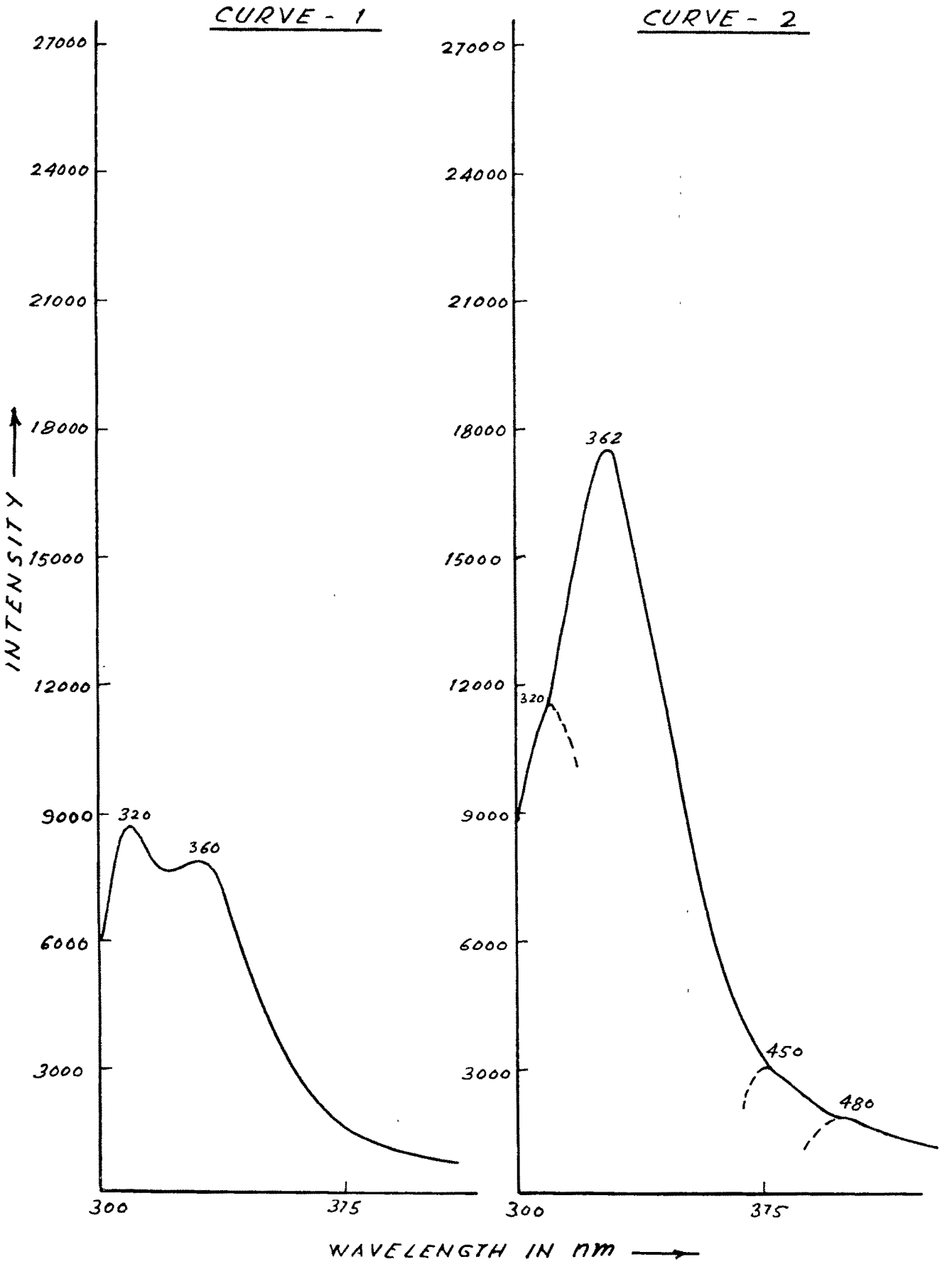

CURVE - 1
CURVE - 2
27000
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
320
360
362
320
450
480
300
375
300
375
WAVELENGTH IN mm

FIG. 8

Fig. 9 : Excitation spectra of NaCl:Tl specimens for 320 nm emission. Specimens annealed at 500°C for 24 hours in evacuated and sealed tube, quenched rapidly to room temperature and subsequently compressed to tablet.

Curve : 1 - For Tl concentration $\sim 10^{-4}$ m.f.
Curve : 2 - " " $\sim 10^{-3}$ m.f.

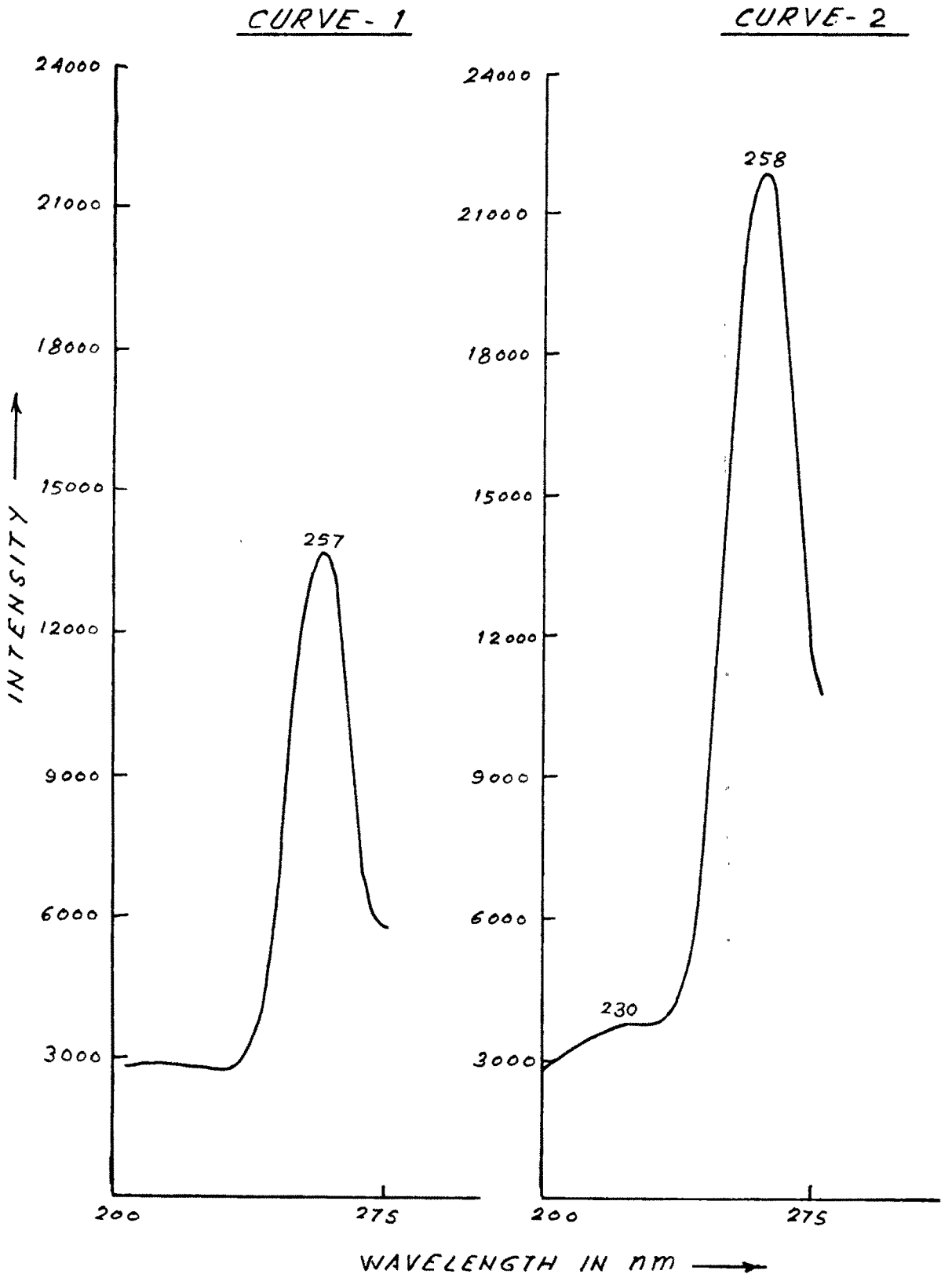

CURVE - 1
CURVE - 2
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
257
258
230
200
275
WAVELENGTH IN mm

FIG. 9

Fig. 10 : Emission spectra of NaCl:Tl specimens upon excitation at 258 nm. Specimens annealed at 500°C for 24 hours in evacuated and sealed tube, quenched rapidly to room temperature and subsequently compressed to tablet.

Curve : 1 - For Tl concentration $\sim 10^{-4}$ m.f.
Curve : 2 - " " $\sim 10^{-3}$ m.f.

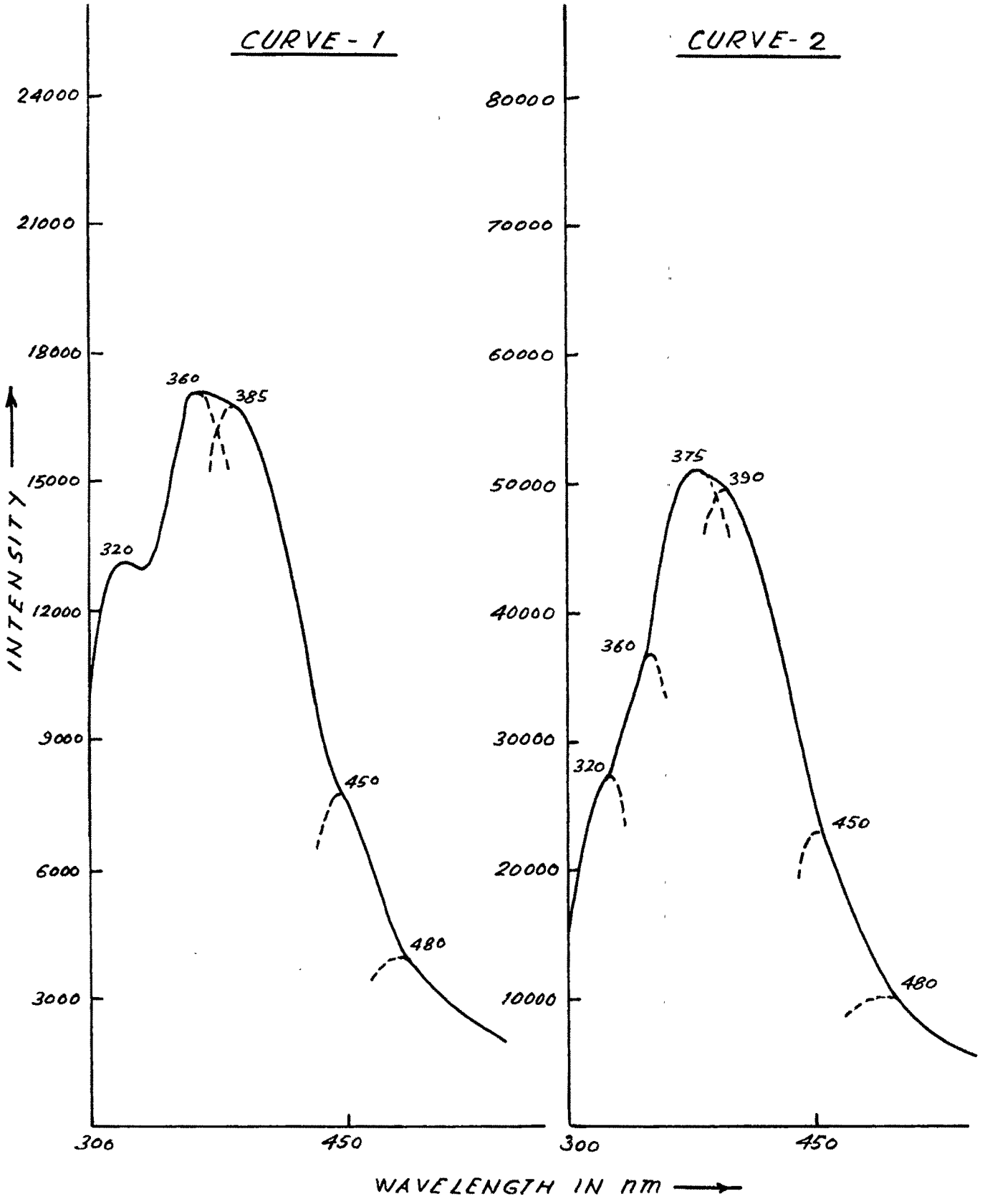

CURVE - 1
CURVE - 2
24000
21000
18000
15000
12000
9000
6000
3000
80000
70000
60000
50000
40000
30000
20000
10000
INTENSITY
360
385
320
450
480
375
390
360
320
450
480
300
450
300
450
WAVELENGTH IN nm

FIG. 10

Fig. 11 : Excitation spectra of NaCl:Tl melt and quenched specimens (powdered) for 325 nm emission.

Curve : 1 - For Tl concentration $\sim 10^{-4}$ m.f.
Curve : 2 - " " $\sim 10^{-3}$ m.f.

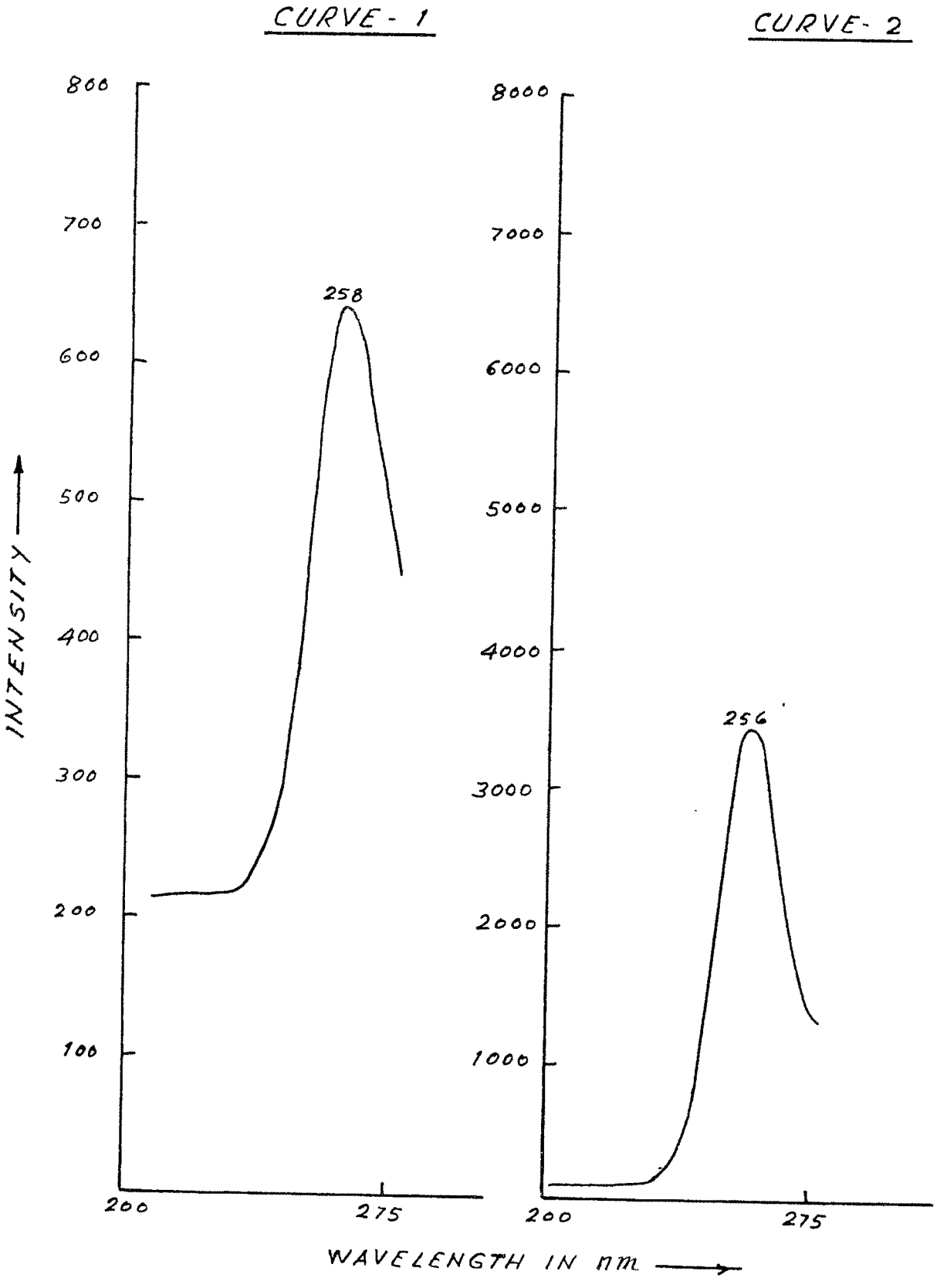

CURVE - 1
CURVE - 2
800
700
600
500
400
300
200
100
8000
7000
6000
5000
4000
3000
2000
1000
258
256
INTENSITY
200
275
200
275
WAVELENGTH IN nm

FIG. 11

Fig. 12 : Emission spectra of NaCl:Tl melt and quenched specimens (powdered) upon excitation at 256 nm.

Curve : 1 - For Tl concentration $\sim 10^{-4}$ m.f.

Curve : 2 - " " $\sim 10^{-3}$ m.f.

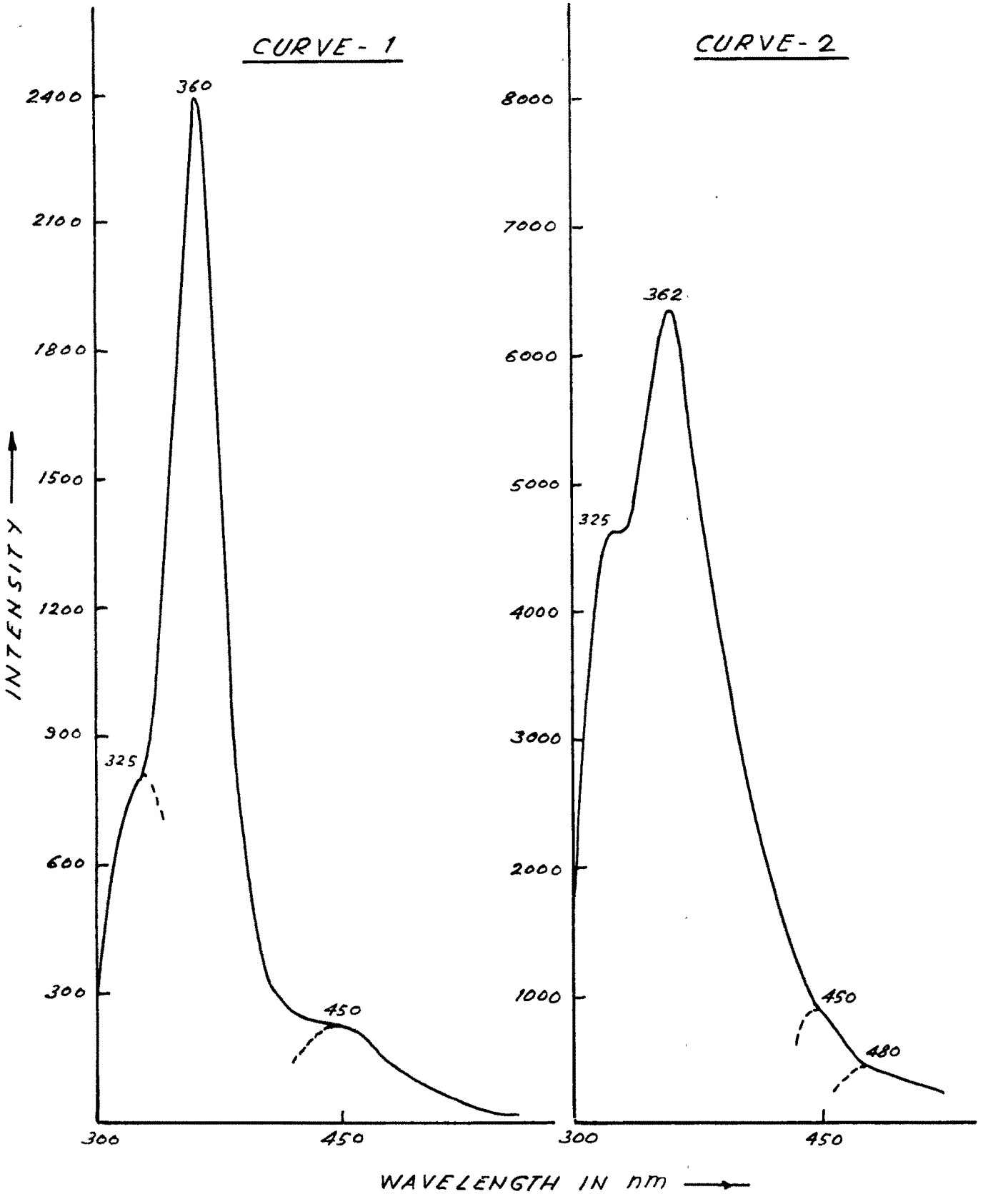

CURVE - 1
CURVE - 2
INTENSITY
WAVELENGTH IN nm
2400
2100
1800
1500
1200
900
600
300
360
325
450
300
450
8000
7000
6000
5000
4000
3000
2000
1000
362
325
450
480
300
450

FIG. 12

Fig. 13 : Excitation spectra of NaCl:Tl specimens for 320 nm emission. Specimens melt and quenched and then compressed to tablets.

Curve : 1 - For Tl concentration $\sim 10^{-4}$ m.f.

Curve : 2 - " " 10^{-3} m.f.

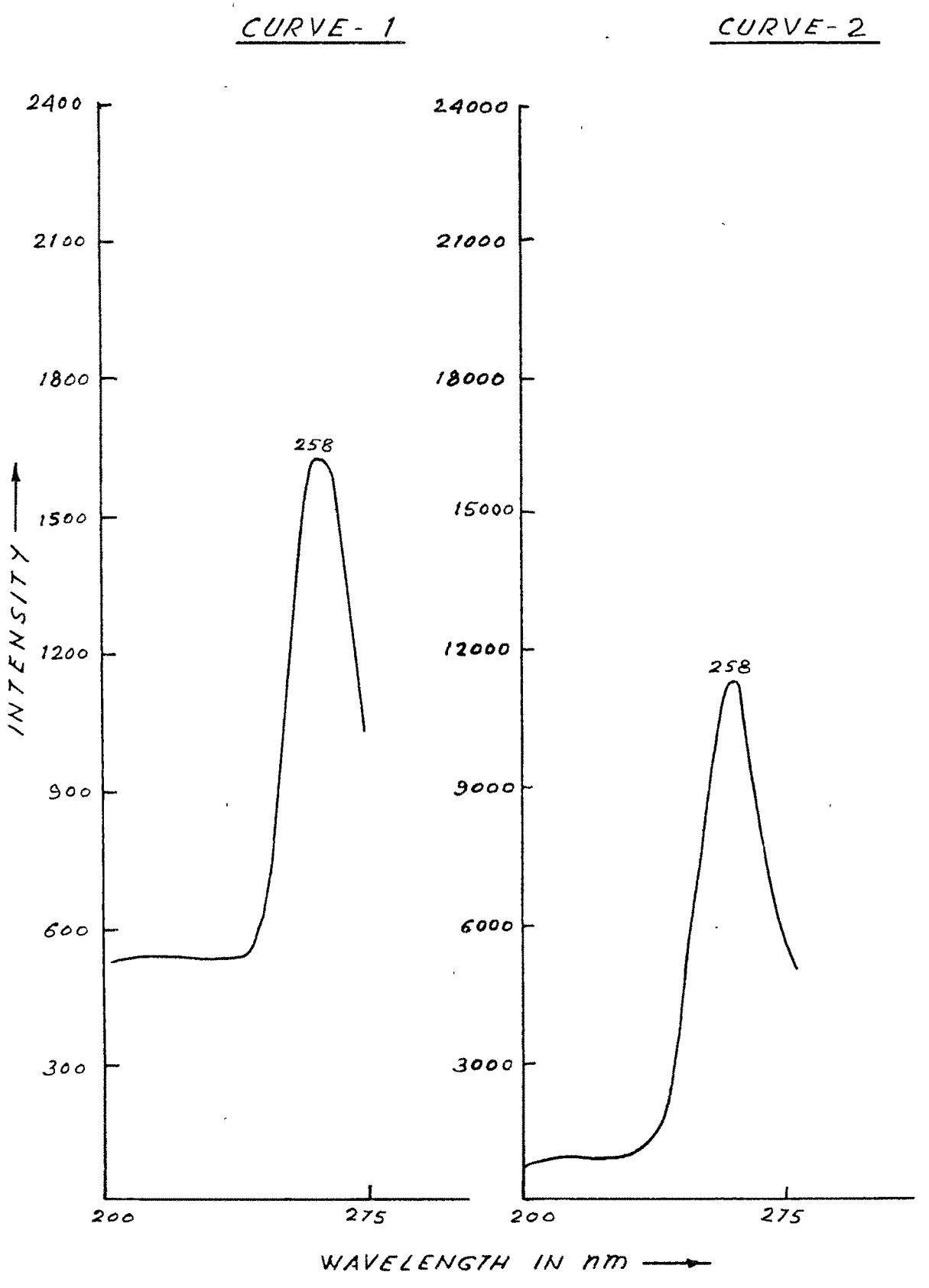

CURVE - 1
CURVE - 2
2400
2100
1800
1500
1200
900
600
300
24000
21000
18000
15000
12000
9000
6000
3000
258
258
INTENSITY
200
275
200
275
WAVELENGTH IN nm

FIG. 13

Fig. 14 : Emission spectra of NaCl:Tl specimens upon excitation at 258 nm. Specimens melt and quenched and then compressed to tablets.

Curve : 1 - For Tl concentration $\sim 10^{-4}$ m.f.
Curve : 2 - " " $\sim 10^{-3}$ m.f.

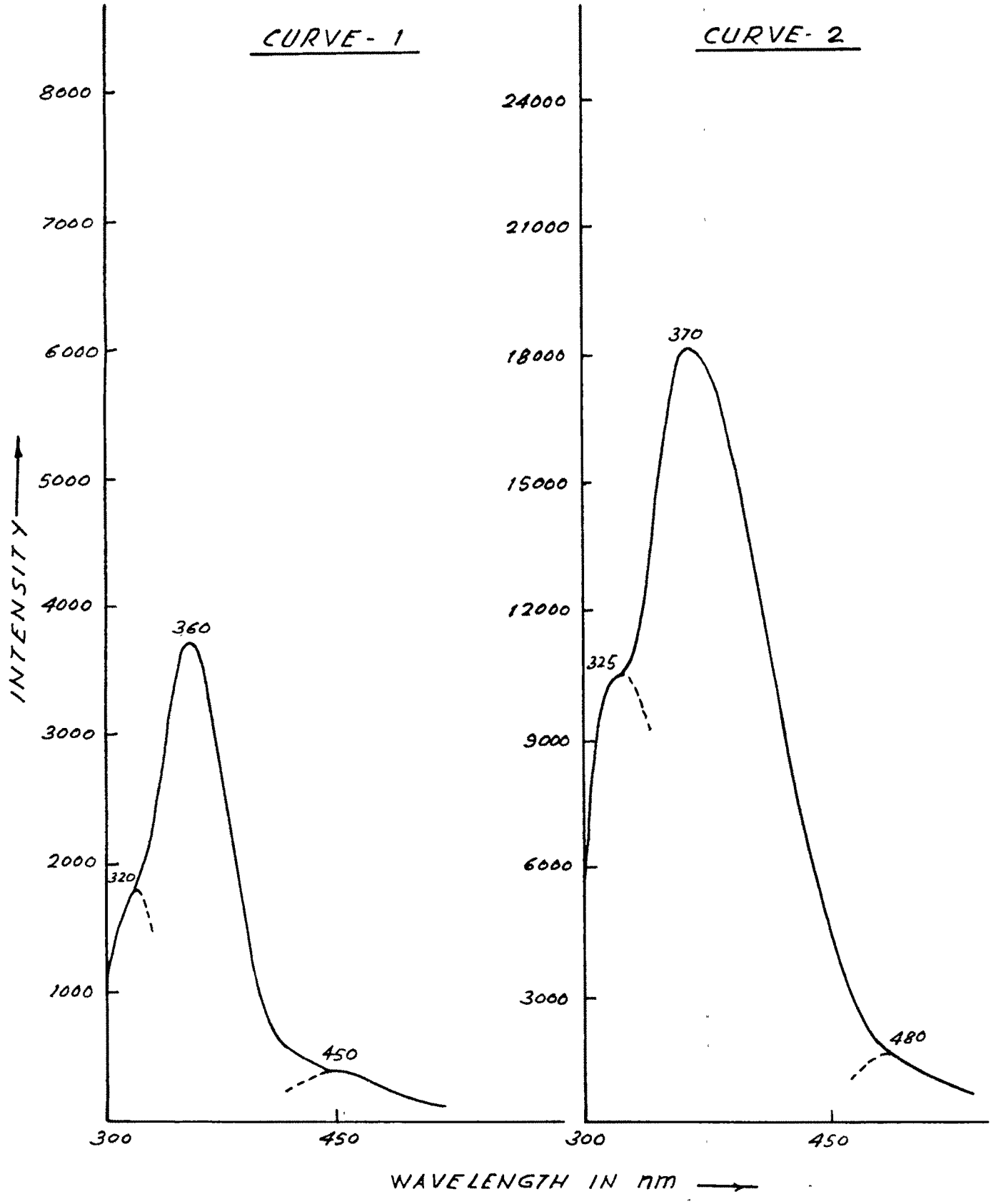

CURVE - 1
CURVE - 2
8000
7000
6000
5000
4000
3000
2000
1000
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
360
320
450
370
325
480
300
450
300
450
WAVELENGTH IN nm

FIG 14

Fig. 15 : Excitation spectrum of NaCl:Tl powder specimen for 360 nm emission. As-received specimen (i.e. as obtained from aqueous solution).

Tl concentration $\sim 10^{-4}$ m.f.

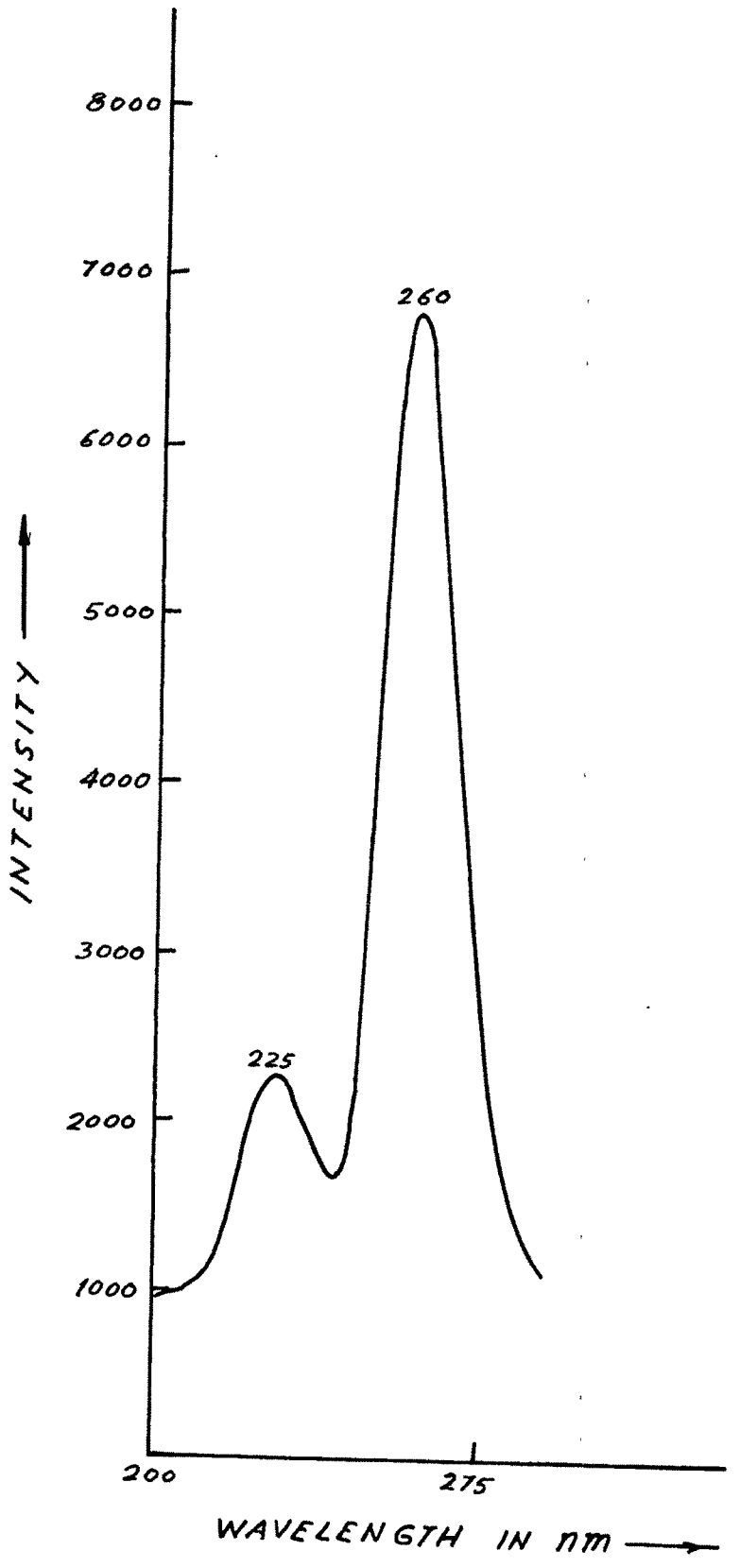

8000
7000
6000
5000
4000
3000
2000
1000
INTENSITY
260
225
200
275
WAVELENGTH IN nm

FIG. 15

Fig. 16 : Emission spectra of NaCl:Tl powder specimen upon excitation at 225 nm (Curve : 1) and at 260 nm (Curve : 2). As-received specimen (i.e. as obtained by crystallization from aqueous solution).

Tl concentration $\sim 10^{-4}$ m.f.

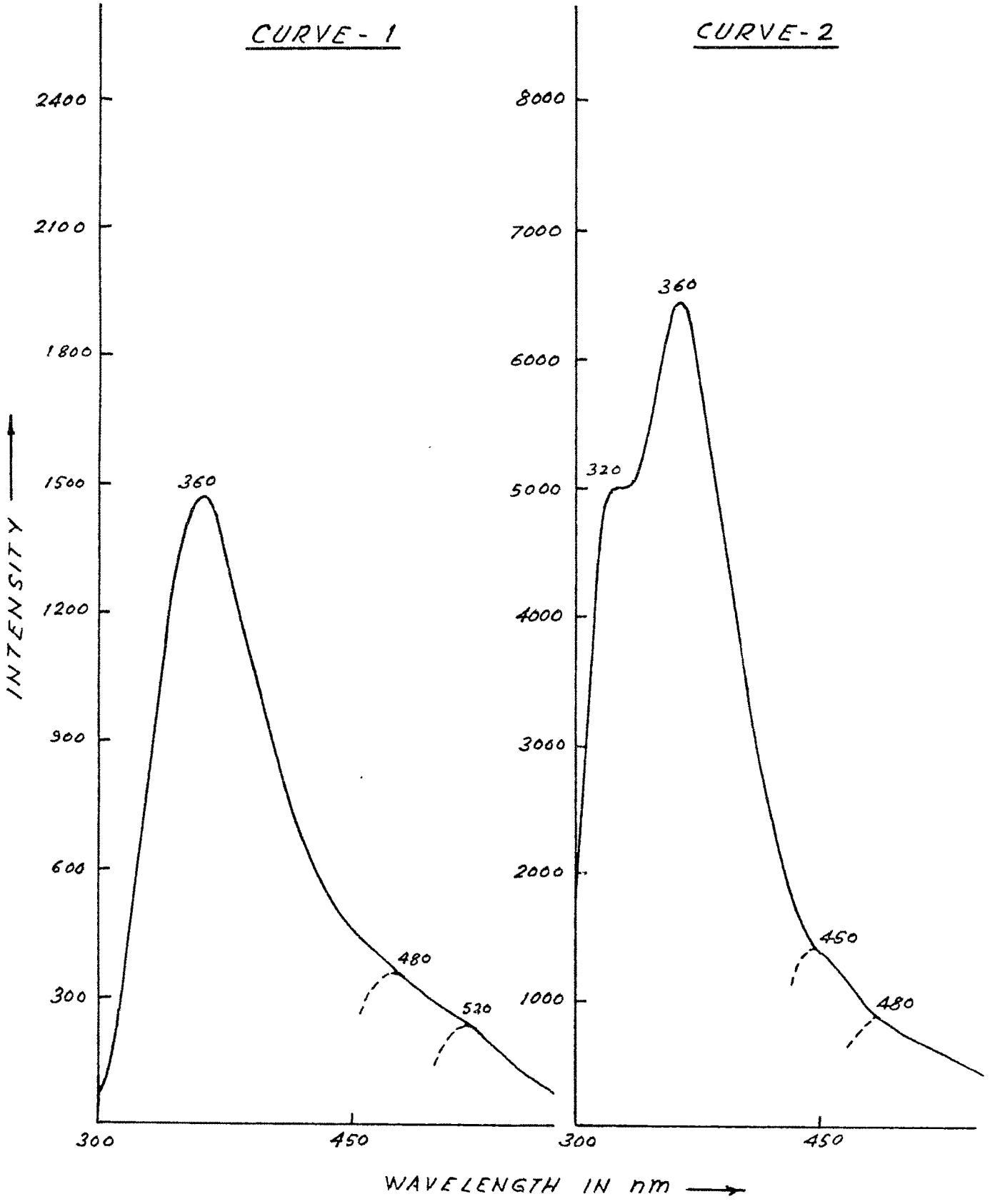

CURVE - 1
CURVE - 2
2400
2100
1800
1500
1200
900
600
300
360
480
530
300
450
8000
7000
6000
5000
4000
3000
2000
1000
360
320
450
480
300
450
INTENSITY
WAVELENGTH IN nm

FIG 16

Fig. 17 : Excitation spectrum of NaCl:Tl
powder specimen for 370 nm emission.
As-received specimen.

Tl concentration $\sim 10^{-3}$ m.f.

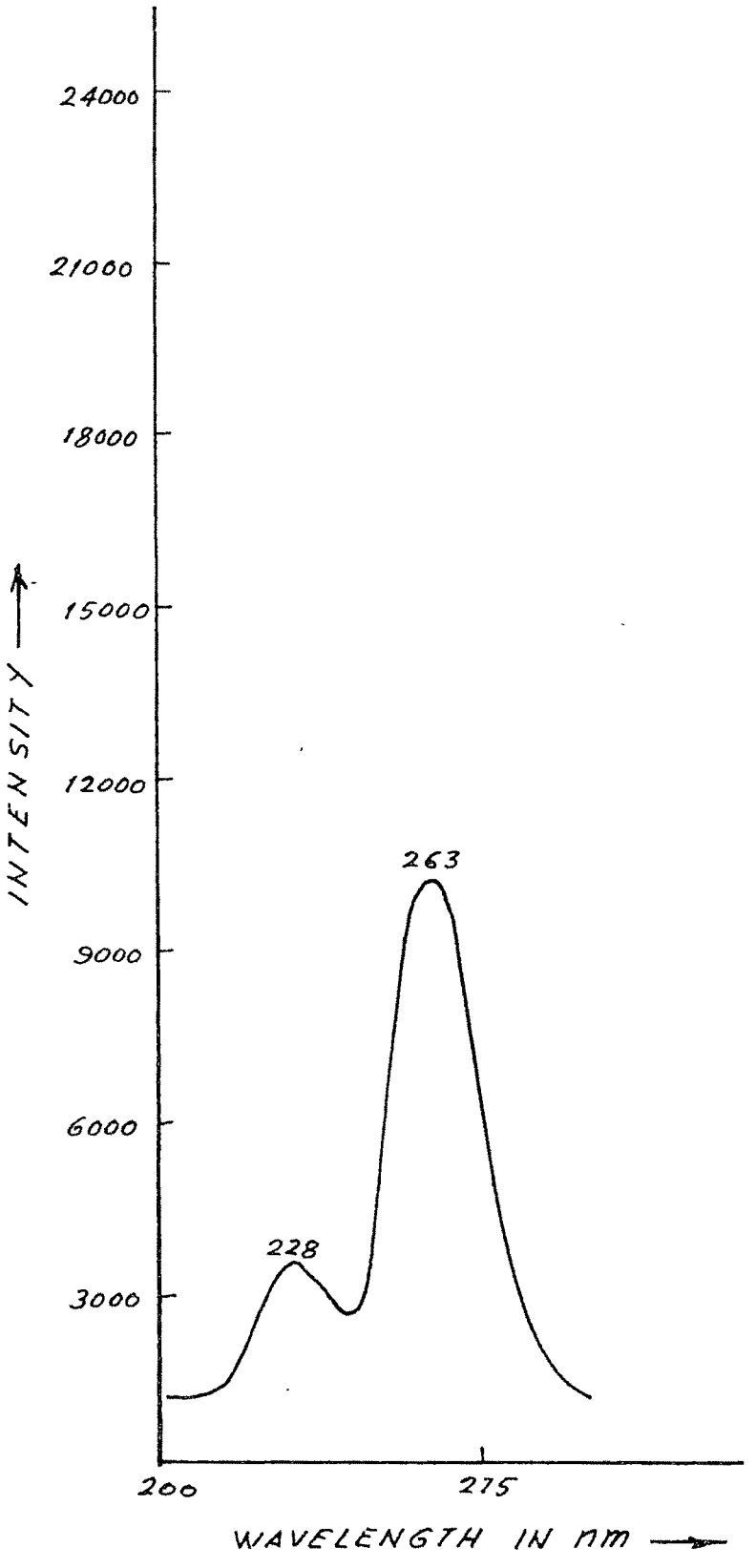

24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
263
228
200
275
WAVELENGTH IN MM

FIG. 17

Fig. 18 : Emission spectra of NaCl:Tl powder specimen upon excitation at 228 nm (Curve : 1) and at 263 nm (Curve : 2). As-received specimen.

Tl concentration $\sim 10^{-3}$ m.f.

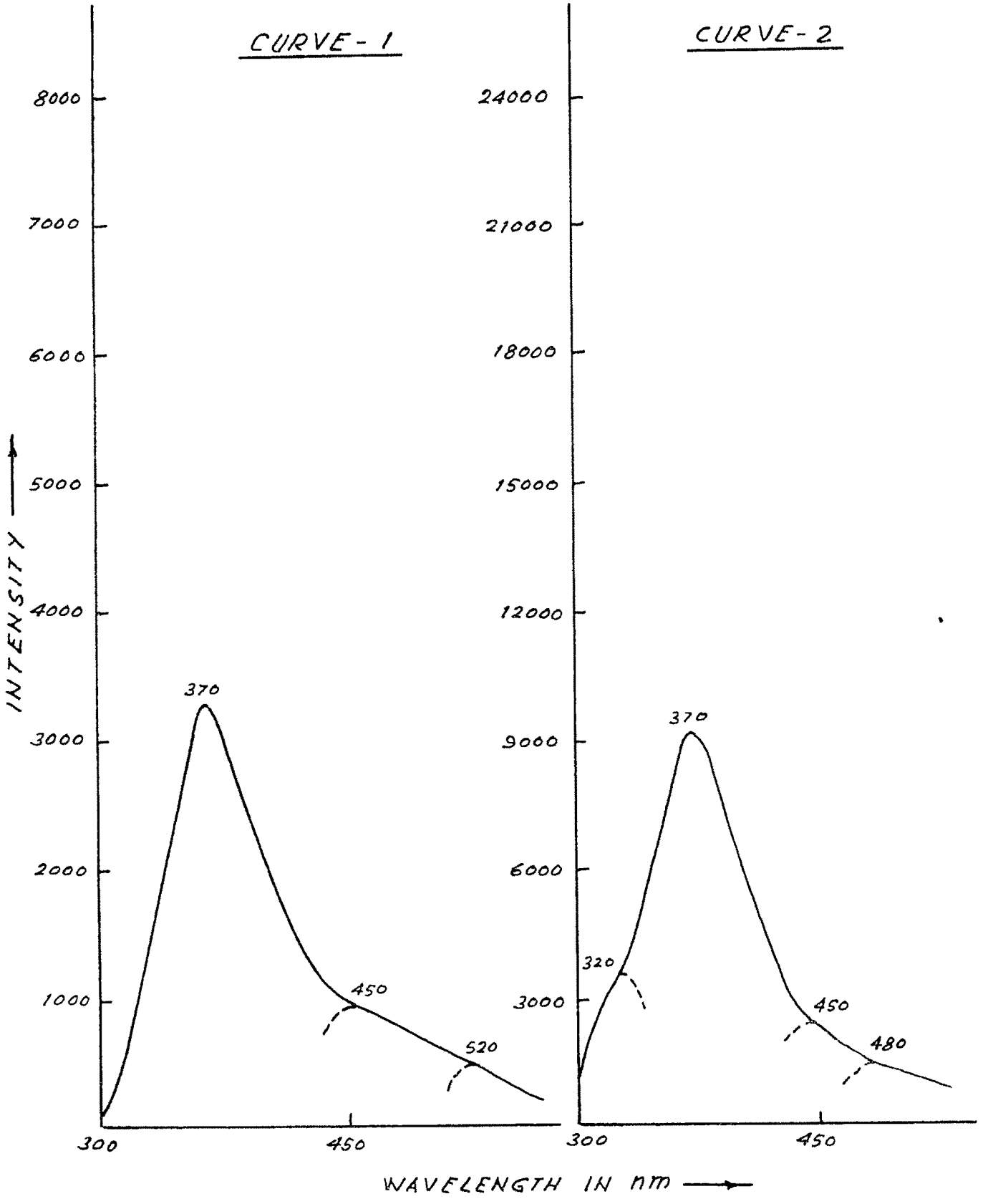

CURVE - 1
CURVE - 2
8000
7000
6000
5000
4000
3000
2000
1000
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
370
450
520
320
480
300
450
WAVELENGTH IN mm

FIG. 18

Fig. 19 : Excitation spectrum of NaCl:Tl
powder specimen for 378 nm emission.
As-received specimen.

Tl concentration $\sim 10^{-2}$ m.f.

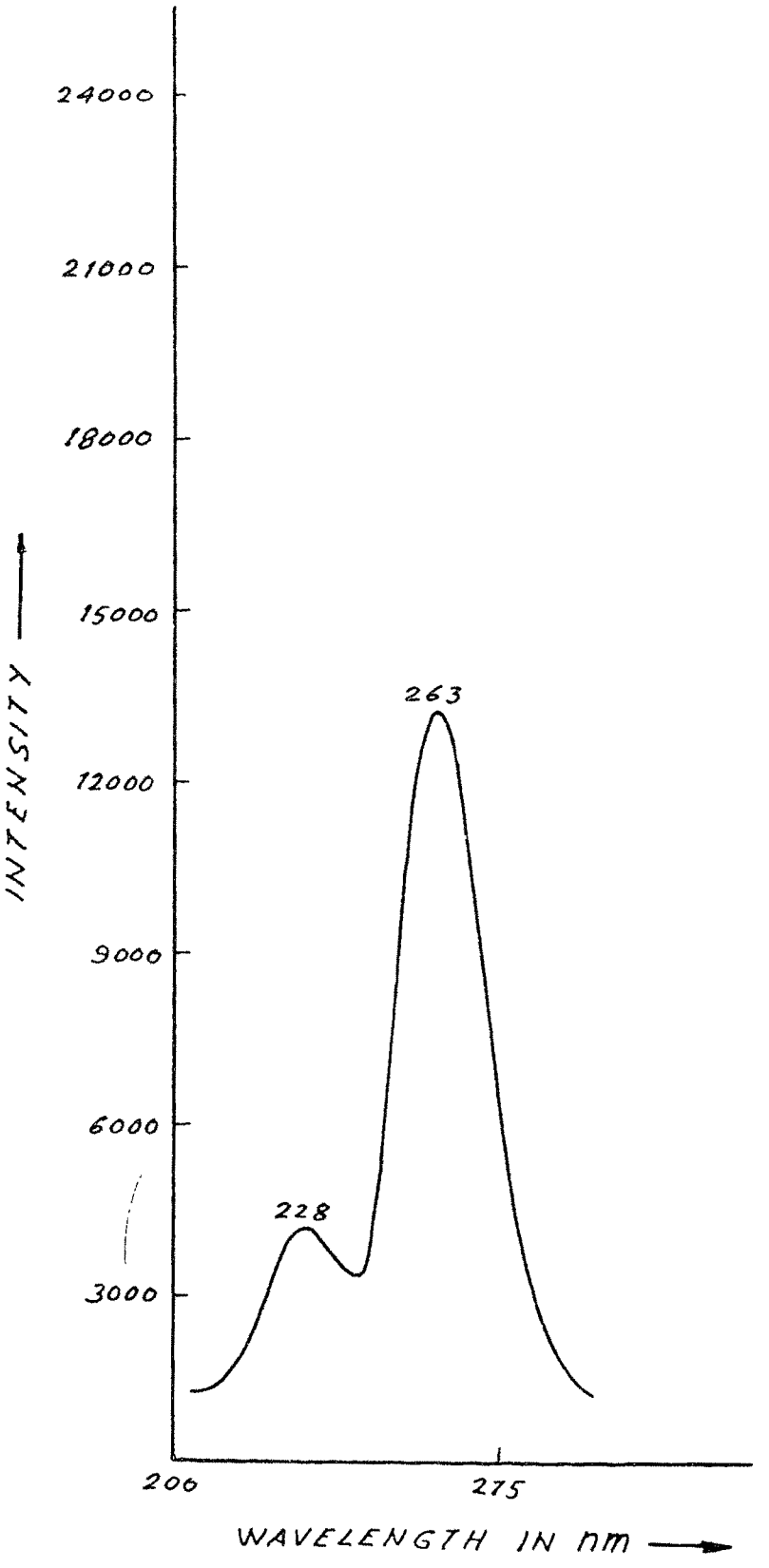

24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
263
228
200
275
WAVELENGTH IN nm

FIG. 19

Fig. 20 : Emission spectra of NaCl:Tl powder specimen upon excitation at 228 nm (Curve : 1) and 263 nm (Curve : 2). As-received specimen.

Tl concentration $\sim 10^{-2}$ m.f.

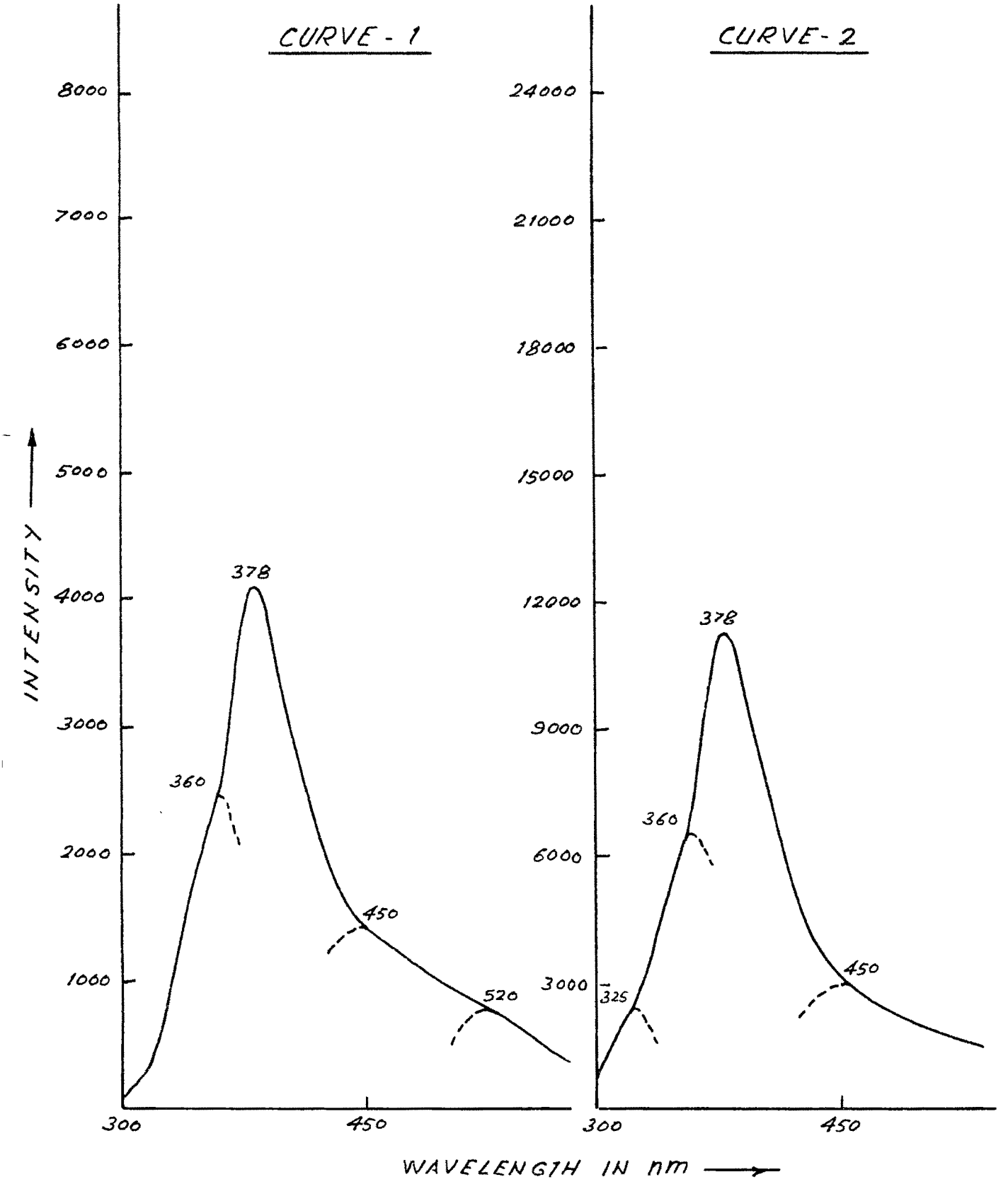

CURVE - 1
CURVE - 2
8000
7000
6000
5000
4000
3000
2000
1000
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
378
360
450
520
325
300
450
WAVELENGTH IN nm

FIG. 20

Fig. 21 : Excitation spectrum of NaCl:Tl powder specimen for 384 nm emission. As-received specimen.

Tl concentration $\sim 10^{-1}$ m.f.

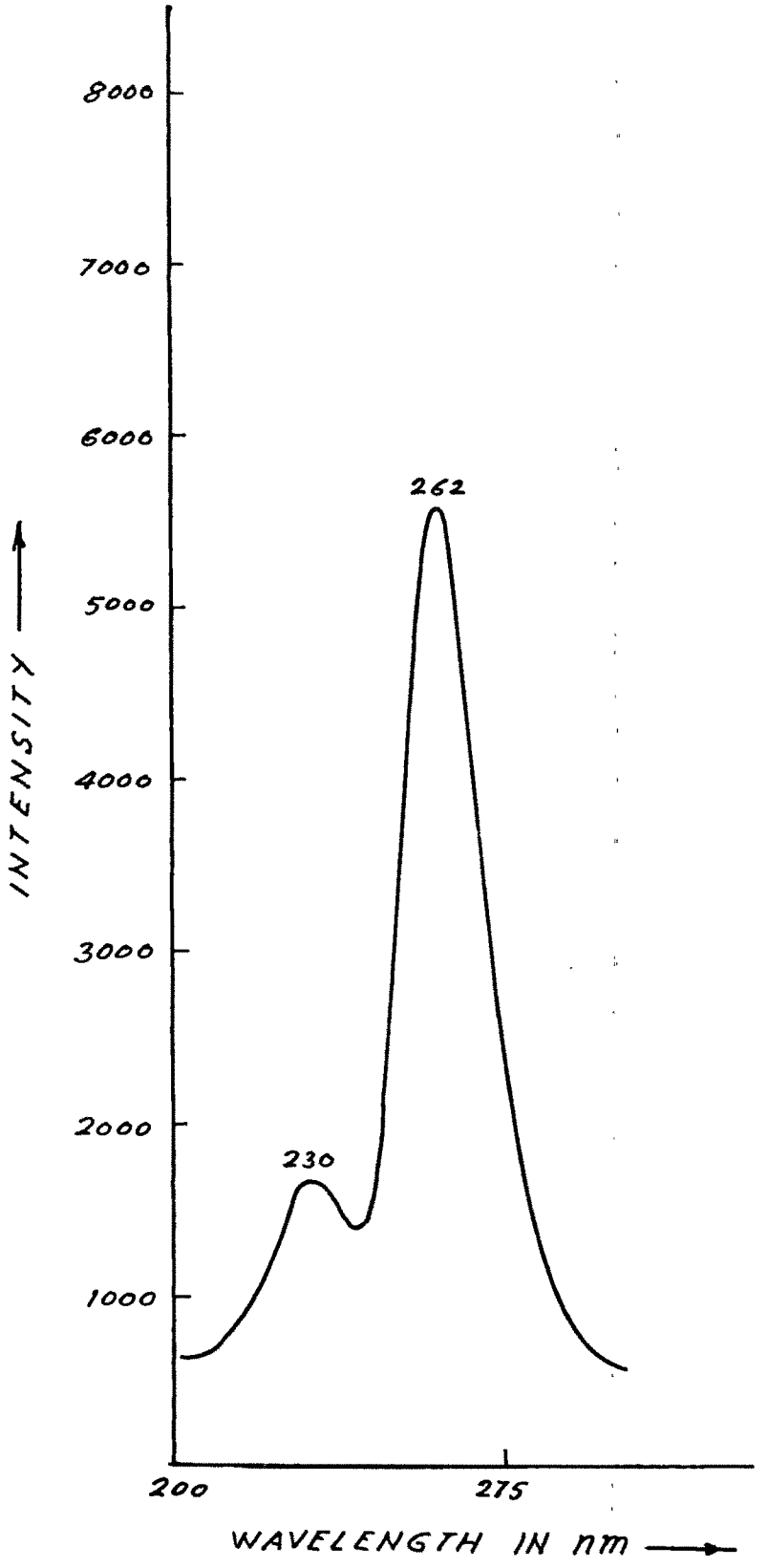

8000
7000
6000
5000
4000
3000
2000
1000
INTENSITY
262
230
200
275
WAVELENGTH IN nm

FIG. 21

Fig. 22 : Emission spectra of NaCl:Tl powder specimen upon excitation at 230 nm (Curve : 1) and at 262 nm (Curve : 2). As-received specimen.

Tl concentration $\sim 10^{-1}$ m.f.

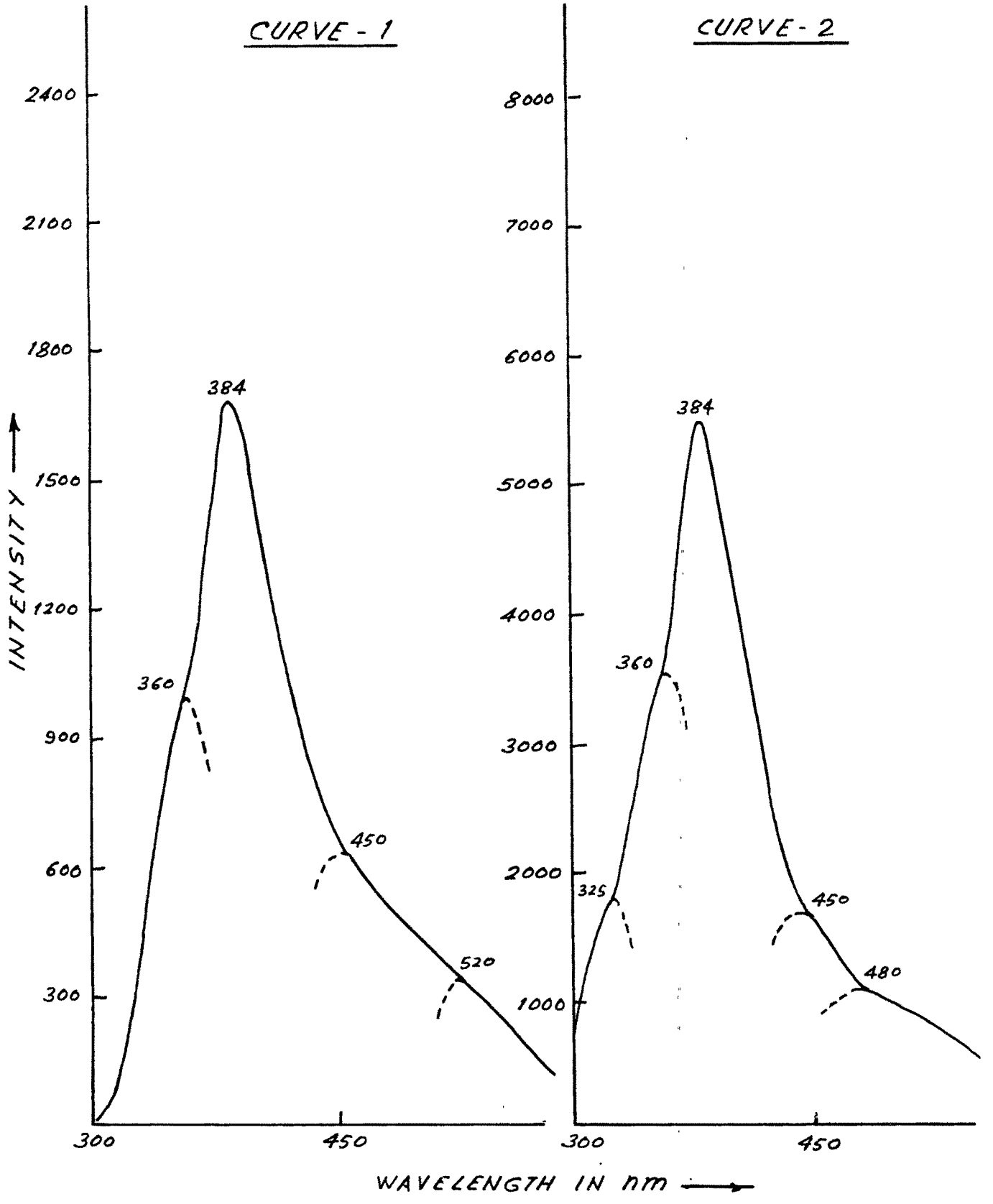

CURVE - 1
CURVE - 2
INTENSITY
2400
2100
1800
1500
1200
900
600
300
8000
7000
6000
5000
4000
3000
2000
1000
384
360
450
520
325
480
300
450
WAVELENGTH IN nm

FIG. 22

Fig. 23 : Excitation spectrum of NaCl:Tl, as-received specimen compressed to tablet, for 390 nm emission.

Tl concentration $\sim 10^{-4}$ m.f.

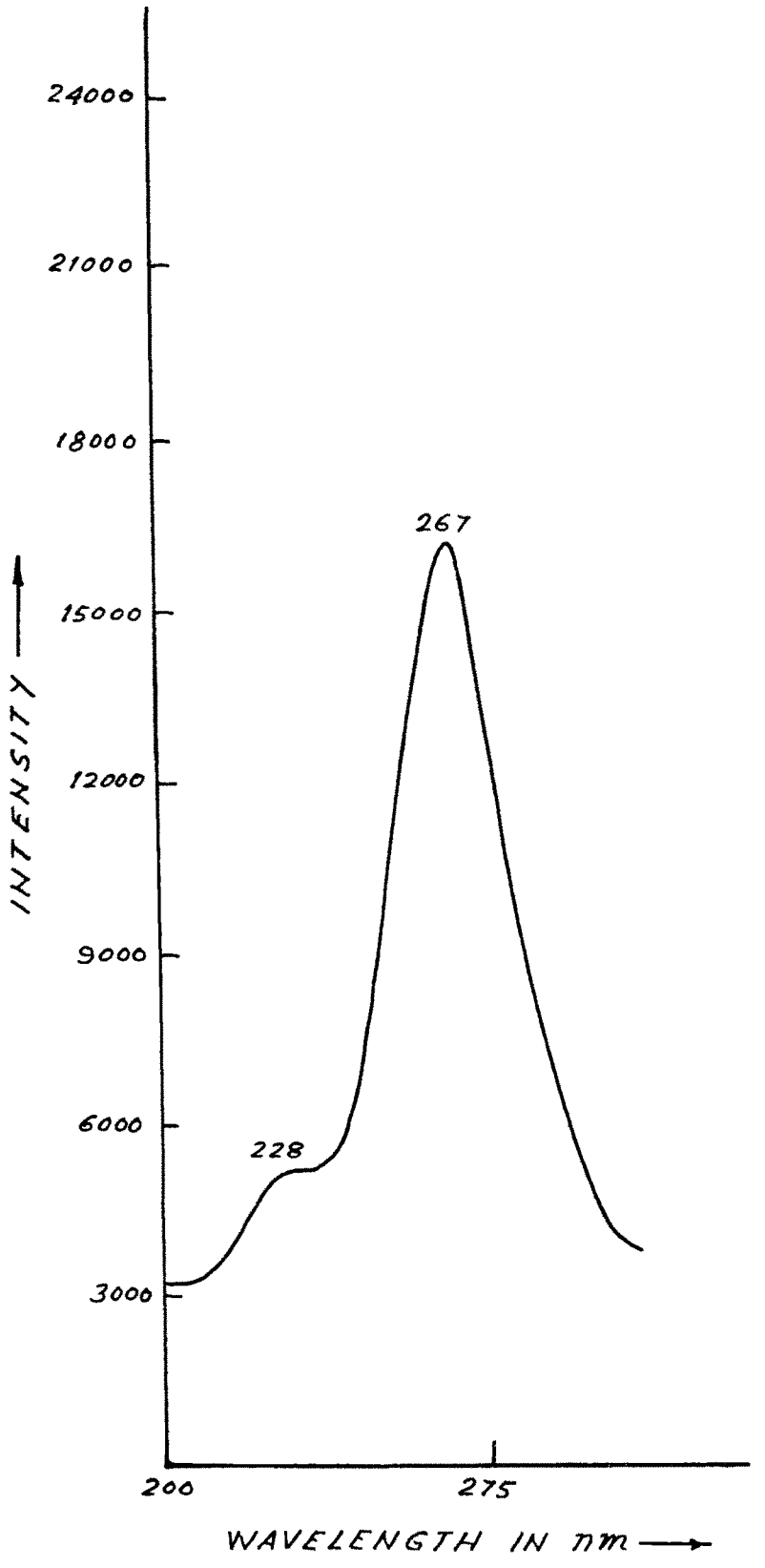

24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
267
228
200
275
WAVELENGTH IN nm

FIG. 23

Fig. 24 : Emission spectra of NaCl:Tl, as-received specimen compressed to tablet, upon excitation at 228 nm (Curve : 1) and at 267 nm (Curve : 2).

Tl concentration $\sim 10^{-4}$ m.f.

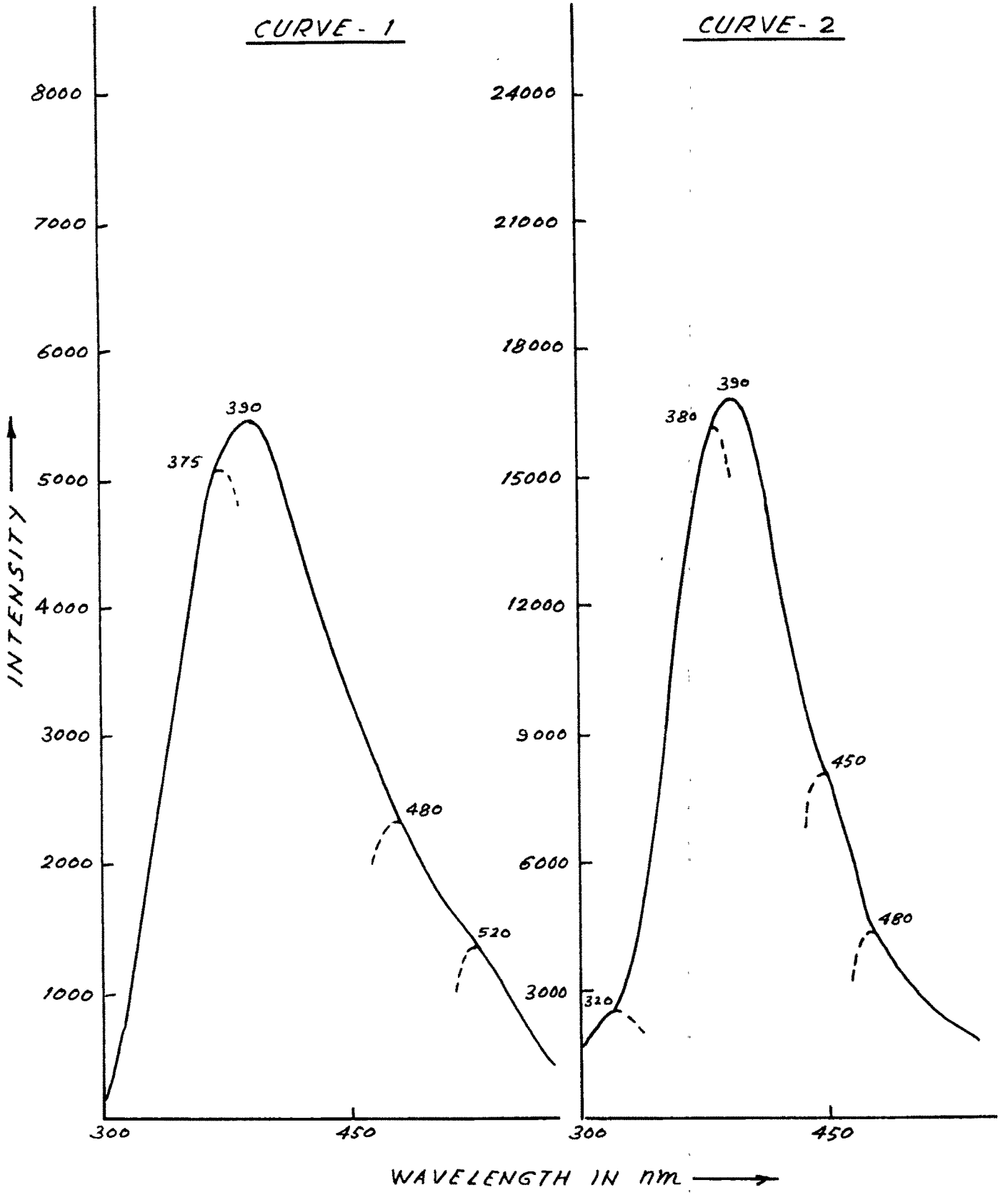

CURVE - 1
CURVE - 2
8000
7000
6000
5000
4000
3000
2000
1000
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
390
375
480
520
390
380
450
480
320
300
450
300
450
WAVELENGTH IN nm

FIG. 24

Fig. 25 : Excitation spectrum of NaCl:Tl, as-received specimen compressed to tablet, for 390 nm emission.

Tl concentration $\sim 10^{-3}$ m.f.

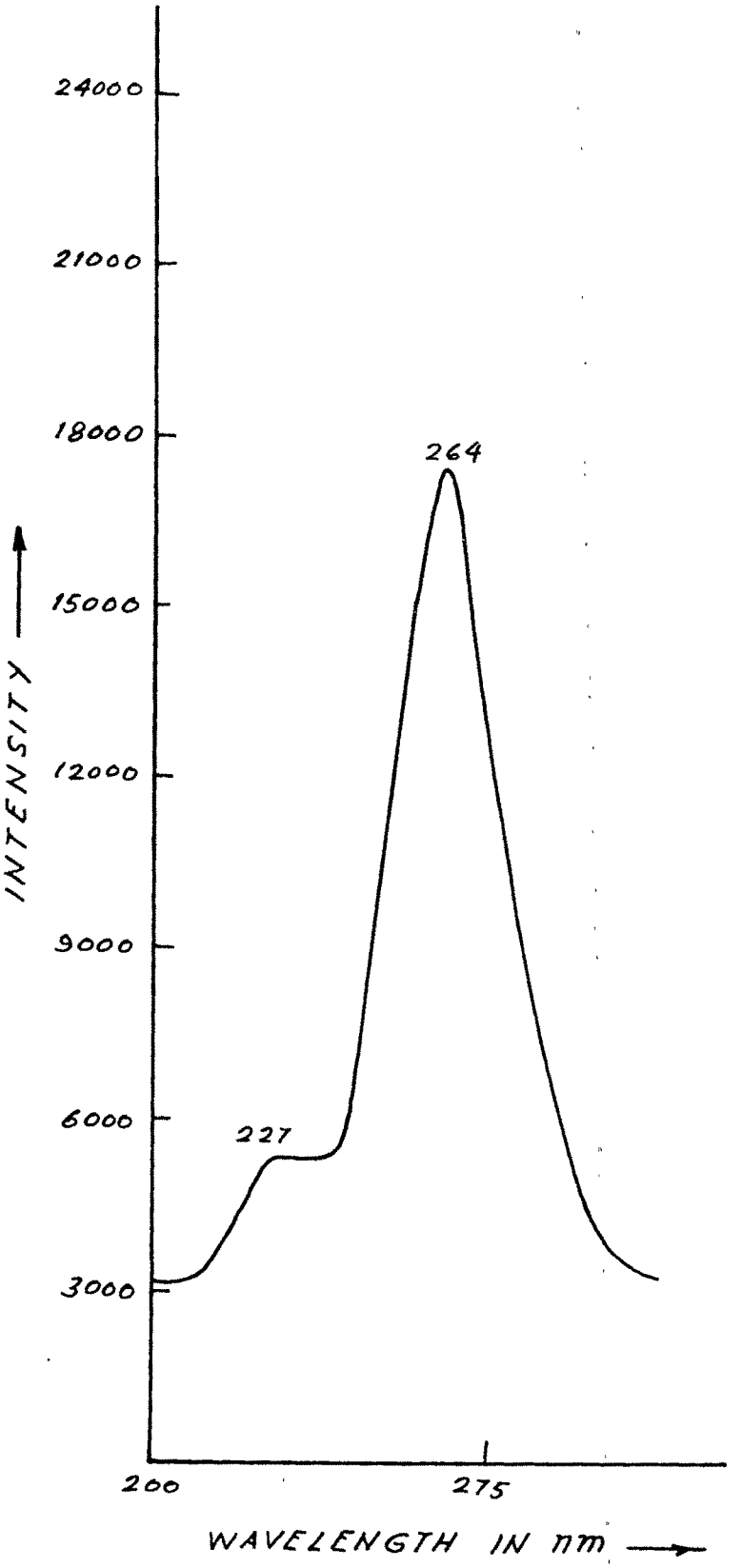

24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
264
227
200
275
WAVELENGTH IN nm

FIG. 25

Fig. 26 : Emission spectra of NaCl:Tl, as-received specimen compressed to tablet, upon excitation at 227 nm (Curve : 1) and at 264 nm (Curve : 2).

Tl concentration $\sim 10^{-3}$ m.f.

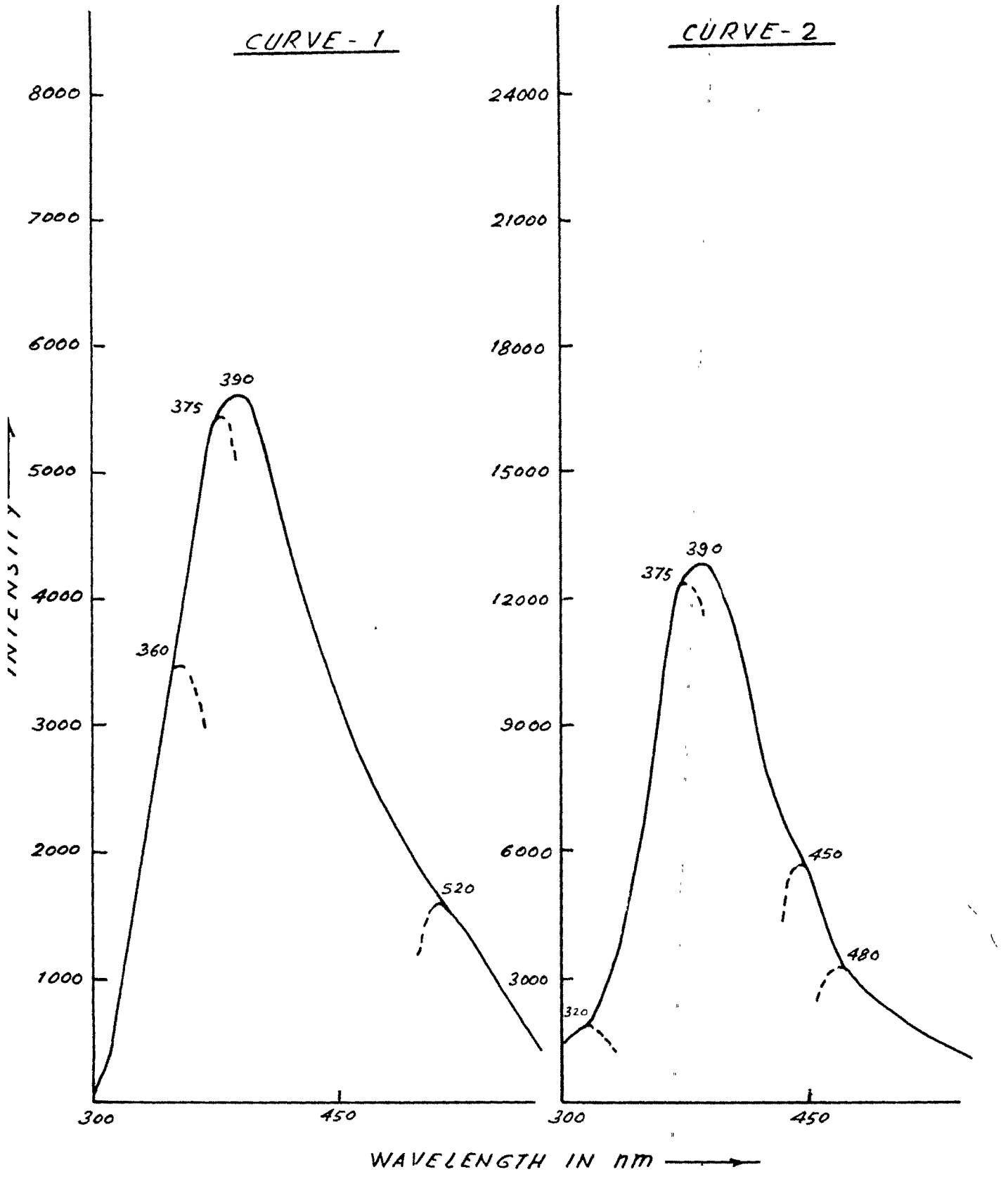

CURVE - 1
CURVE - 2
INTENSITY
8000
7000
6000
5000
4000
3000
2000
1000
24000
21000
18000
15000
12000
9000
6000
3000
390
375
360
520
390
375
450
480
320
300
450
300
450
WAVELENGTH IN nm

FIG. 26

Fig. 27 : Excitation spectrum of NaCl:Tl,
as-received specimen compressed to
tablet, for 392 nm emission.

Tl concentration $\sim 10^{-2}$ m.f.

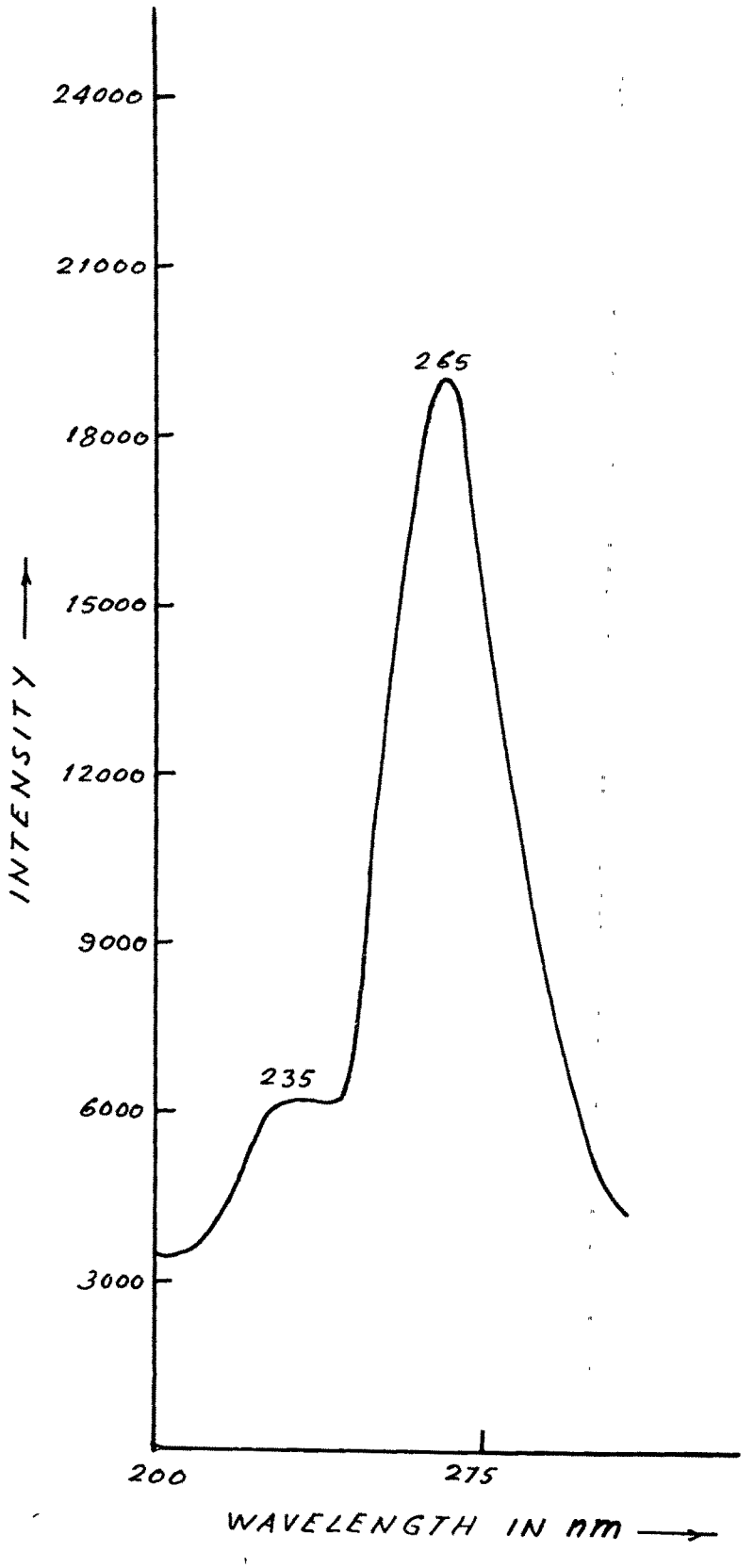

24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
265
235
200
275
WAVELENGTH IN nm

FIG. 27

Fig. 28 : Emission spectra of NaCl:Tl, as-received specimen compressed to tablet, upon excitation at 235 nm (Curve : 1) and 265 nm (Curve : 2).

Tl concentration $\sim 10^{-2}$ m.f.

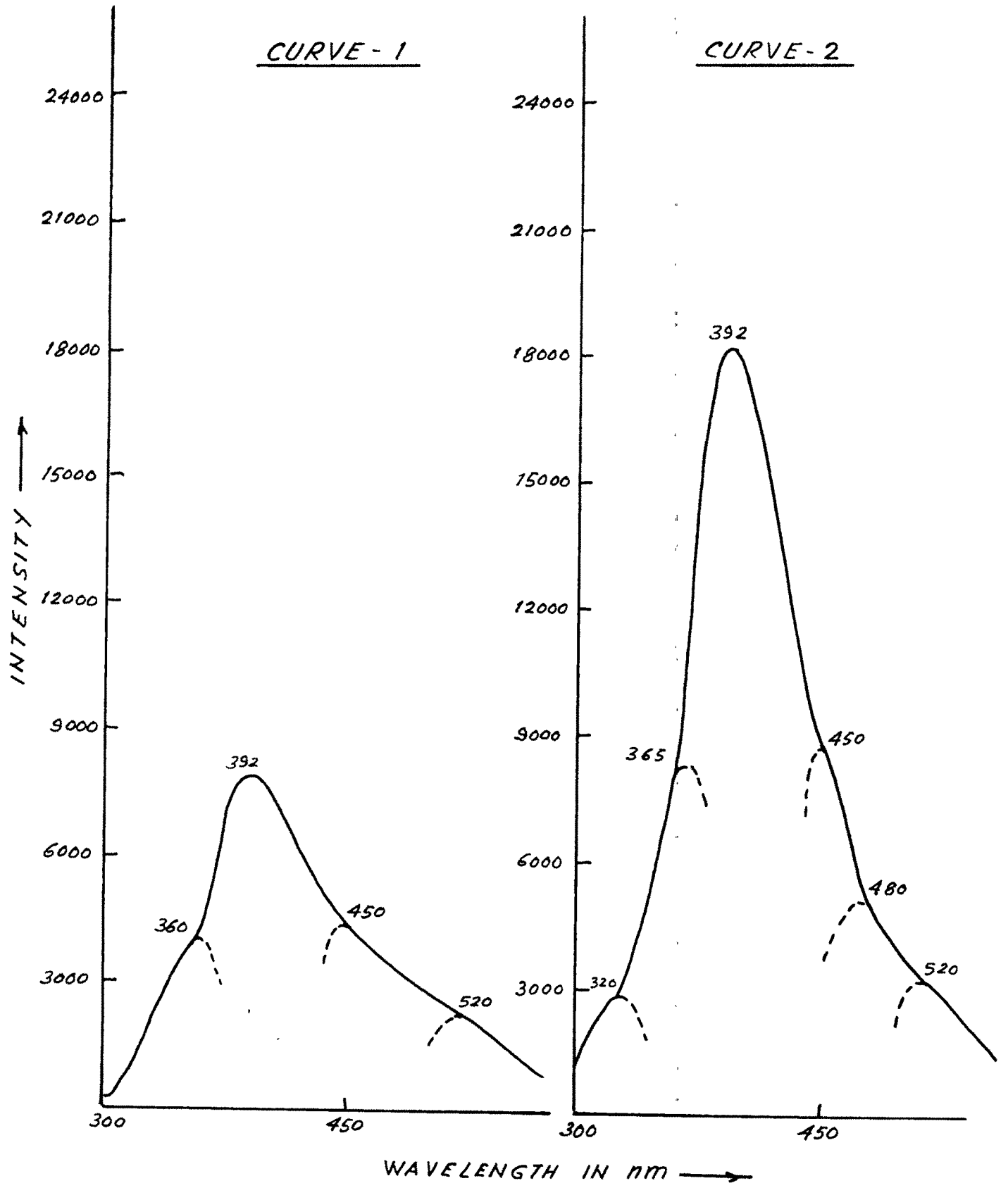

CURVE - 1
CURVE - 2
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
392
360
450
520
365
320
480
300
450
WAVELENGTH IN nm

FIG. 28

Fig. 29 : Excitation spectrum of NaCl:Tl, as-received specimen compressed to tablet, for 395 nm emission.

Tl concentration $\sim 10^{-1}$ m.f.

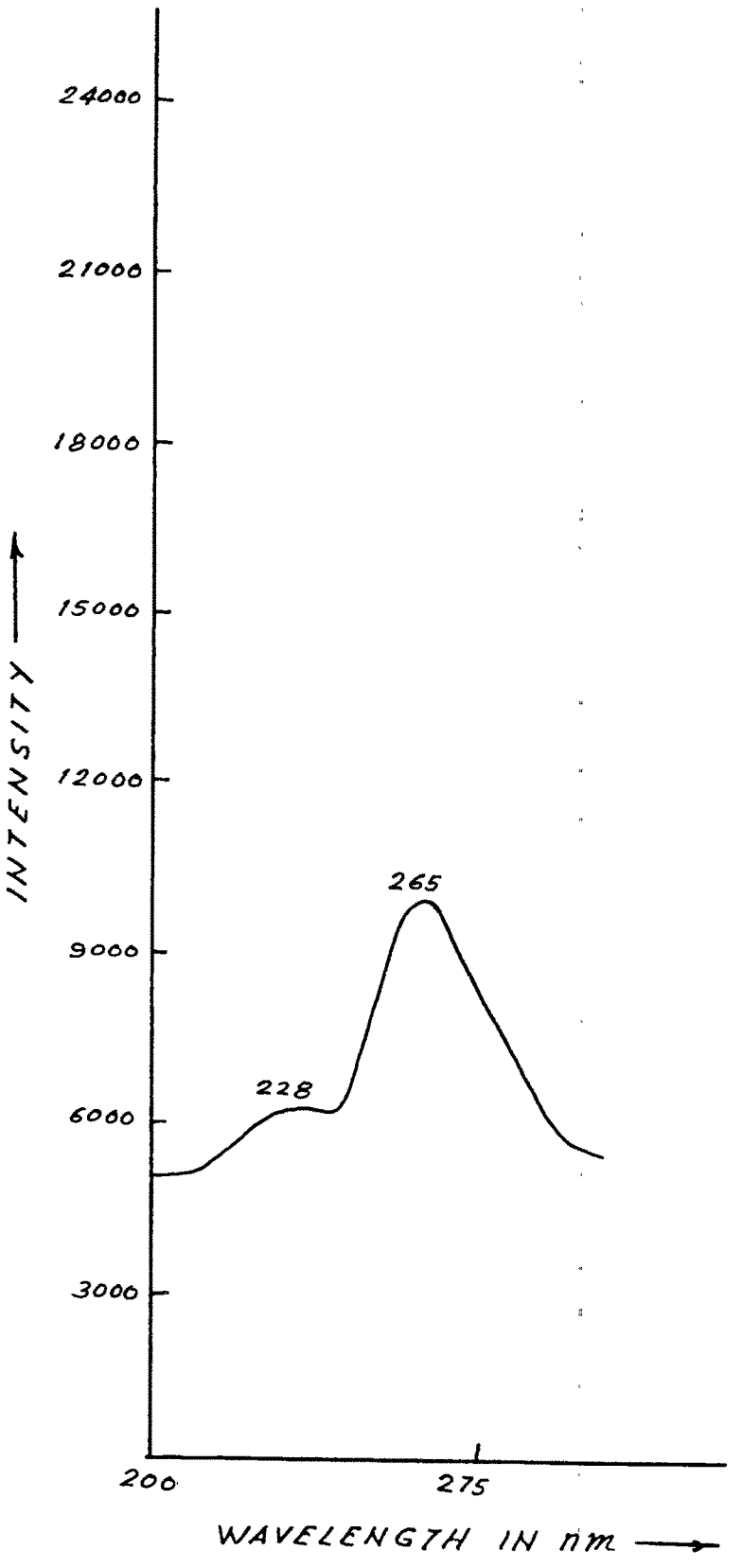

24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
265
228
200
275
WAVELENGTH IN nm

FIG. 29

Fig. 30 : Emission spectra of NaCl:Tl, as-received specimen compressed to tablet, upon excitation at 228 nm (Curve : 1) and at 265 nm (Curve : 2).

Tl concentration $\sim 10^{-1}$ m.f.

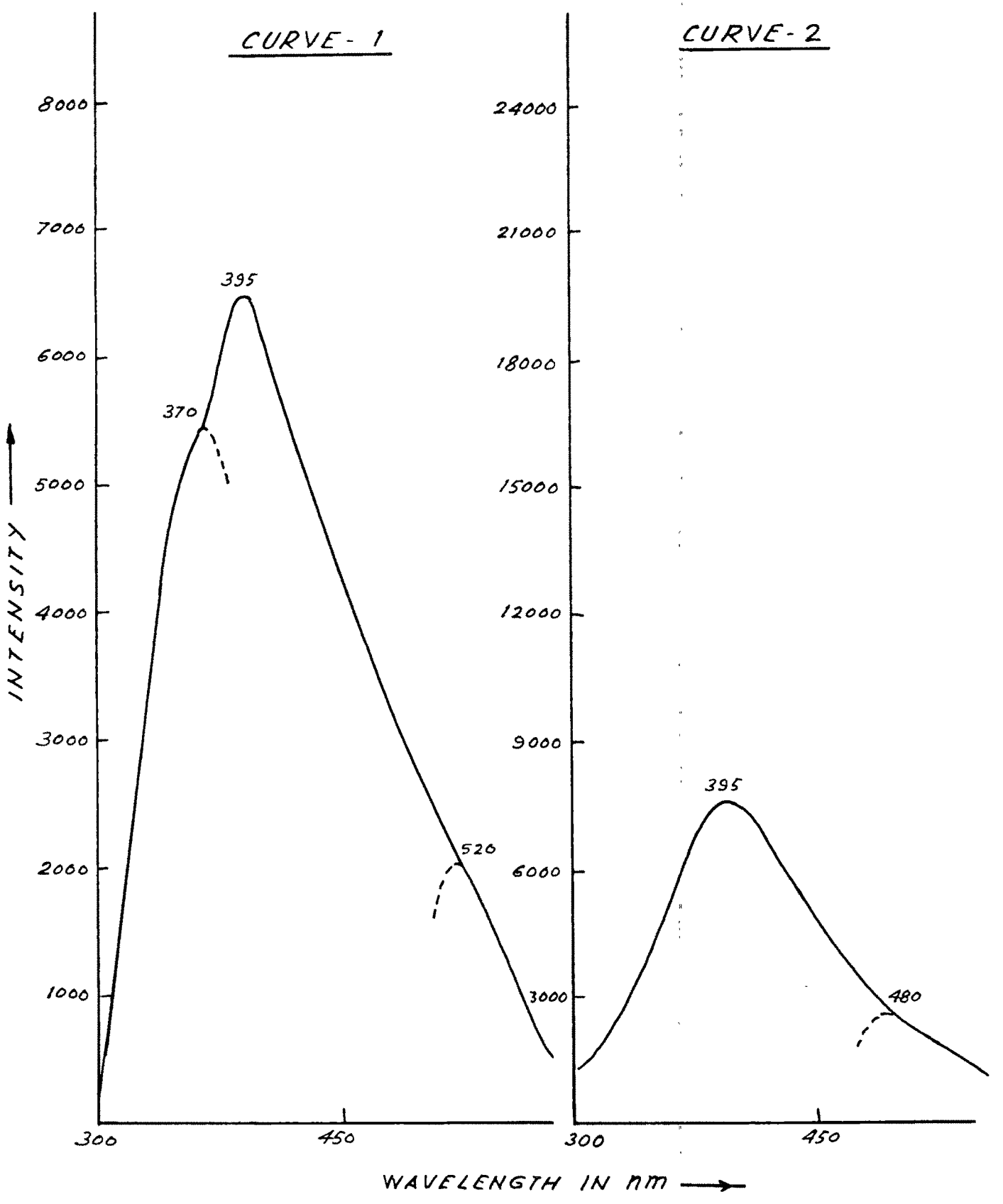

CURVE - 1
CURVE - 2
8000
7000
6000
5000
4000
3000
2000
1000
24000
21000
18000
15000
12000
9000
6000
3000
395
370
520
395
480
INTENSITY
300
450
300
450
WAVELENGTH IN nm

FIG. 30

Fig. 31 : Excitation spectrum of NaCl:Tl powder specimen for 364 nm emission. Specimen was annealed at 500°C in evacuated and sealed tube for 24 hours and then quenched rapidly to room temperature.

Tl concentration $\sim 10^{-2}$ m.f.

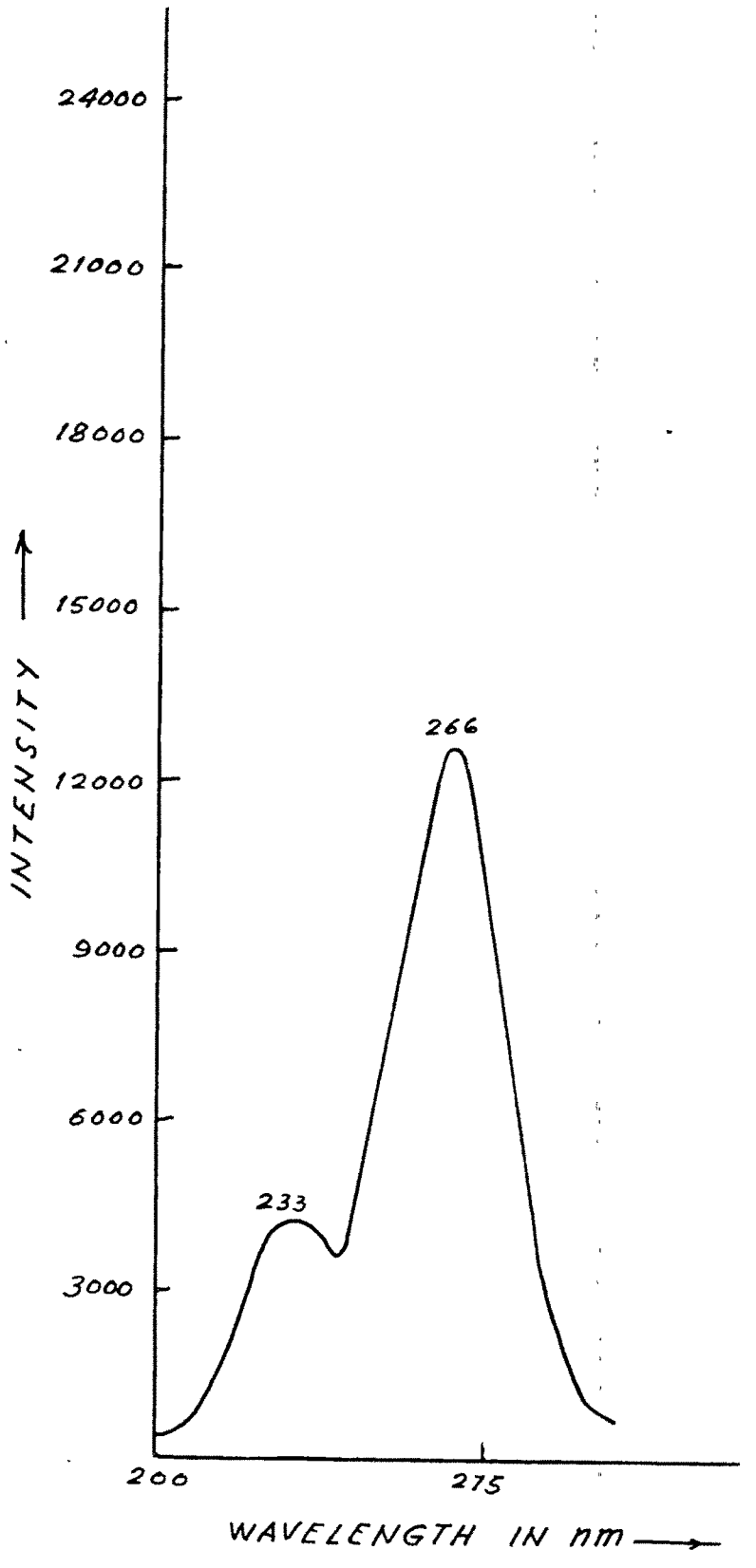

24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
266
233
200
275
WAVELENGTH IN nm

FIG. 31

Fig. 32 : Emission spectra of NaCl:Tl powder specimen upon excitation at 233 nm (Curve : 1) and at 266 nm (Curve : 2). Specimen was annealed at 500°C in evacuated and sealed tube for 24 hours and then quenched rapidly to room remperature.

Tl concentration $\sim 10^{-2}$ m.f.

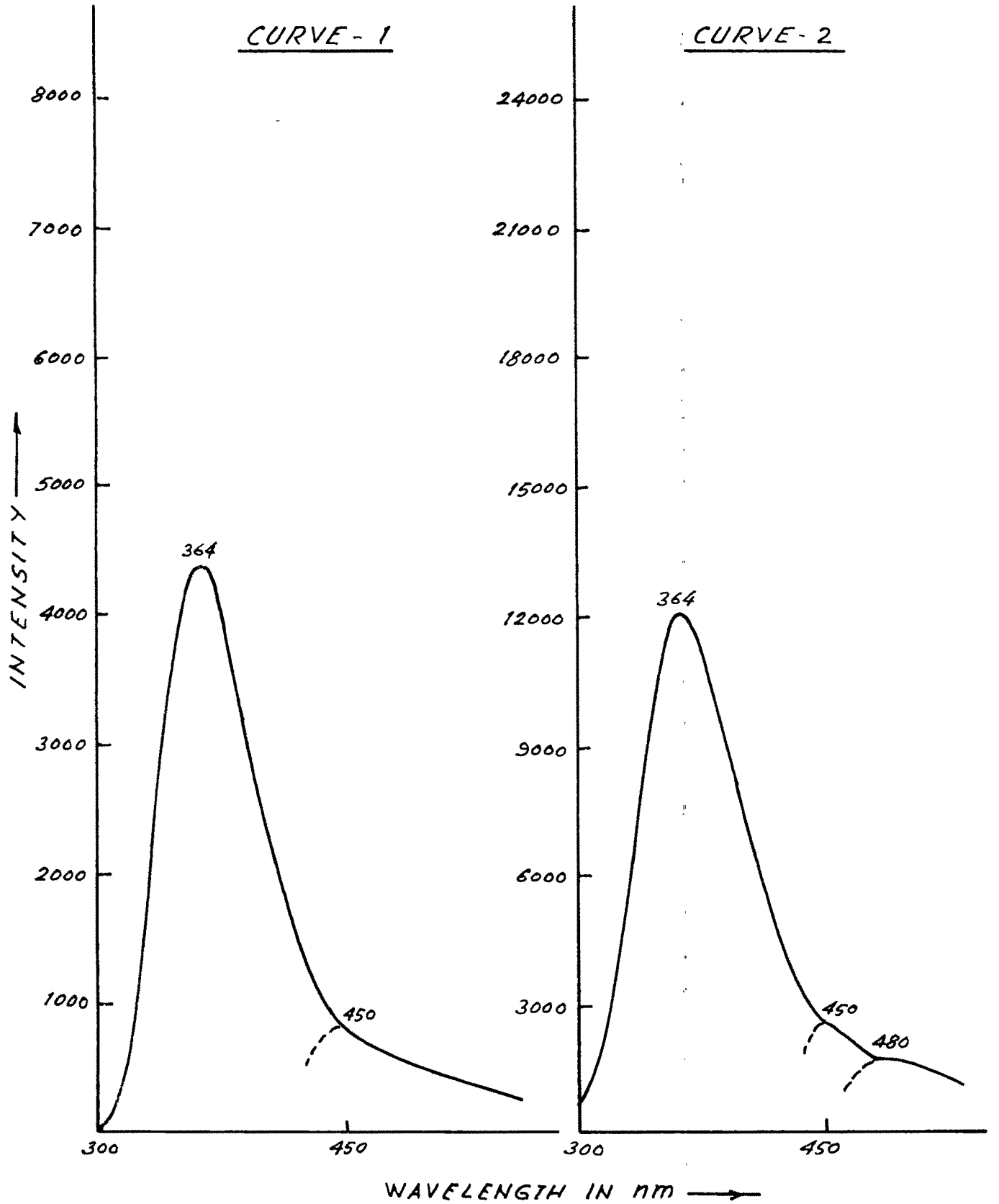

CURVE - 1
CURVE - 2
8000
7000
6000
5000
4000
3000
2000
1000
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
364
450
480
300
450
WAVELENGTH IN nm

FIG. 32

Fig. 33 : Excitation spectrum of NaCl:Tl powder specimen for 372 nm emission. Specimen was annealed at 500°C in evacuated and sealed tube for 24 hours and then quenched rapidly to room temperature.

Tl concentration $\sim 10^{-1}$ m.f.

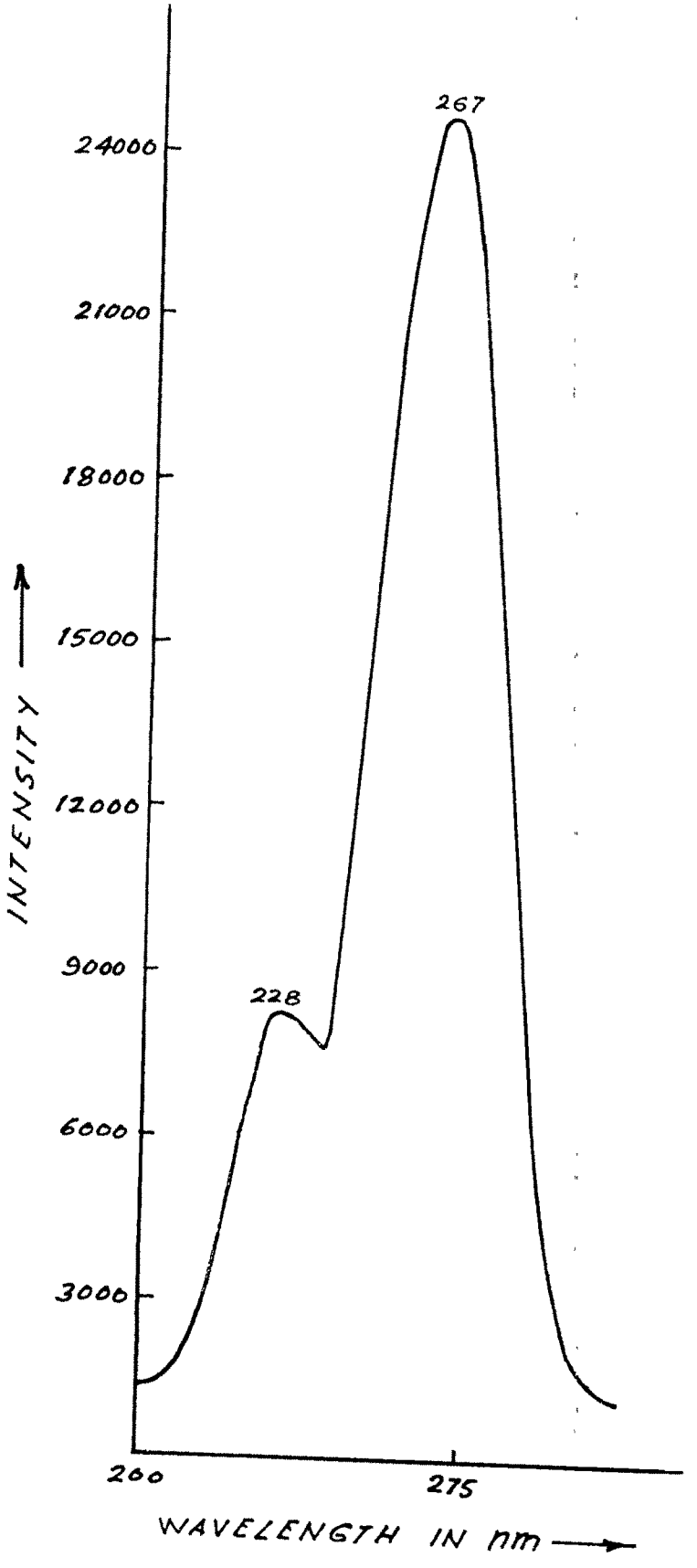

267
24000
21000
18000
15000
12000
9000
228
6000
3000
INTENSITY
200
275
WAVELENGTH IN nm

FIG. 33

Fig. 34 : Emission spectra of NaCl:Tl powder specimens upon excitation at 228 nm (Curve : 1) and at 267 nm (Curve : 2). Specimen was annealed at 500°C in evacuated sealed tube for 24 hours and then quenched rapidly to room temperature.

Tl concentration $\sim 10^{-1}$ m.f.

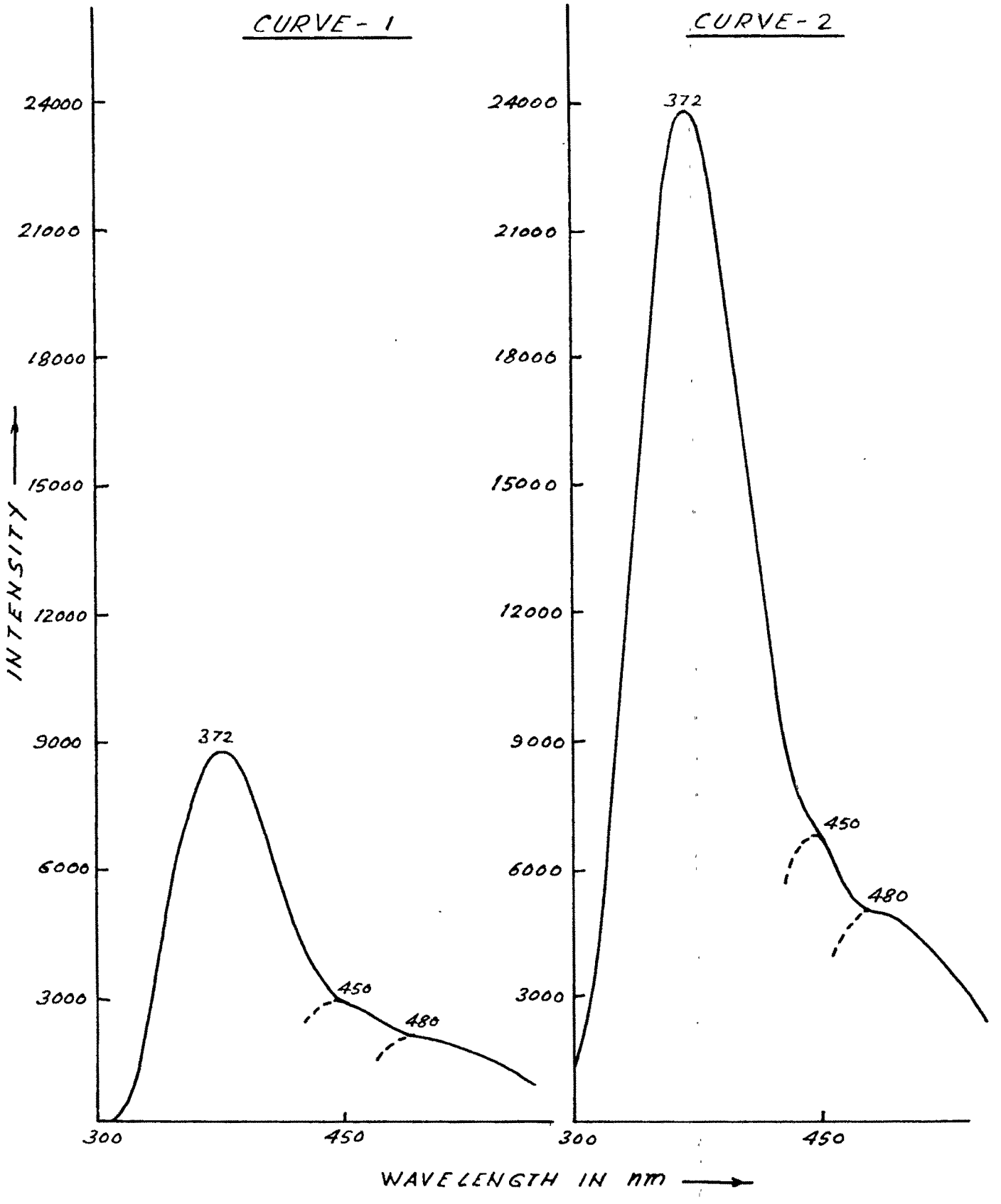

CURVE - 1
CURVE - 2
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
372
450
480
300
450
WAVELENGTH IN nm

FIG. 34

Fig. 35 : Excitation spectrum of NaCl:Tl specimen for 375 nm emission. Specimen annealed and quenched from 500°C in evacuated and sealed tube and subsequently compressed to tablet.

Tl concentration $\sim 10^{-2}$ m.f.

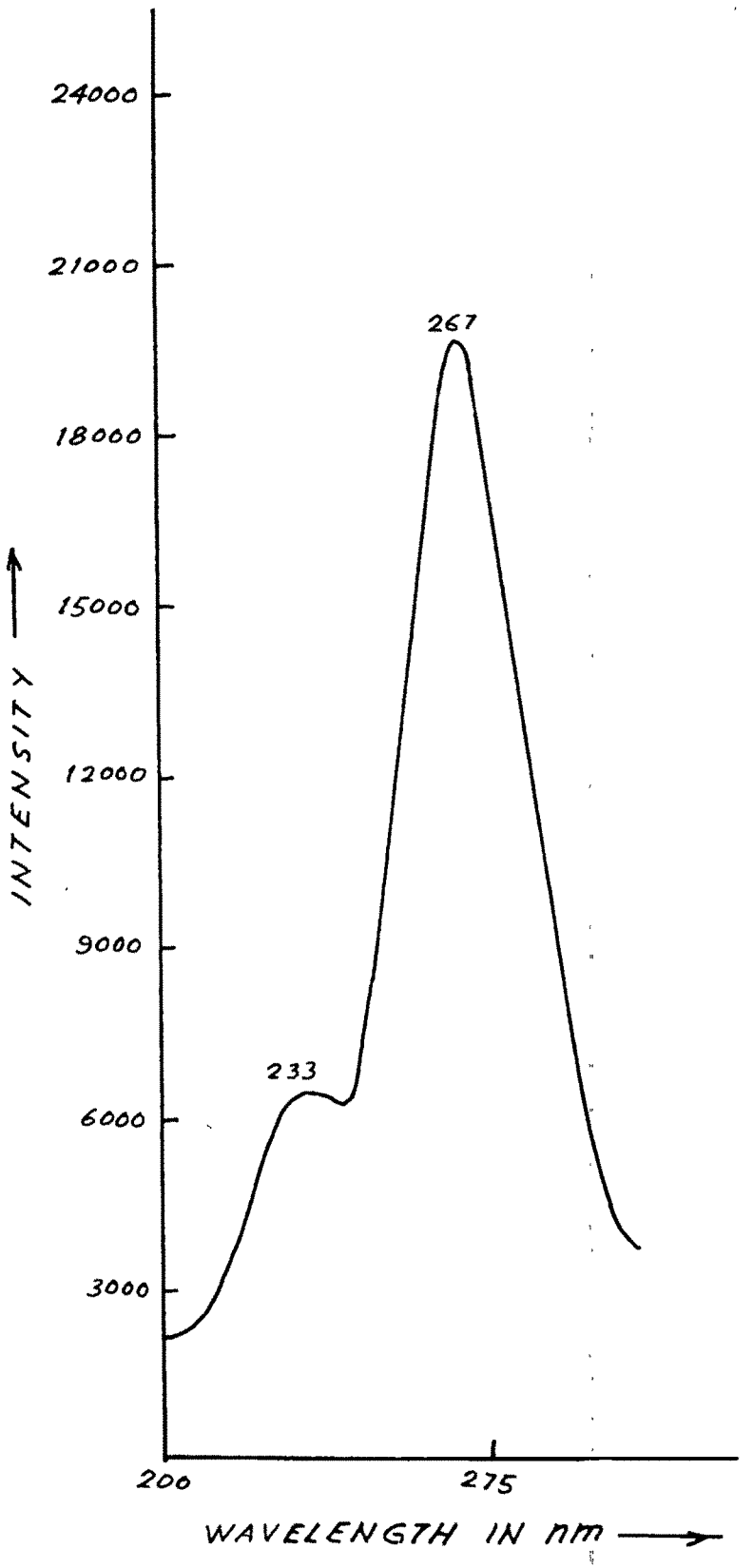

24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
267
233
200
275
WAVELENGTH IN nm

FIG. 35

Fig. 36 : Emission spectra of NaCl:Tl specimens upon excitation at 233 nm (Curve : 1) and at 267 nm (Curve : 2). Specimens annealed and quenched from 500°C in evacuated and sealed tube and subsequently compressed to tablet.

Tl concentration $\sim 10^{-2}$ m.f.

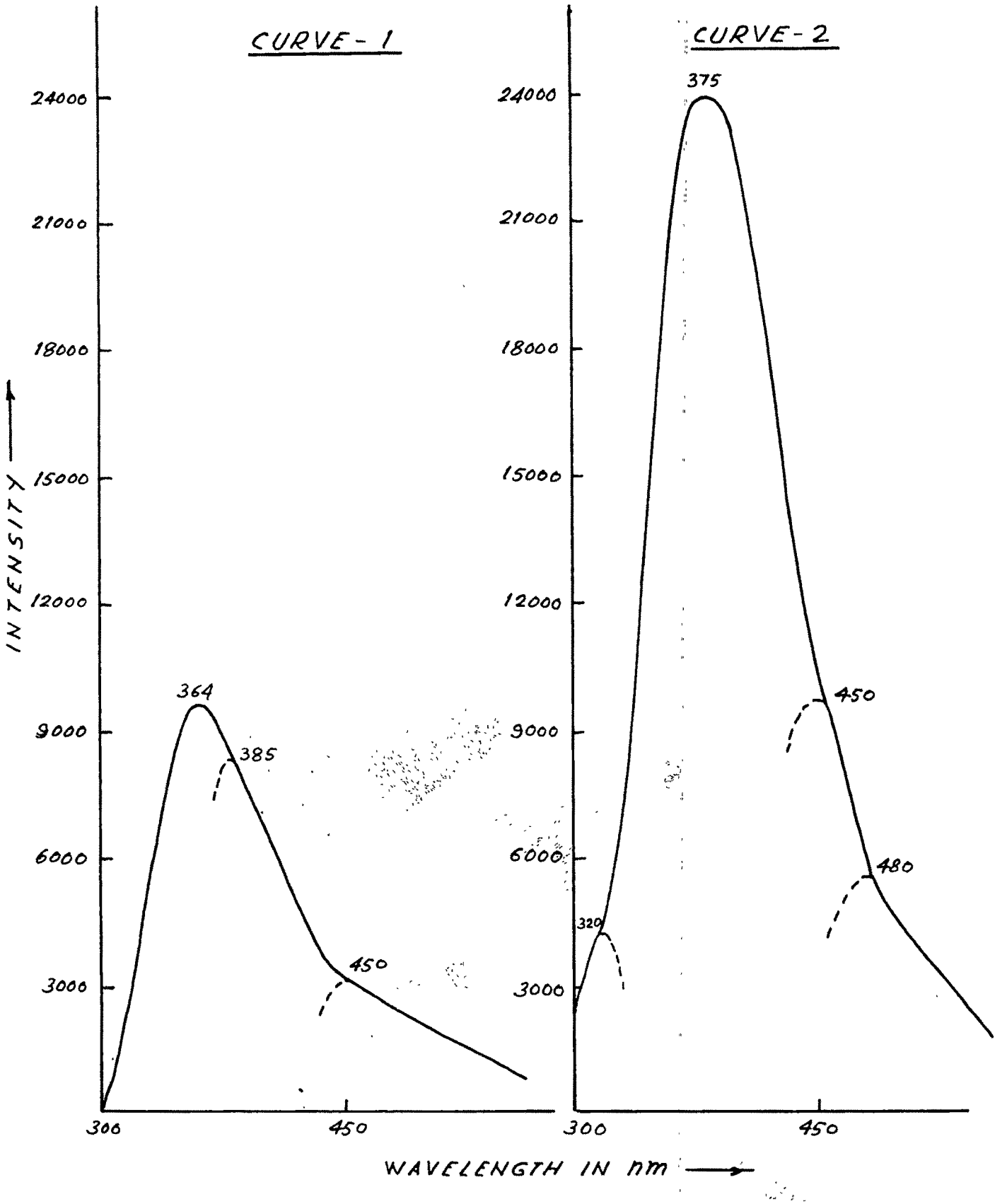

CURVE - 1
CURVE - 2
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
364
385
450
375
450
480
320
300
450
WAVELENGTH IN nm

FIG. 36

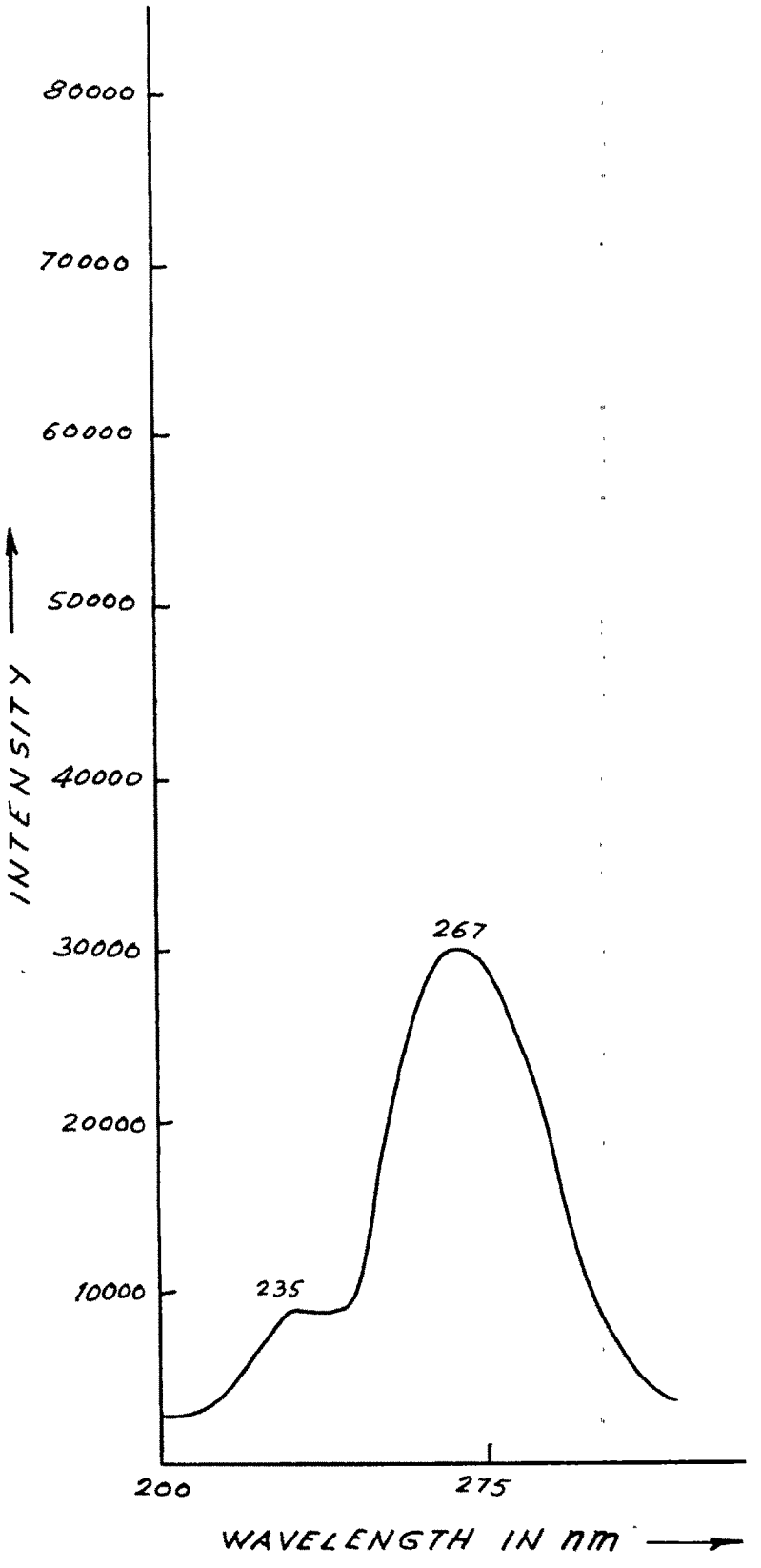

80000
70000
60000
50000
40000
30000
20000
10000
INTENSITY
267
235
200
275
WAVELENGTH IN nm

FIG. 37

Fig. 38 : Emission spectra of NaCl:Tl specimen upon excitation at 235 nm (Curve : 1) and 267 nm (Curve : 2). Specimen annealed and quenched from 500°C in evacuated and sealed tube and subsequently compressed to tablet.

Tl concentration $\sim 10^{-1}$ m.f.

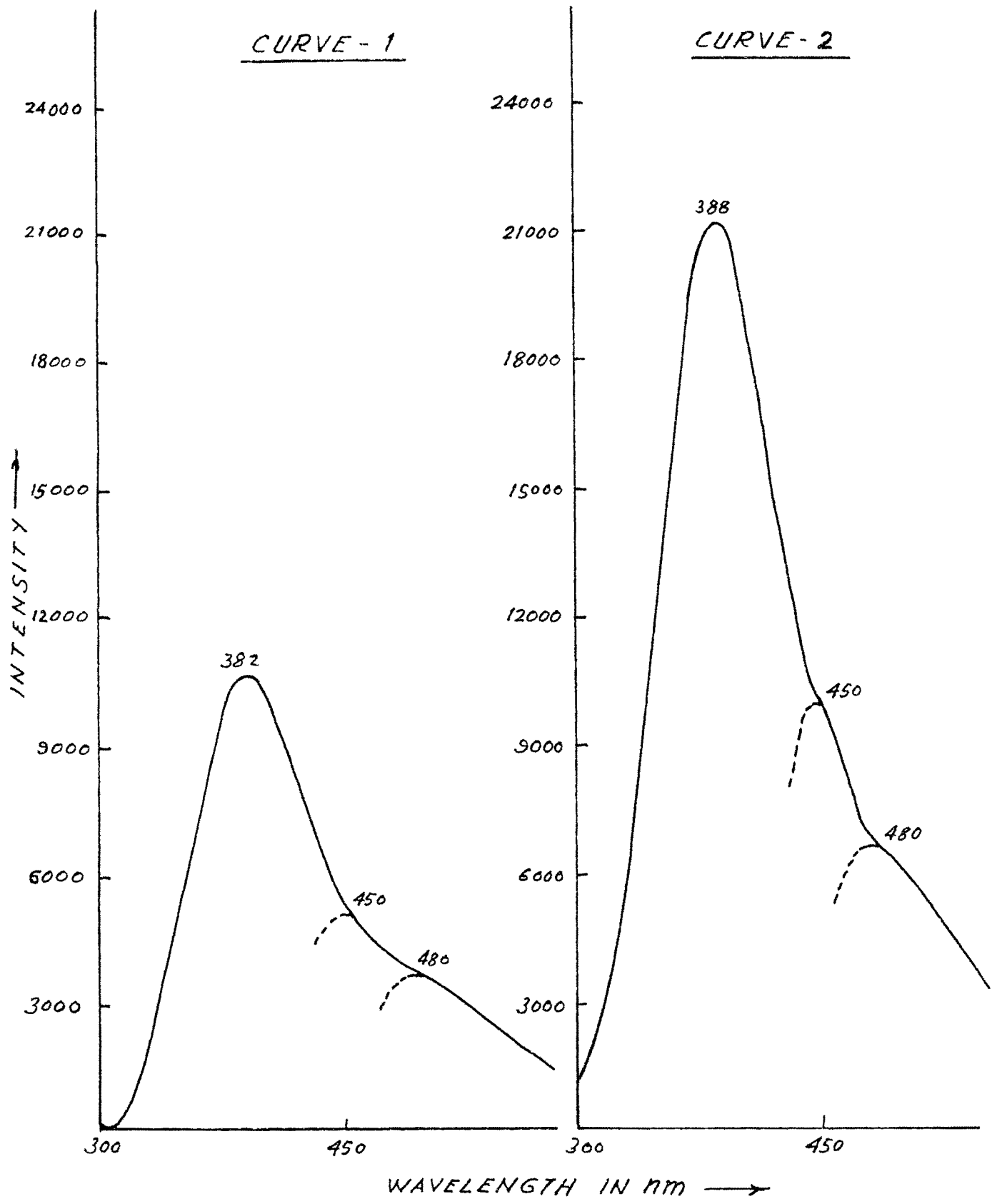

CURVE - 1
CURVE - 2
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
382
388
450
480
300
450
WAVELENGTH IN mm

FIG. 38

Fig. 39 : Excitation spectra of NaCl:Tl melt and quenched specimens (powdered) for 375 nm emission.

Curve : 1 - For Tl concentration $\sim 10^{-2}$ m.f.
Curve : 2 - " " $\sim 10^{-1}$ m.f.

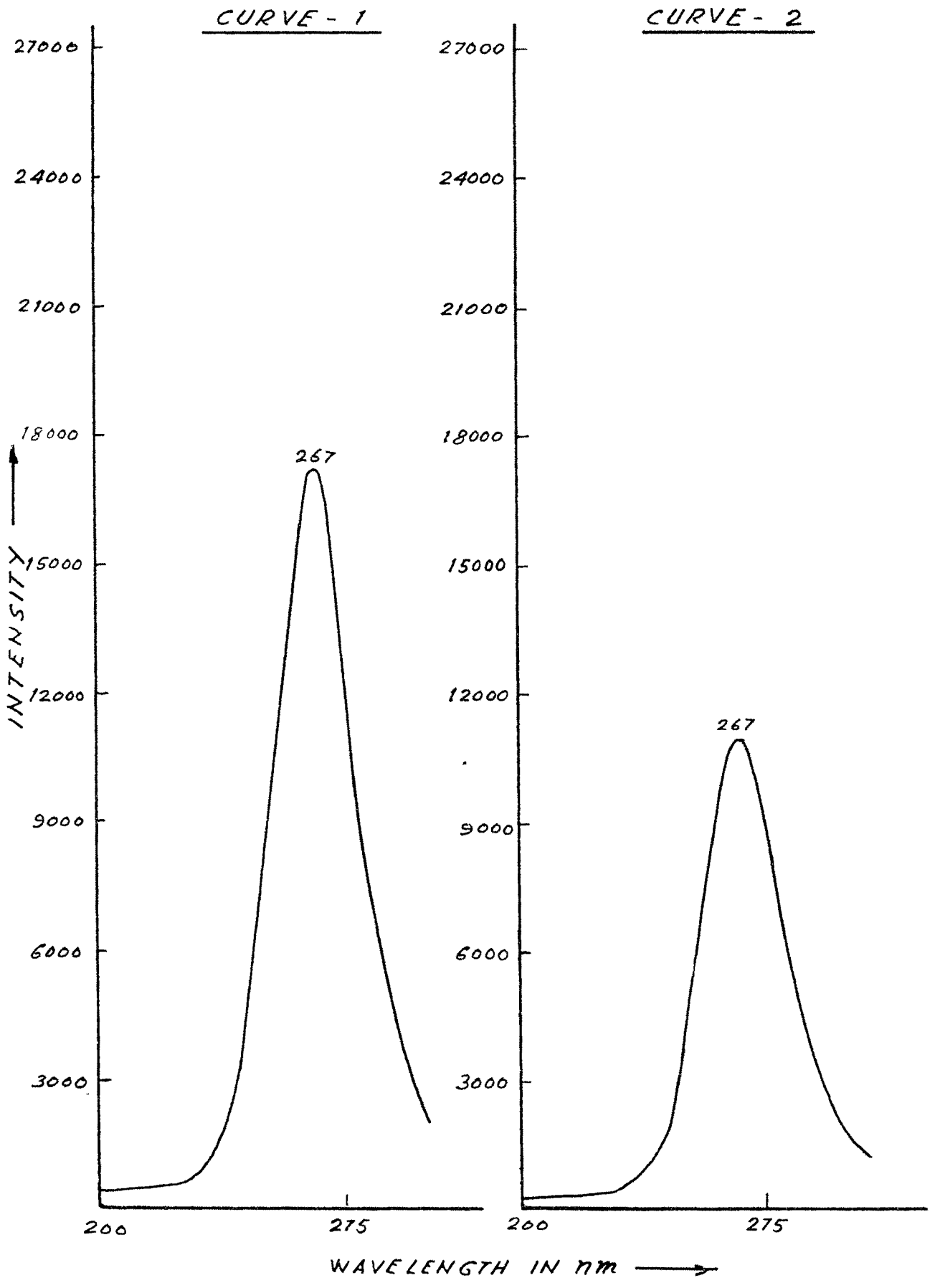

CURVE - 1
CURVE - 2
27000
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
267
267
200
275
200
275
WAVELENGTH IN nm

FIG. 39

Fig. 40 : Emission spectra of NaCl:Tl melt and quenched specimens (powdered) upon excitation at 267 nm.

Curve : 1 - For Tl concentration $\sim 10^{-2}$ m.f.

Curve : 2 - " " $\sim 10^{-1}$ m.f.

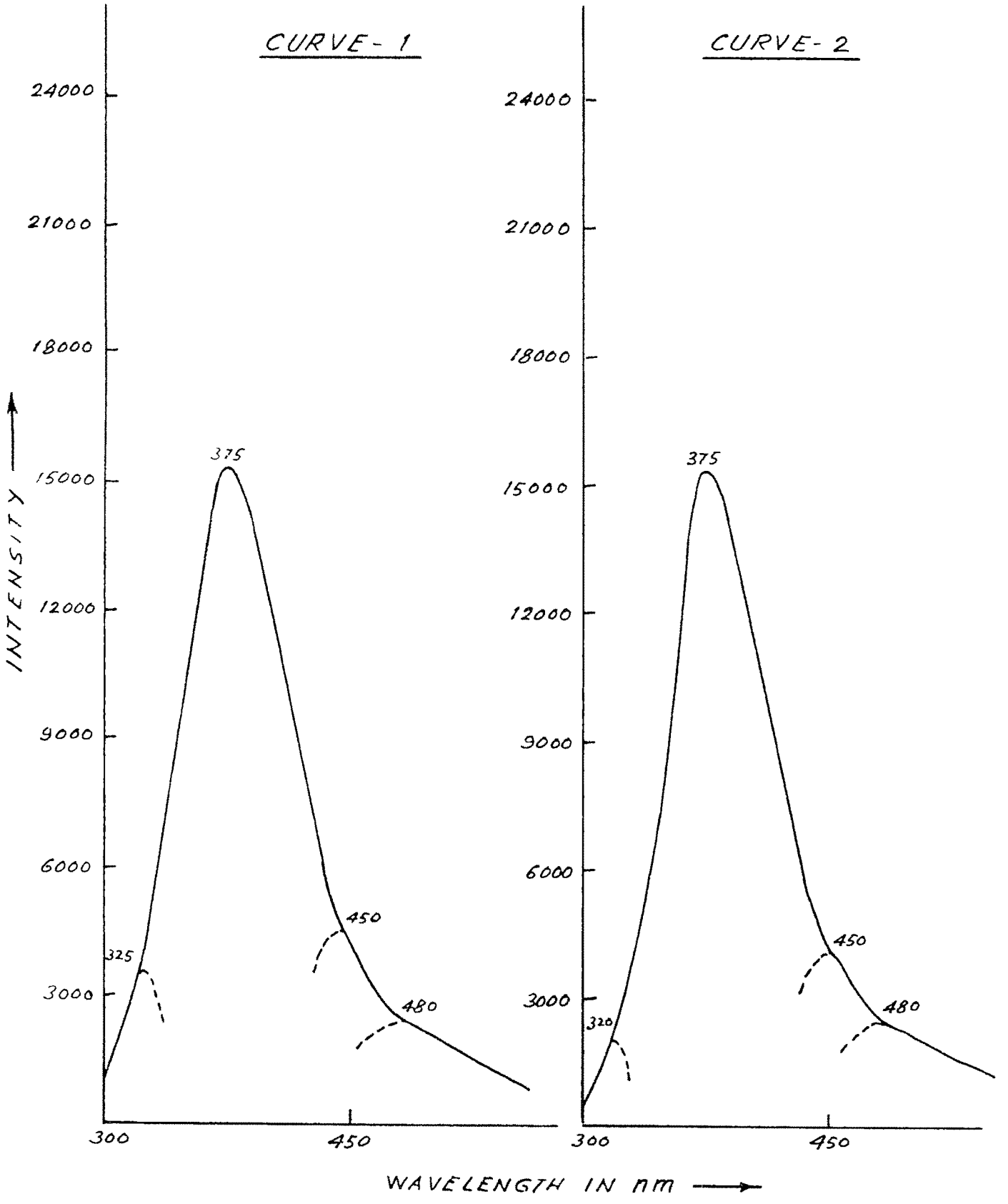

CURVE-1
CURVE-2
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
375
325
450
480
320
300
450
WAVELENGTH IN nm

FIG. 40

Fig. 41 : Excitation spectra of NaCl:Tl melt and quenched specimens (tabletted) for 390 nm emission.

Curve : 1 - For Tl concentration $\sim 10^{-2}$ m.f.

Curve : 2 - " " $\sim 10^{-1}$ m.f.

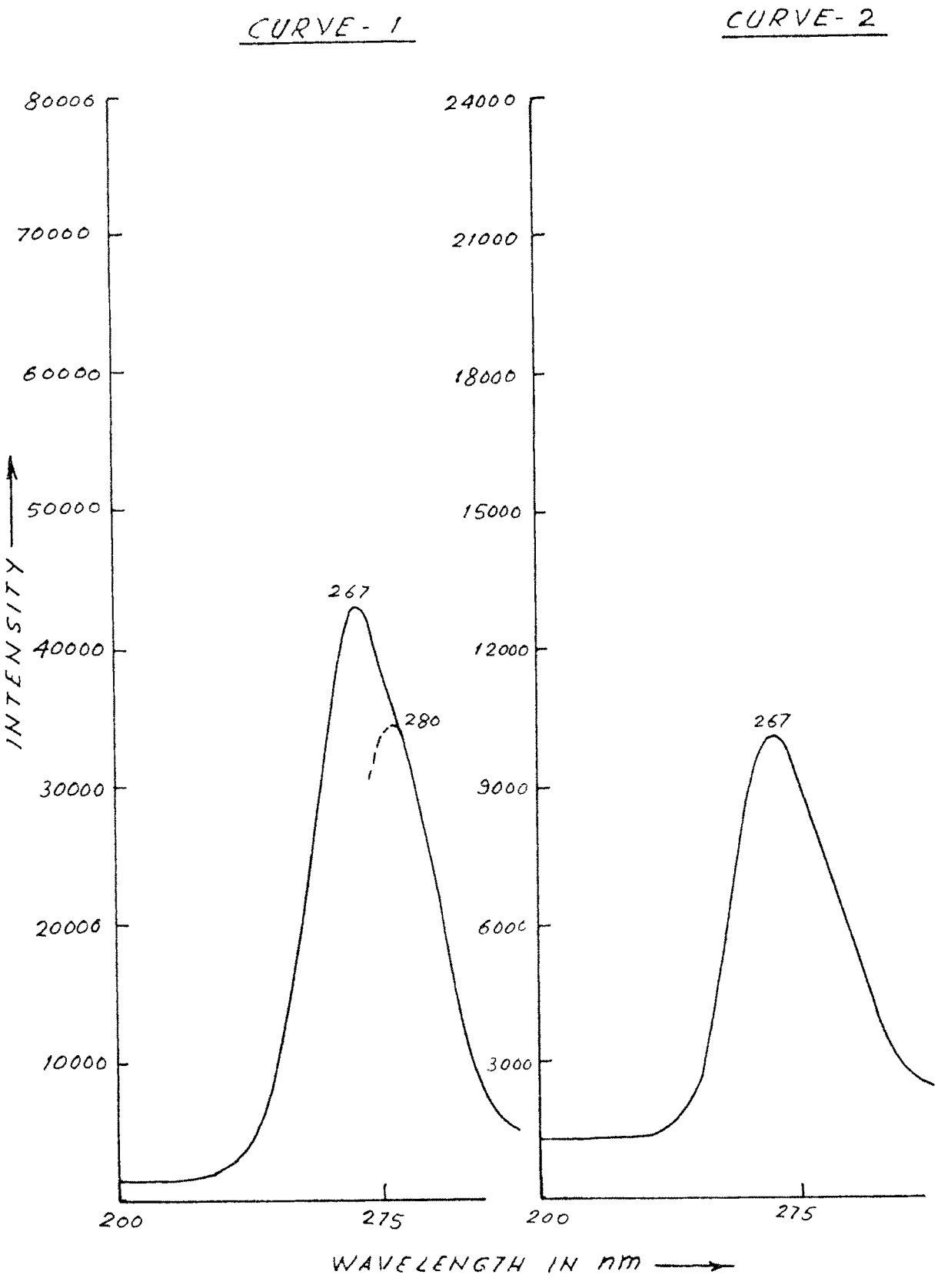

CURVE - 1
CURVE - 2
80000
70000
60000
50000
40000
30000
20000
10000
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
267
280
267
200
275
200
275
WAVELENGTH IN nm

FIG 41

Fig. 42 : Emission spectra of NaCl:Tl melt and quenched specimens (tabletted) upon excitation at 267 nm.

Curve : 1 - For Tl concentration $\sim 10^{-2}$ m.f.

Curve : 2 - " " $\sim 10^{-1}$ m.f.

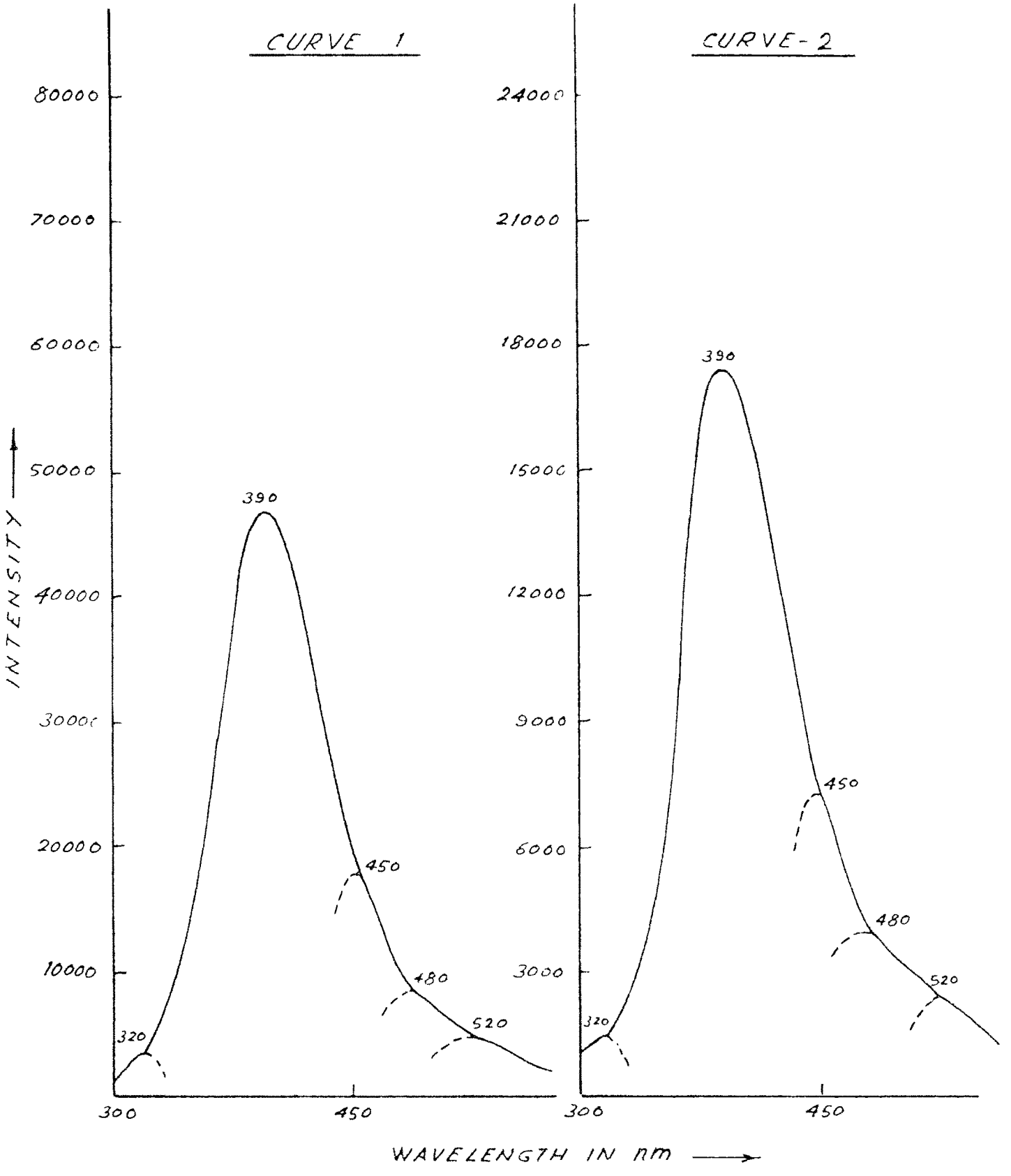

CURVE 1
CURVE-2
80000
70000
60000
50000
40000
30000
20000
10000
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
390
450
480
520
320
300
450
WAVELENGTH IN nm

FIG 42

Fig. 43 : Excitation spectra of NaCl:Tl powder specimen for 450 nm emission (Curve : a), 480 nm emission (Curve : b) and 520 nm emission (Curve : c). As-received specimens (i.e. as obtained by crystallization from aqueous solution).

Tl concentration $\sim 10^{-4}$ m.f.

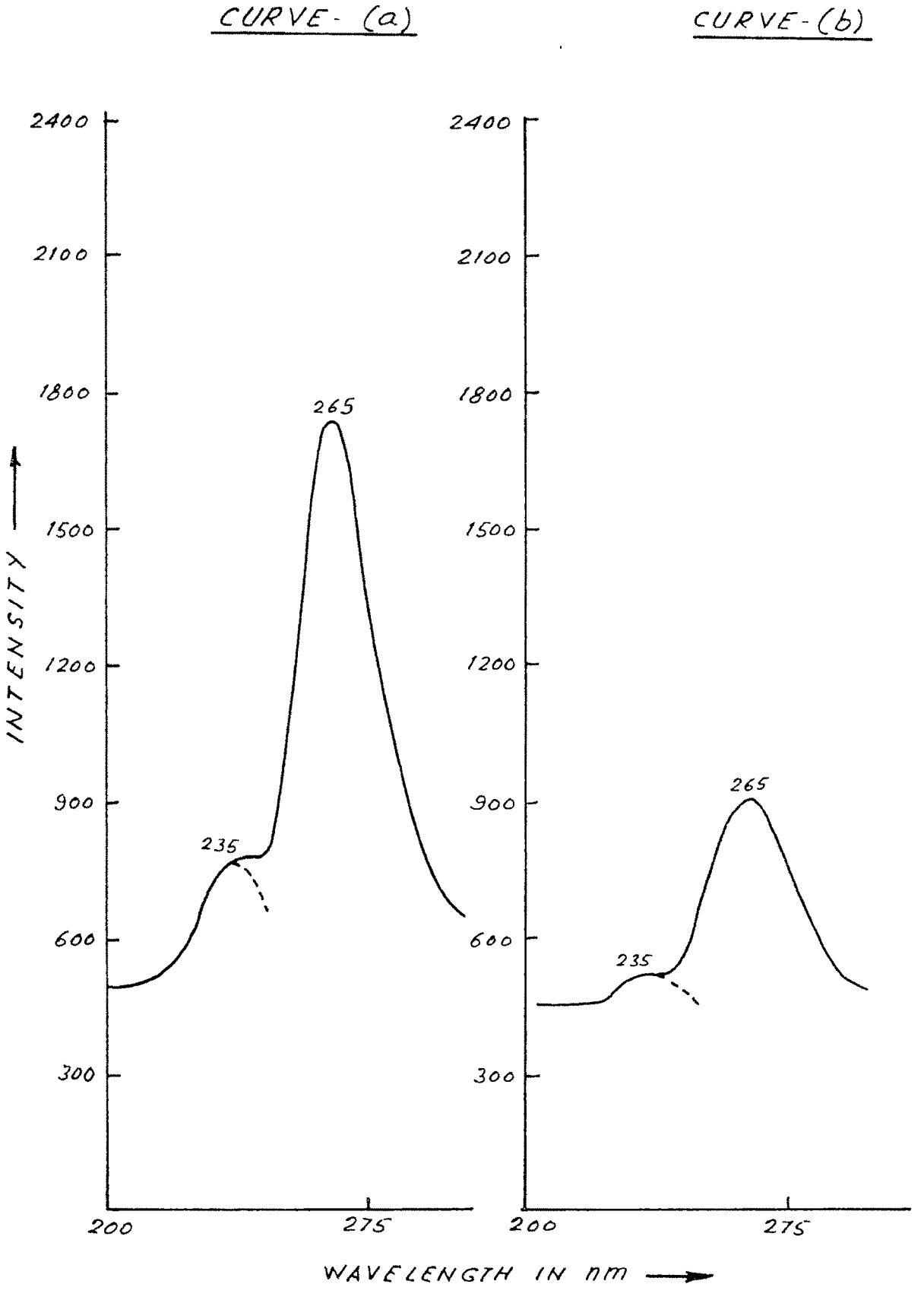

CURVE- (a)
CURVE-(b)
2400
2100
1800
1500
1200
900
600
300
INTENSITY
265
235
200
275
WAVELENGTH IN nm

FIG. 43

CURVE - (c)

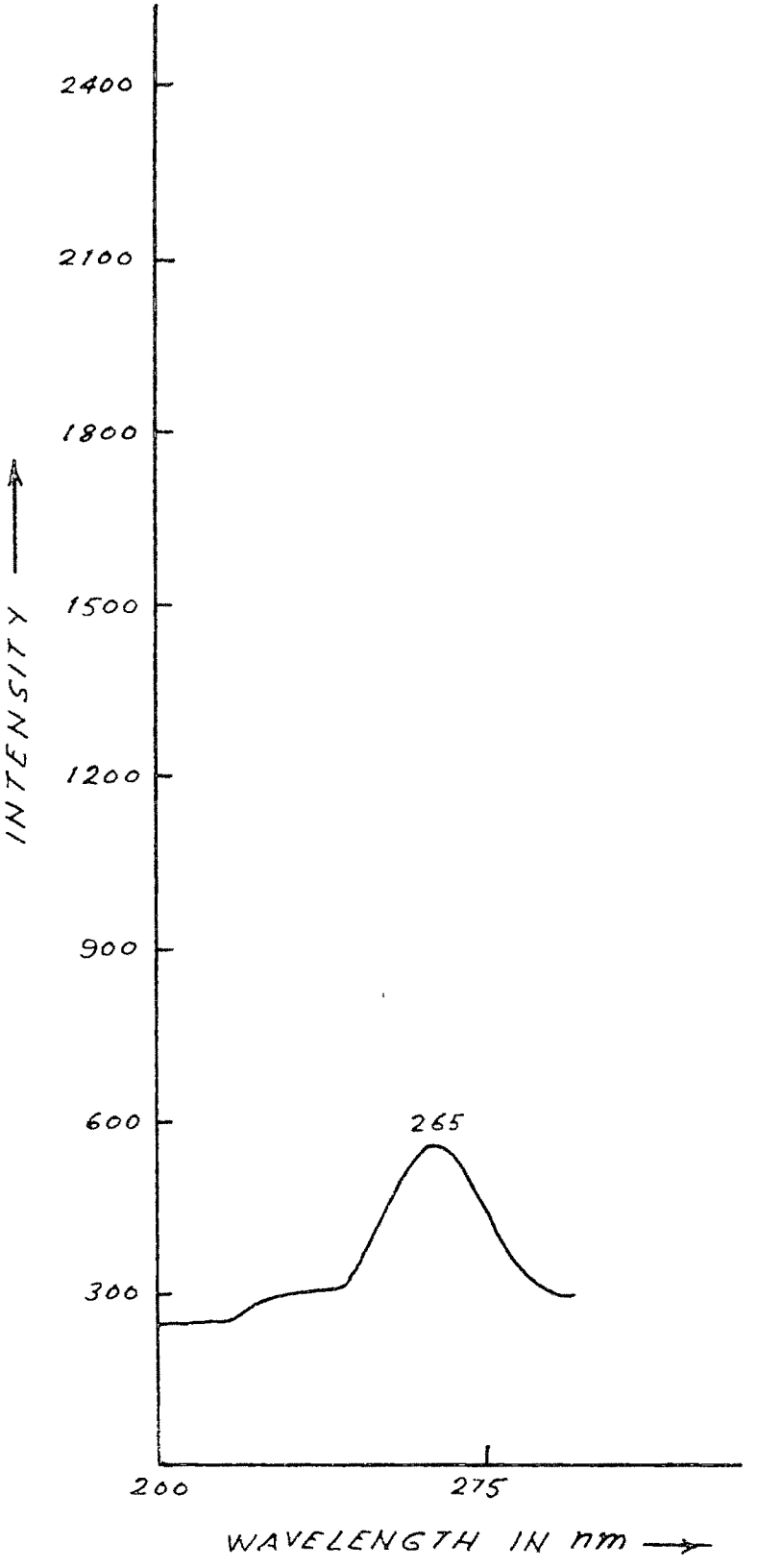


FIG. 43

Fig. 44 : Excitation spectra of NaCl:Tl powder specimen for 450 nm emission (Curve : a), 480 nm emission (Curve : b), and 520 nm emission (Curve : c). As-received specimens (i.e. as obtained by crystallization from aqueous solution).

Tl concentration $\backsim 10^{-2}$ m.f.

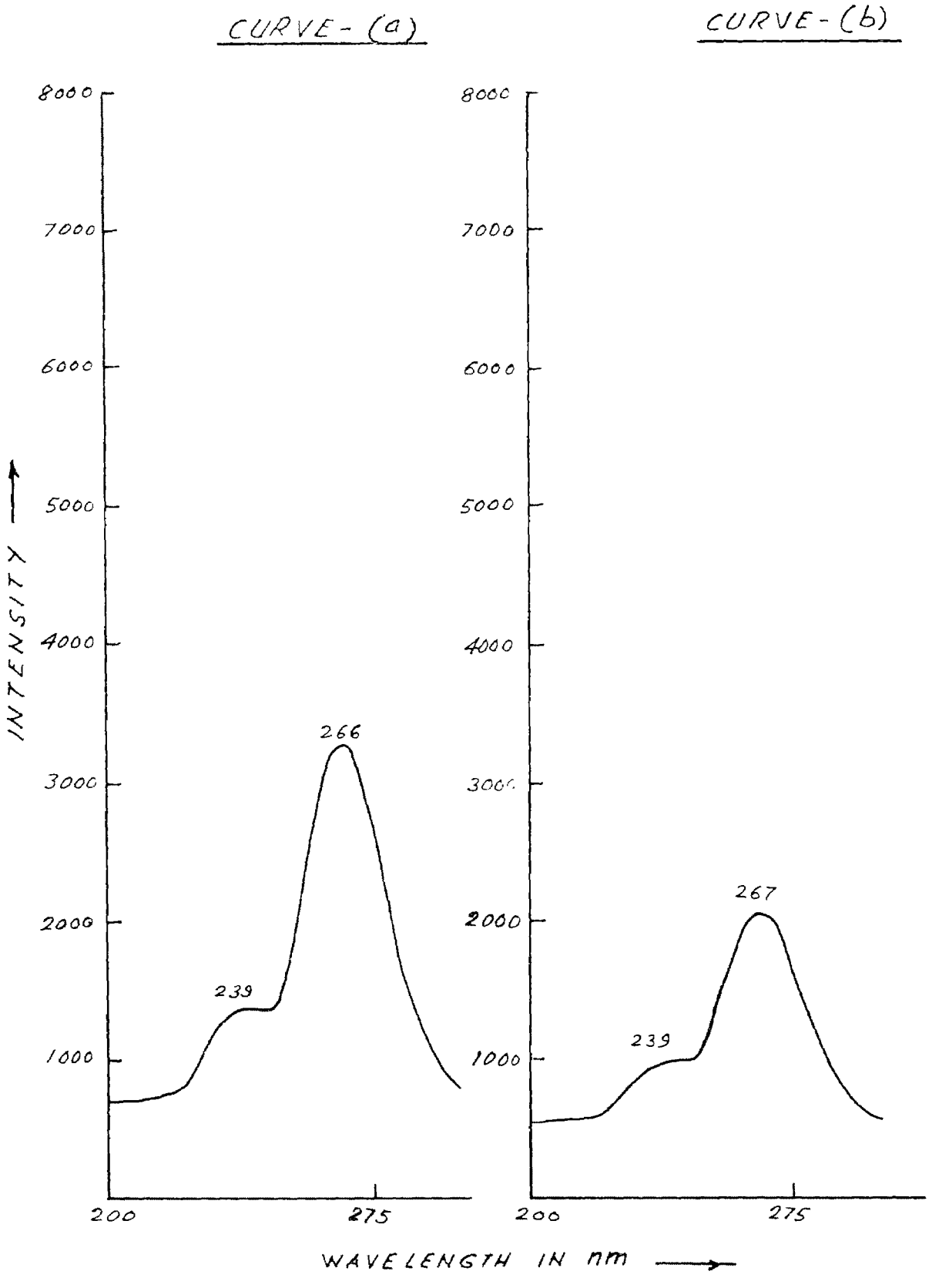

CURVE - (a)
CURVE - (b)
8000
7000
6000
5000
4000
3000
2000
1000
INTENSITY
266
239
267
239
200
275
200
275
WAVELENGTH IN nm

FIG 44

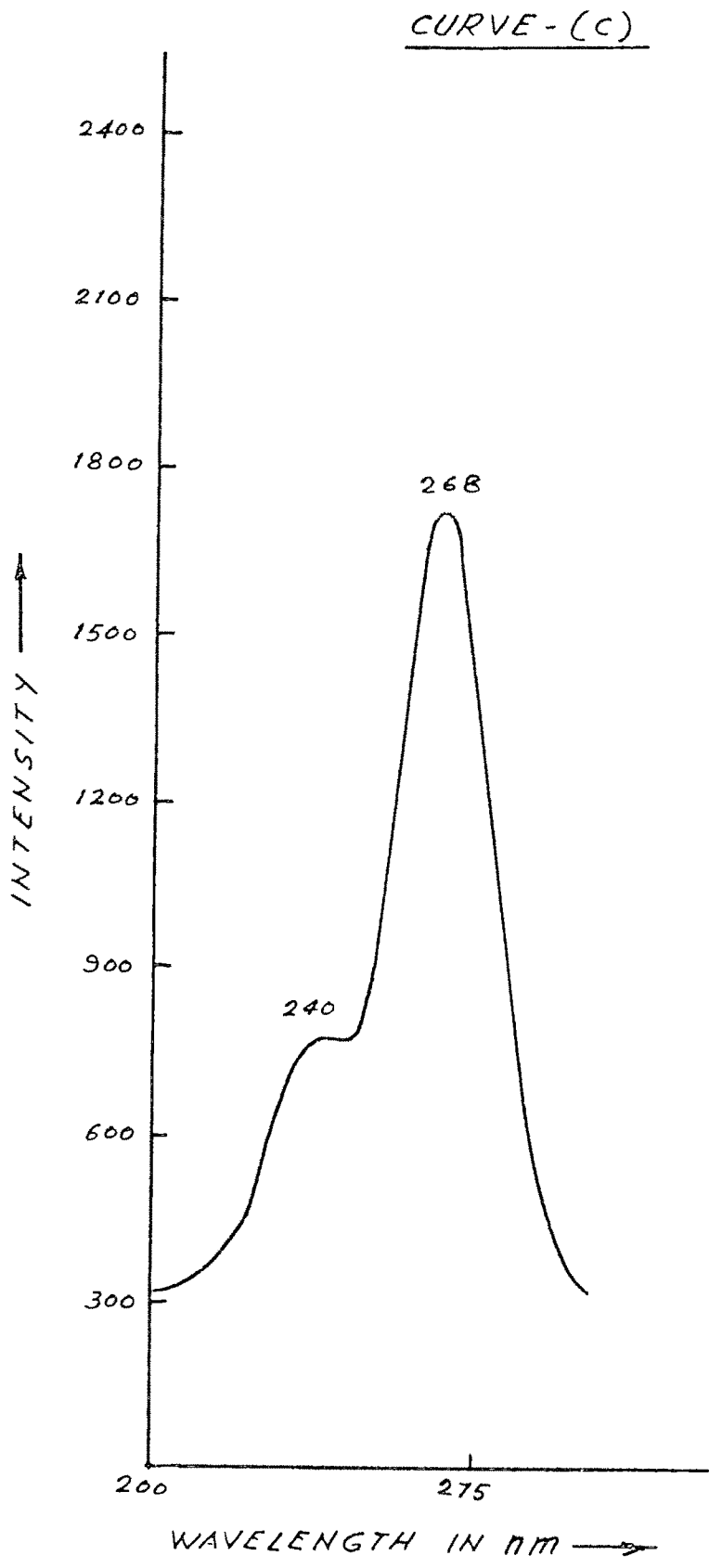

CURVE - (C)
2400
2100
1800
1500
1200
900
600
300
INTENSITY
268
240
200
275
WAVELENGTH IN nm

FIG. 44

Fig. 45 : Excitation spectra of NaCl:Tl specimen compressed into tablet for 450 nm emission (Curve : a) and 480 nm emission (Curve : b). As-received specimens.

Tl concentration $\sim 10^{-4}$ m.f.

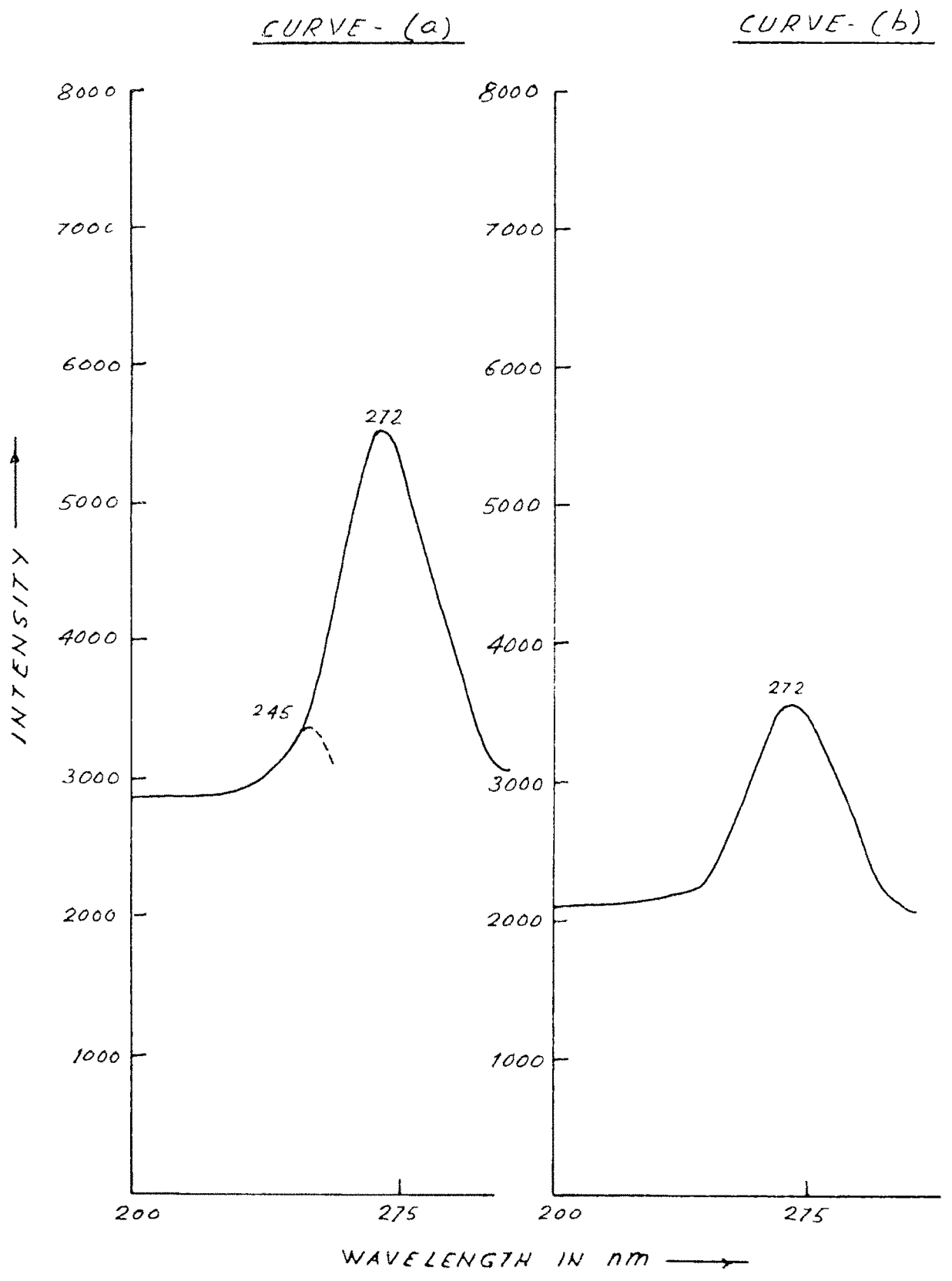

CURVE- (a)
CURVE- (b)
8000
7000
6000
5000
4000
3000
2000
1000
INTENSITY
272
245
272
200
275
200
275
WAVELENGTH IN nm

FIG. 45

Fig. 46 : Excitation spectra of NaCl:Tl as-received specimen compressed to tablet for 450 nm emission (Curve : a), 480 nm emission (Curve : b) and 520 nm emission (Curve : c).

Tl concentration $\sim 10^{-2}$ m.f.

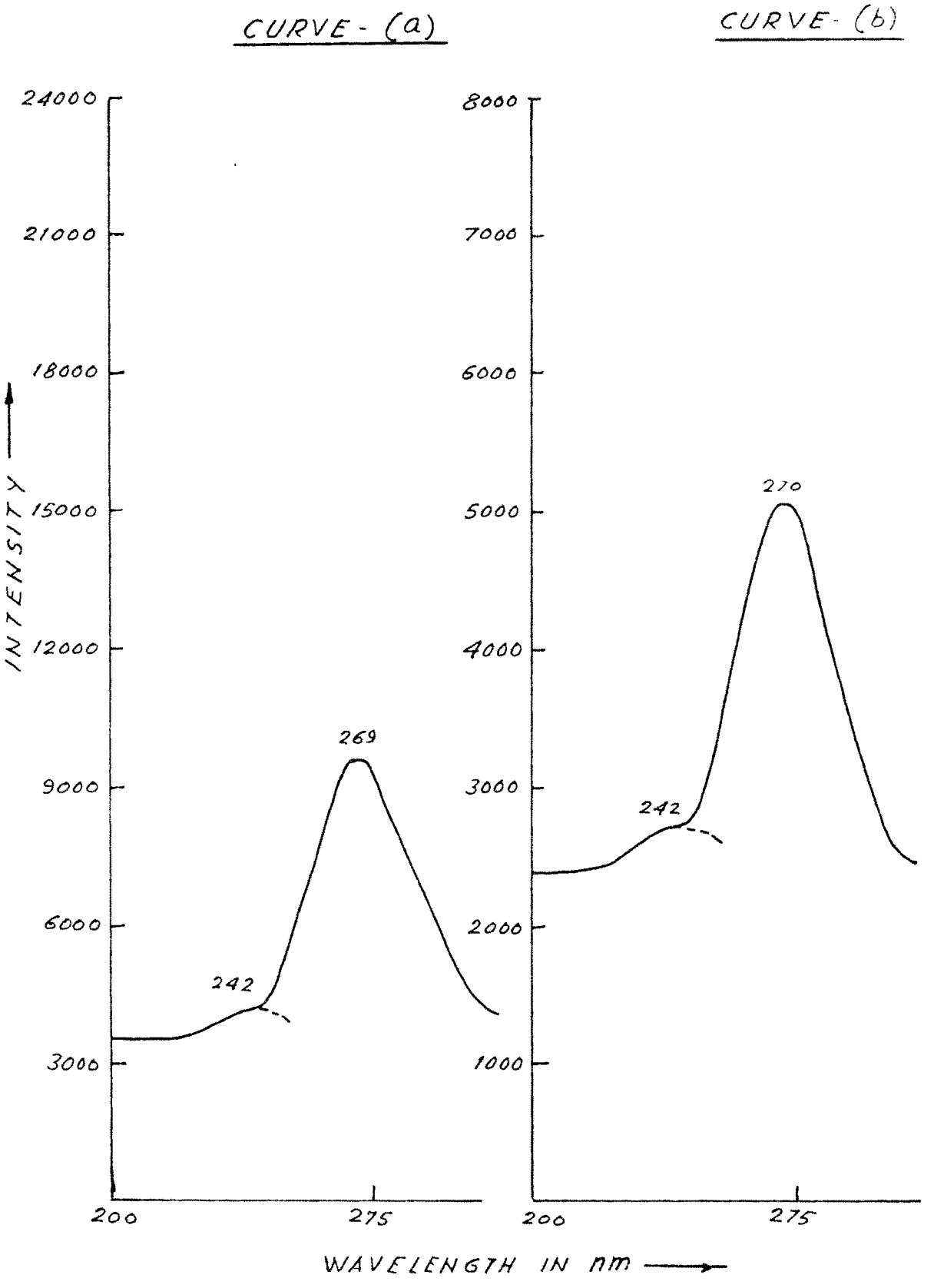

CURVE - (a)
CURVE - (b)
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
269
242
200
275
8000
7000
6000
5000
4000
3000
2000
1000
270
242
200
275
WAVELENGTH IN nm

FIG 46

CURVE - (c)

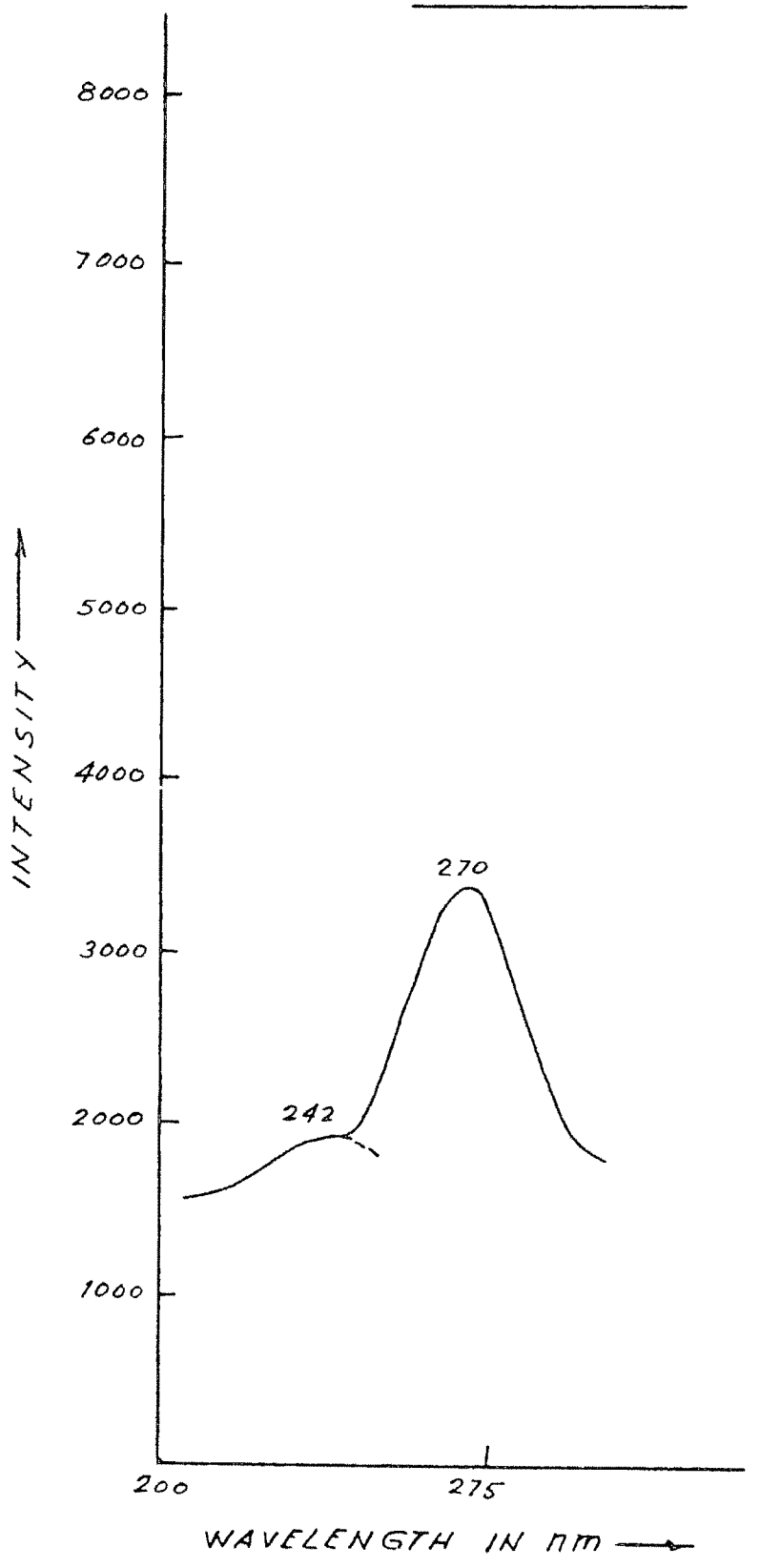


FIG 46

Fig. 47 : Excitation spectra of NaCl:Tl powder specimens for 450 nm emission (Curve : a), 480 nm emission (Curve : b) and 520 nm emission (Curve : c). Specimen annealed at 500°C in evacuated and sealed tube for 24 hours and then quenched rapidly to room temperature.

Tl concentration $\sim 10^{-2}$ m.f.

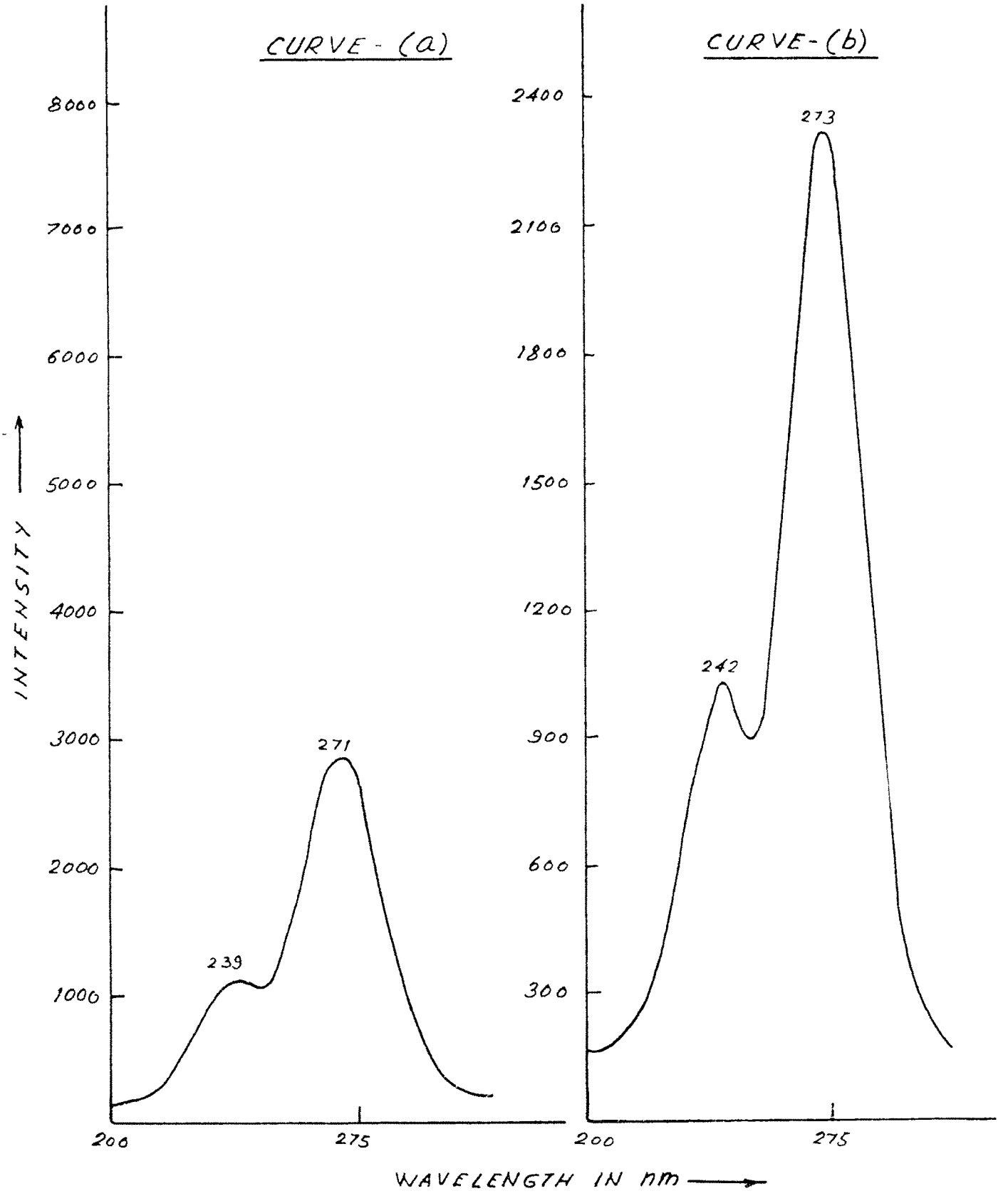

CURVE - (a)
CURVE - (b)
8000
7000
6000
5000
4000
3000
2000
1000
2400
2100
1800
1500
1200
900
600
300
INTENSITY
271
239
273
242
200
275
200
275
WAVELENGTH IN nm

FIG. 47

CURVE (C)

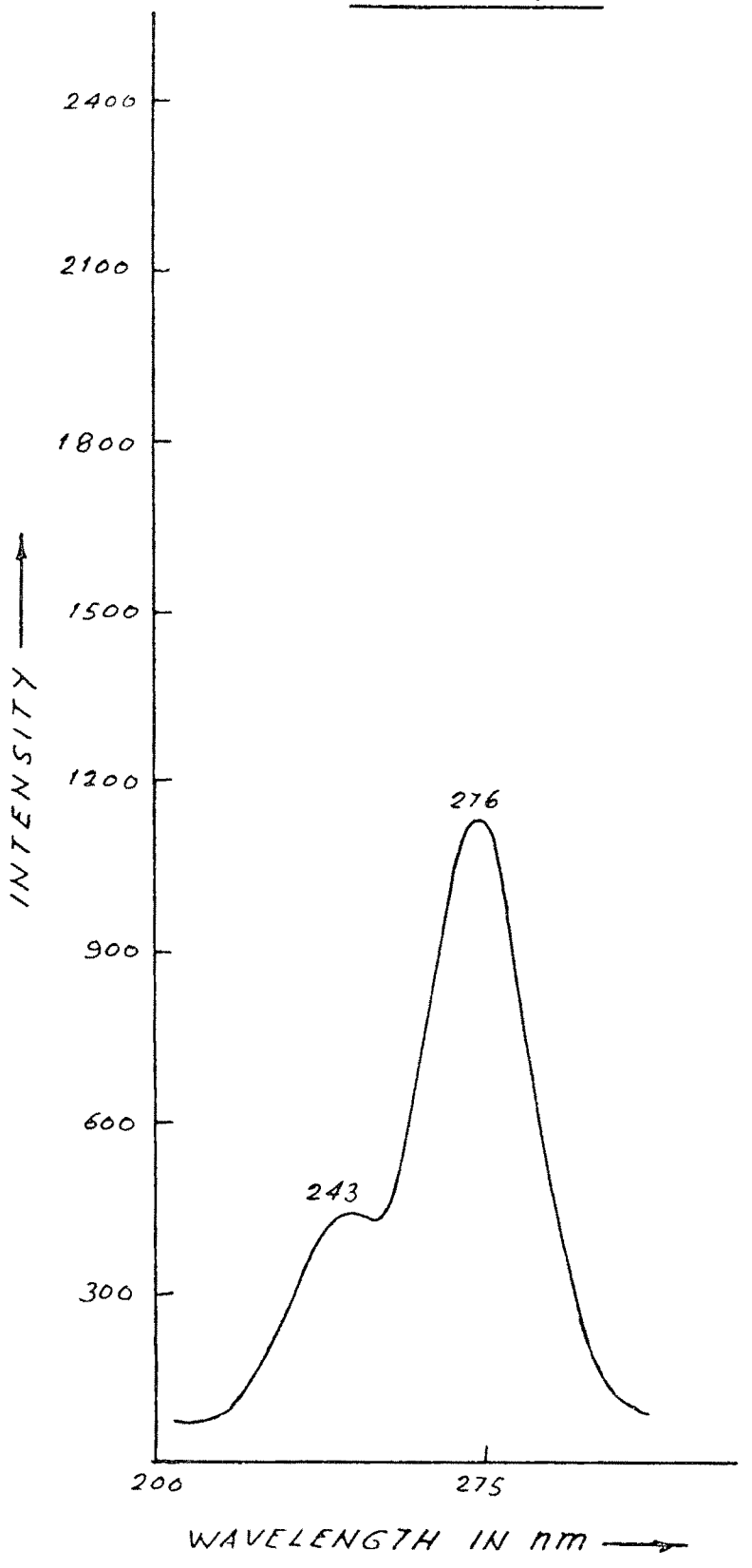


FIG. 47

Fig. 48 : Excitation spectra of NaCl:Tl specimens compressed to tablet for 450 nm emission (Curve : a), 480 nm emission (Curve : b) and 520 nm emission (Curve : c). Specimen annealed and quenched from 500°C in evacuated and sealed tube and then compressed to tablet.

Tl concentration $\sim 10^{-2}$ m.f.

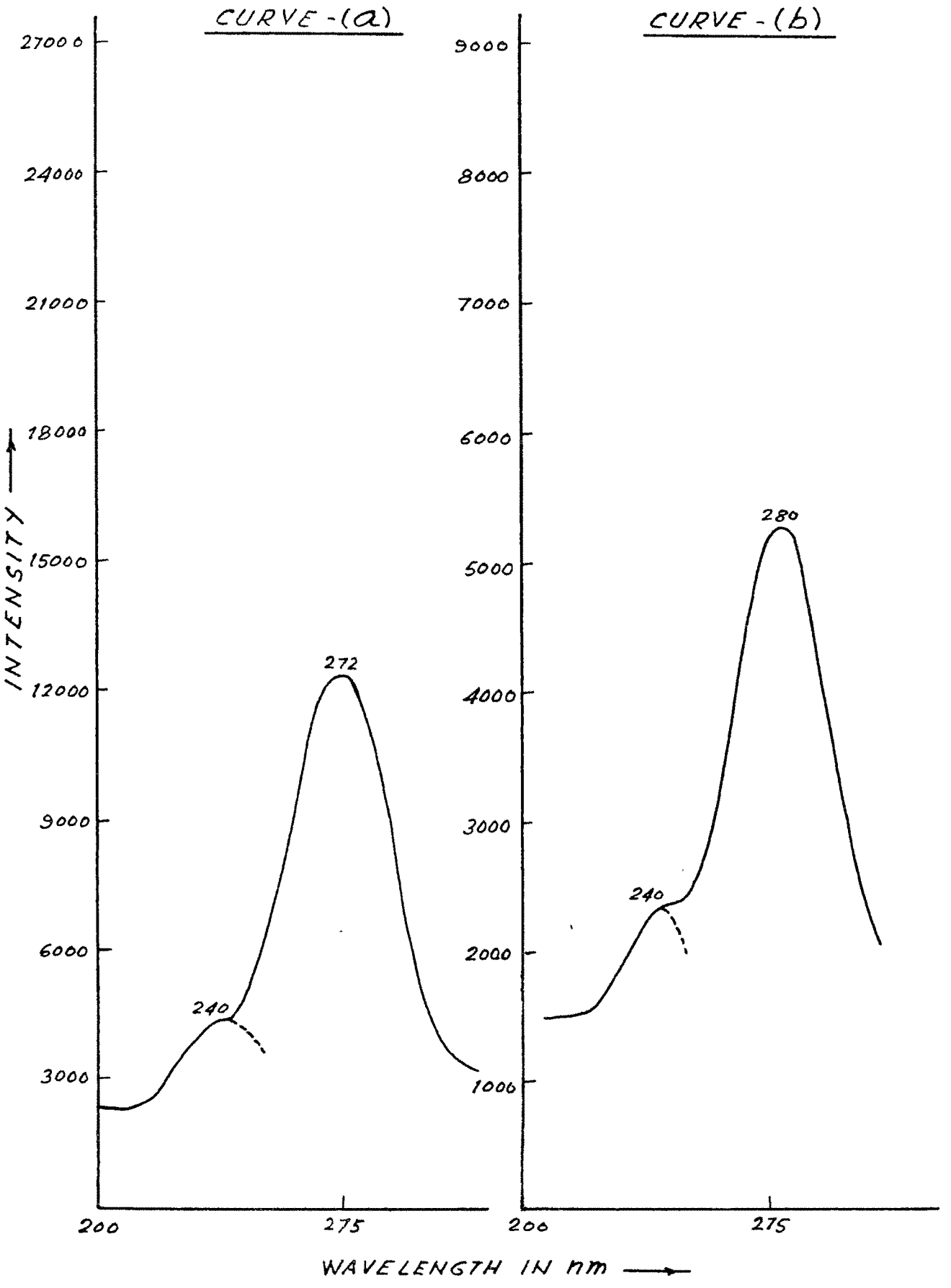

CURVE - (a)
CURVE - (b)
27000
24000
21000
18000
15000
12000
9000
6000
3000
9000
8000
7000
6000
5000
4000
3000
2000
1000
INTENSITY
272
240
280
240
200
275
200
275
WAVELENGTH IN nm

FIG 48

CURVE - (c)

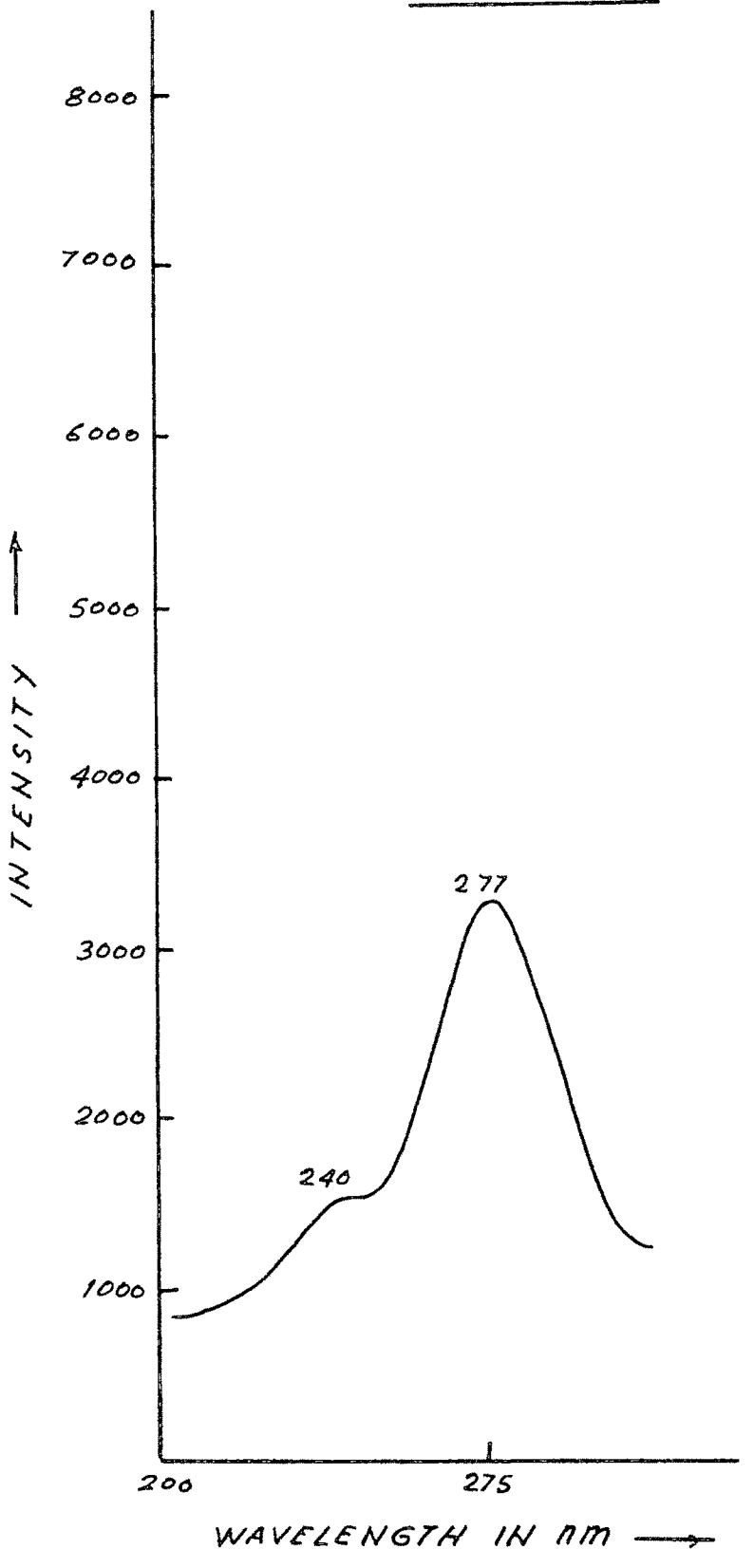


FIG. 48

Fig. 49 : Excitation spectra of NaCl:Tl melt and quenched specimen (powdered) for 450 nm emission (Curve : a), 480 nm emission (Curve : b) and 520 nm emission (Curve : c).

Tl concentration $\sim 10^{-2}$ m.f.

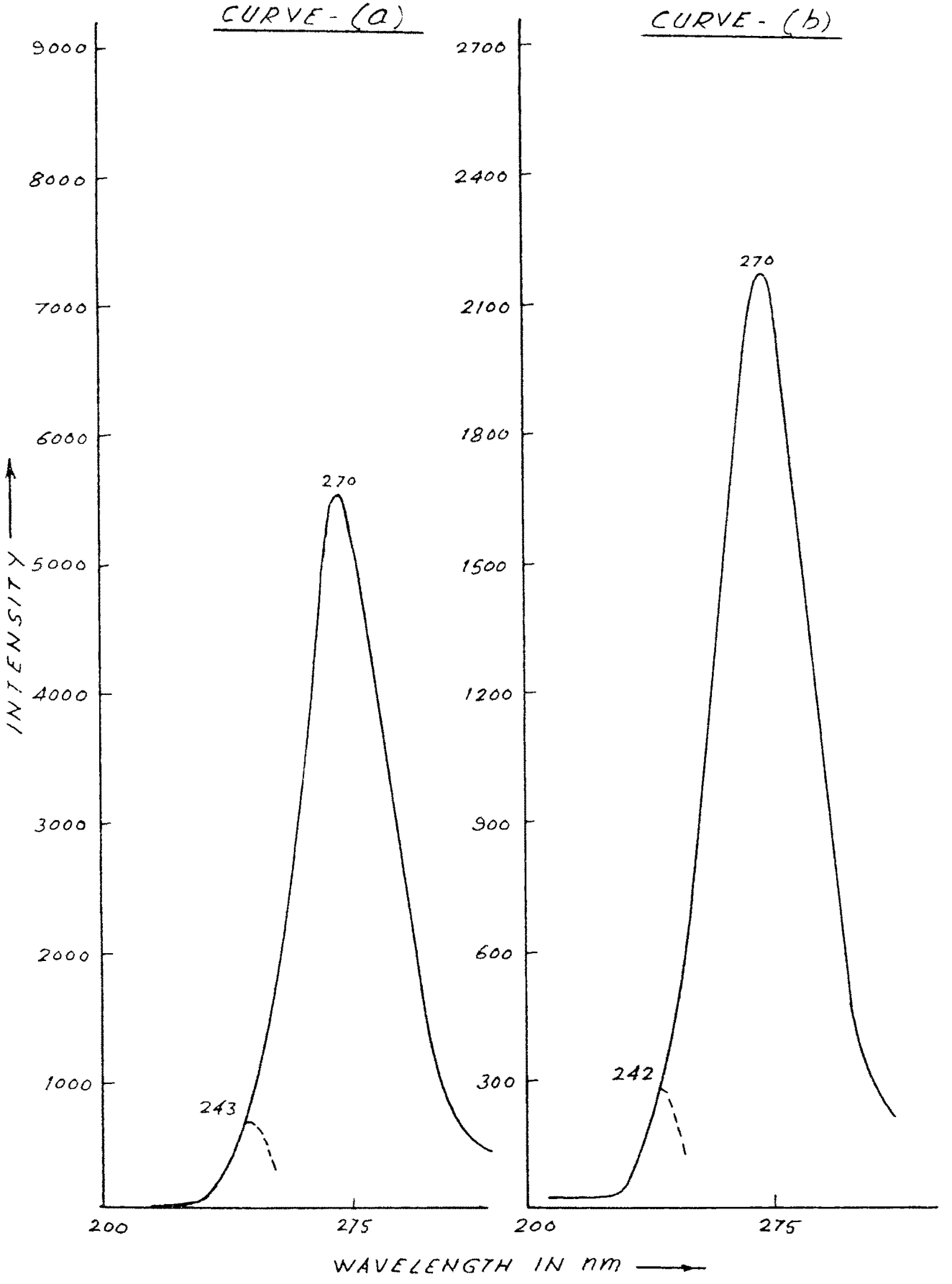

CURVE - (a)
CURVE - (b)
9000
8000
7000
6000
5000
4000
3000
2000
1000
2700
2400
2100
1800
1500
1200
900
600
300
270
270
243
242
INTENSITY
200
275
200
275
WAVELENGTH IN nm

FIG 49

CURVE- (C)

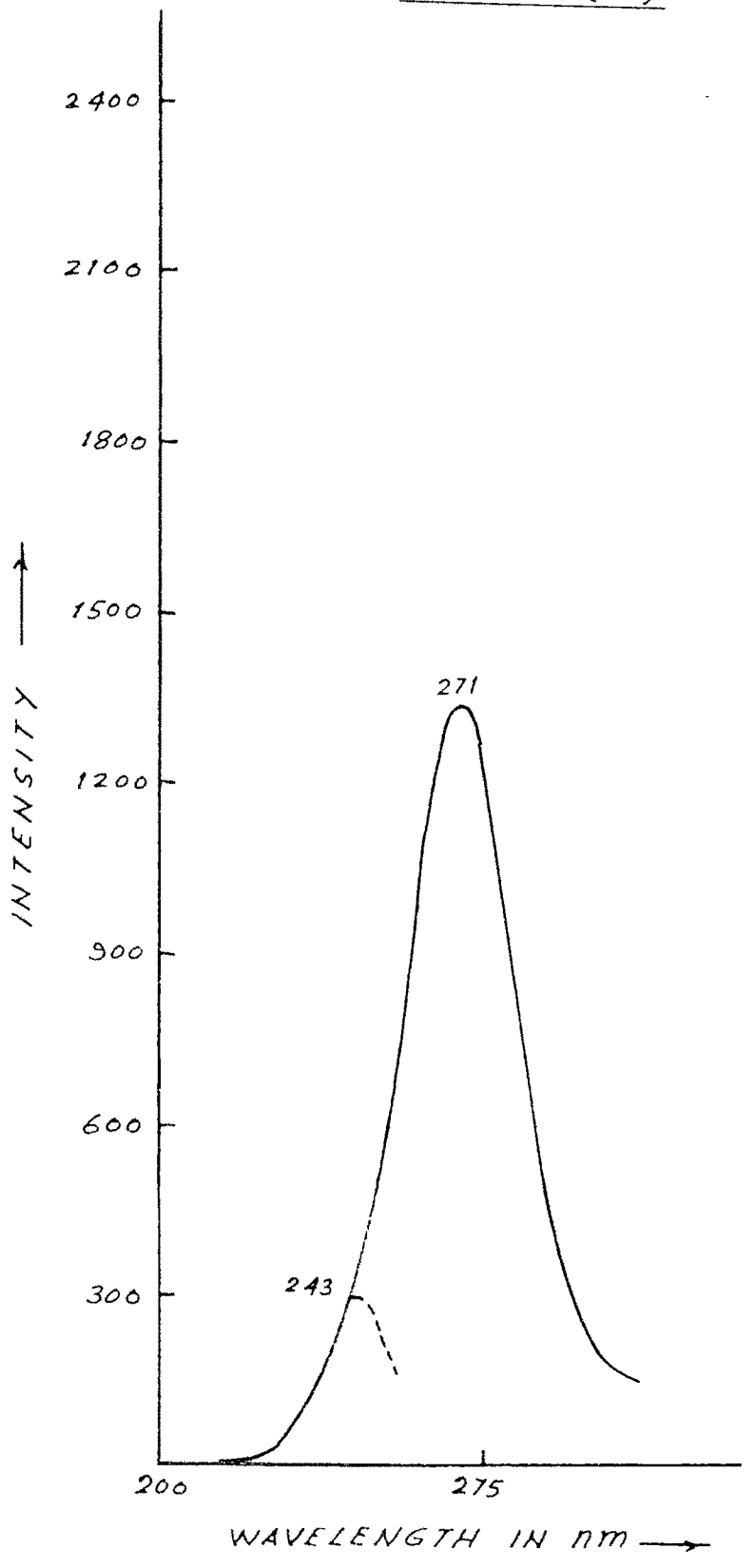


FIG 49

Fig. 50 : Excitation spectra of NaCl:Tl melt and quenched specimen (tabletted) for 450 nm emission (Curve : a) and 480 nm emission (Curve : b).

Tl concentration $\sim 10^{-2}$ m.f.

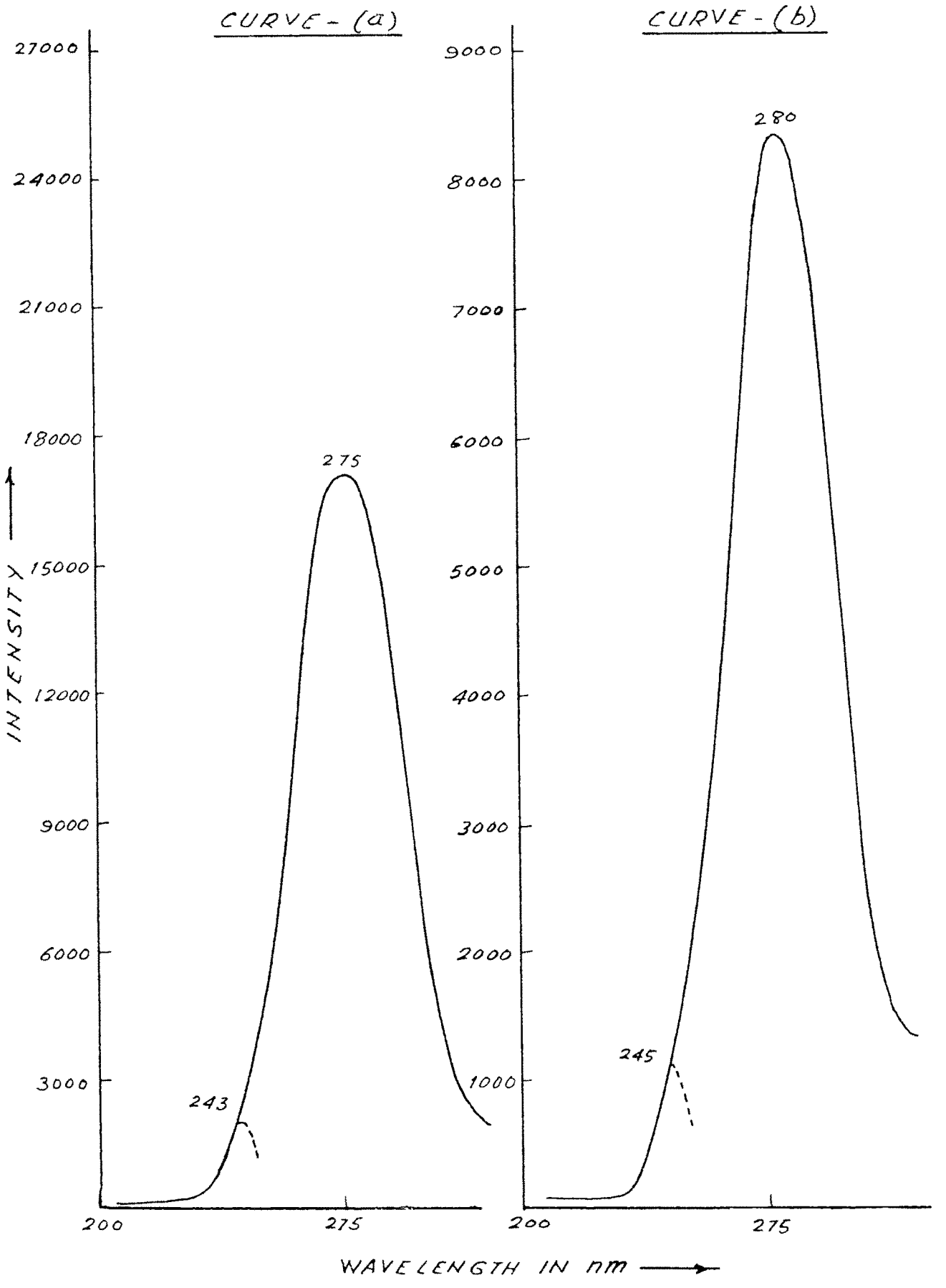

CURVE - (a)
CURVE - (b)
27000
24000
21000
18000
15000
12000
9000
6000
3000
9000
8000
7000
6000
5000
4000
3000
2000
1000
INTENSITY
275
280
243
245
200
275
200
275
WAVELENGTH IN nm

FIG 50

Fig. 51 : Excitation spectrum of TlCl powder (untreated) for 385 nm emission.

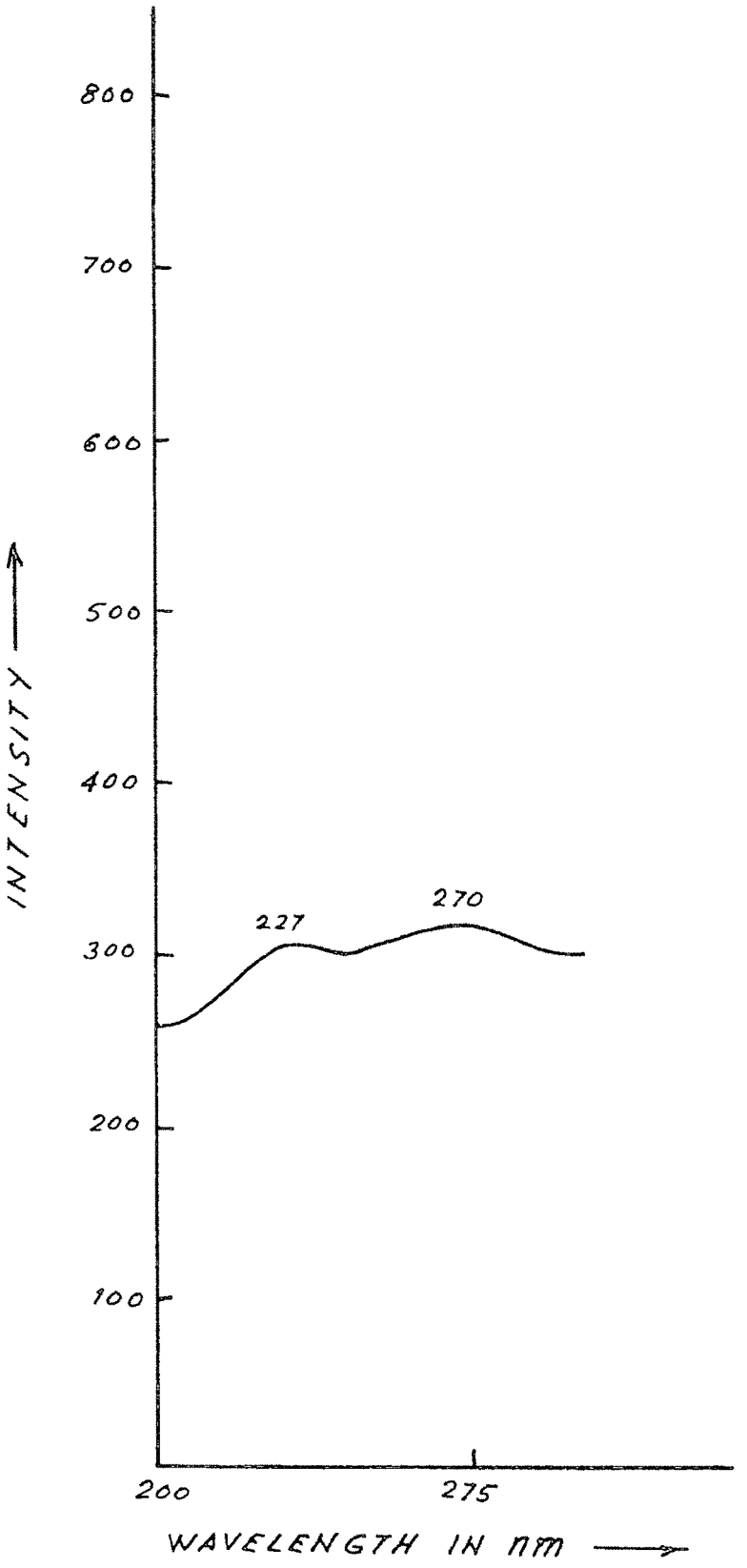

800
700
600
500
400
300
200
100
INTENSITY
227
270
200
275
WAVELENGTH IN nm

FIG. 51

Fig. 52 : Emission spectra of TlCl powder (untreated) upon excitation at 227 nm emission (Curve : 1), 260 nm emission (Curve : 2) and 270 nm emission (Curve : 3).

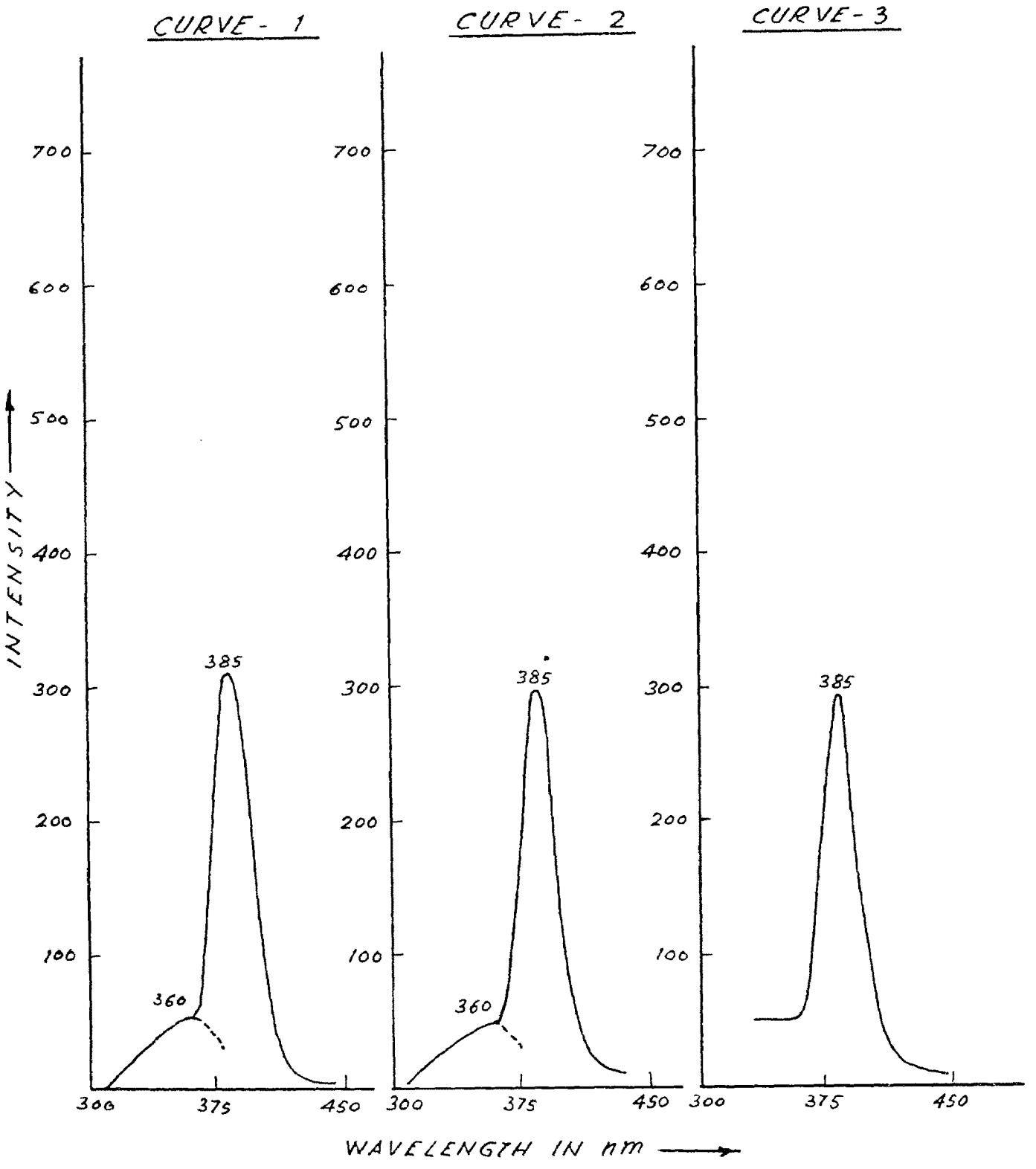

CURVE - 1
CURVE - 2
CURVE - 3
700
600
500
400
300
200
100
INTENSITY
385
360
300
375
450
WAVELENGTH IN mm

FIG. 52

Fig. 53 : Excitation spectrum of TlCl powder compressed to tablet, for 360 nm emission.

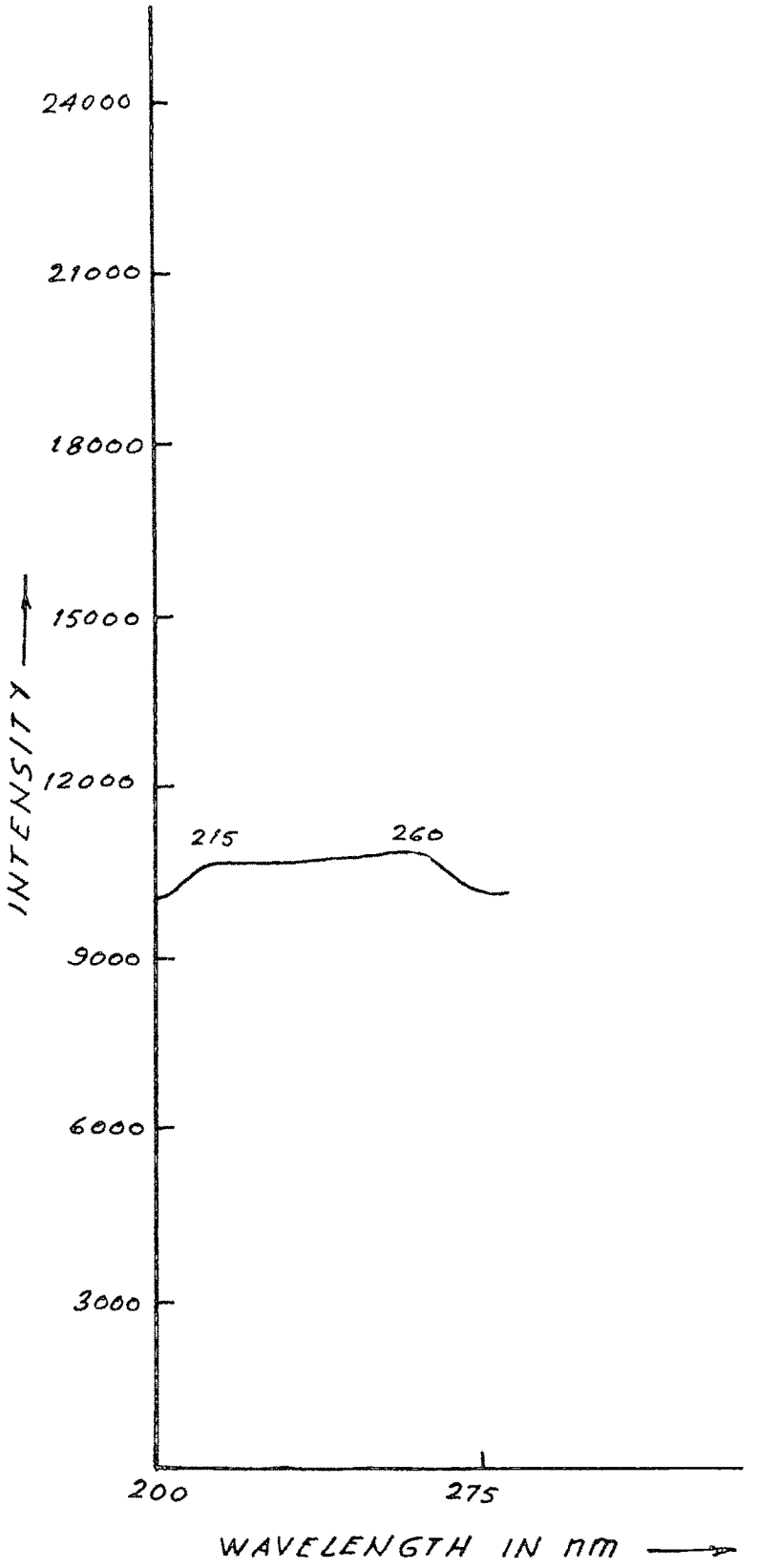

24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
215
260
200
275
WAVELENGTH IN nm

FIG. 53

Fig. 54 : Emission spectra of TlCl powder compressed to tablet upon excitation at 215 nm (Curve : 1) and 260 nm (Curve : 2).

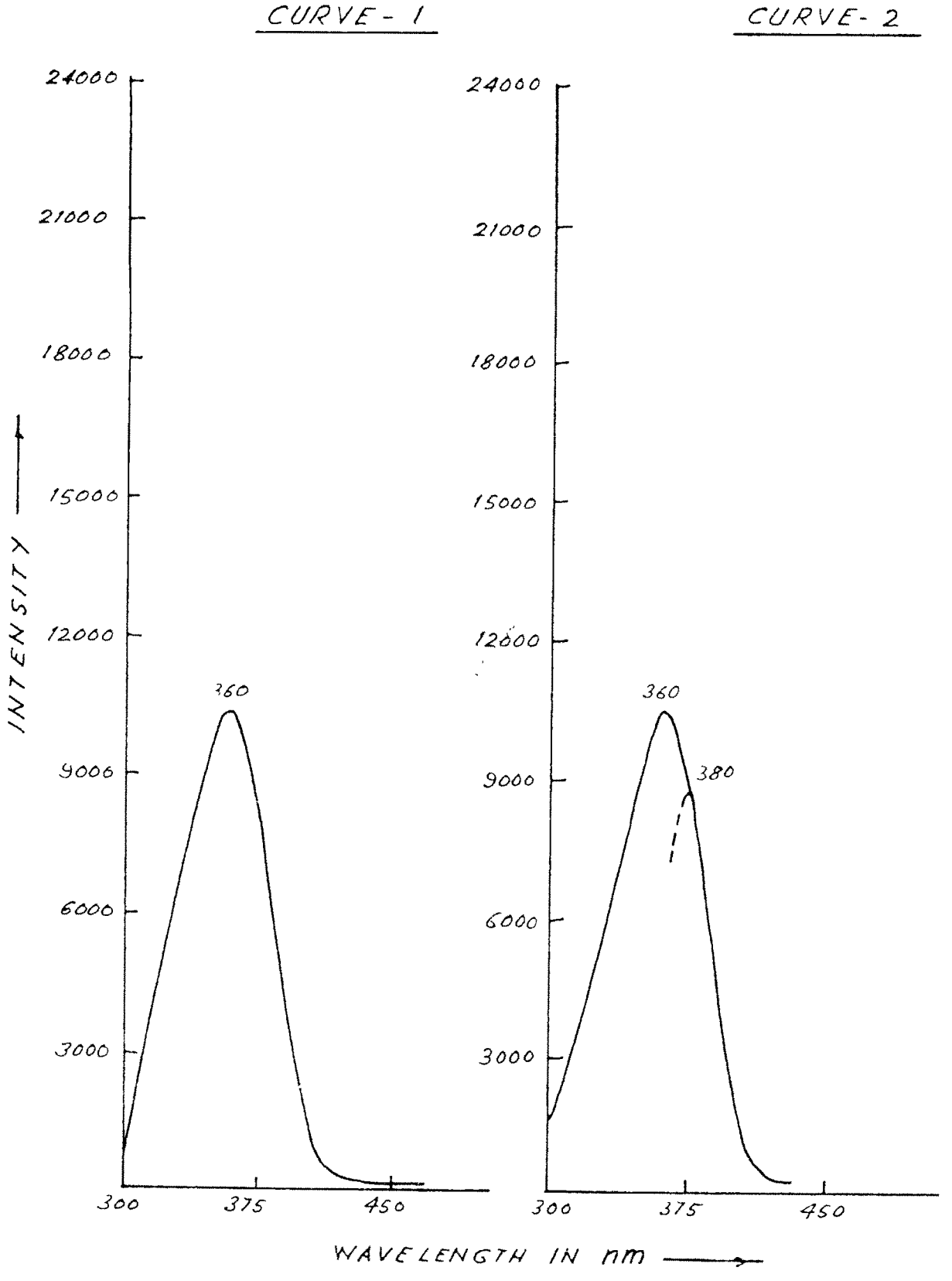

CURVE - 1
CURVE - 2
24000
21000
18000
15000
12000
9000
6000
3000
INTENSITY
360
380
300
375
450
WAVELENGTH IN nm

FIG 54

Fig. 55 : Excitation of aqueous TlCl-solution as a function of TlCl concentration.

Curve : 1 - Saturated TlCl-solution

Curve : 2 - Dilution of the saturated TlCl-solution with water in the proportion of ... 1:1

Curve : 3 - " " " ... 1:2

Curve : 4 - " " " ... 1:3

Curve : 5 - " " " ... 1:5

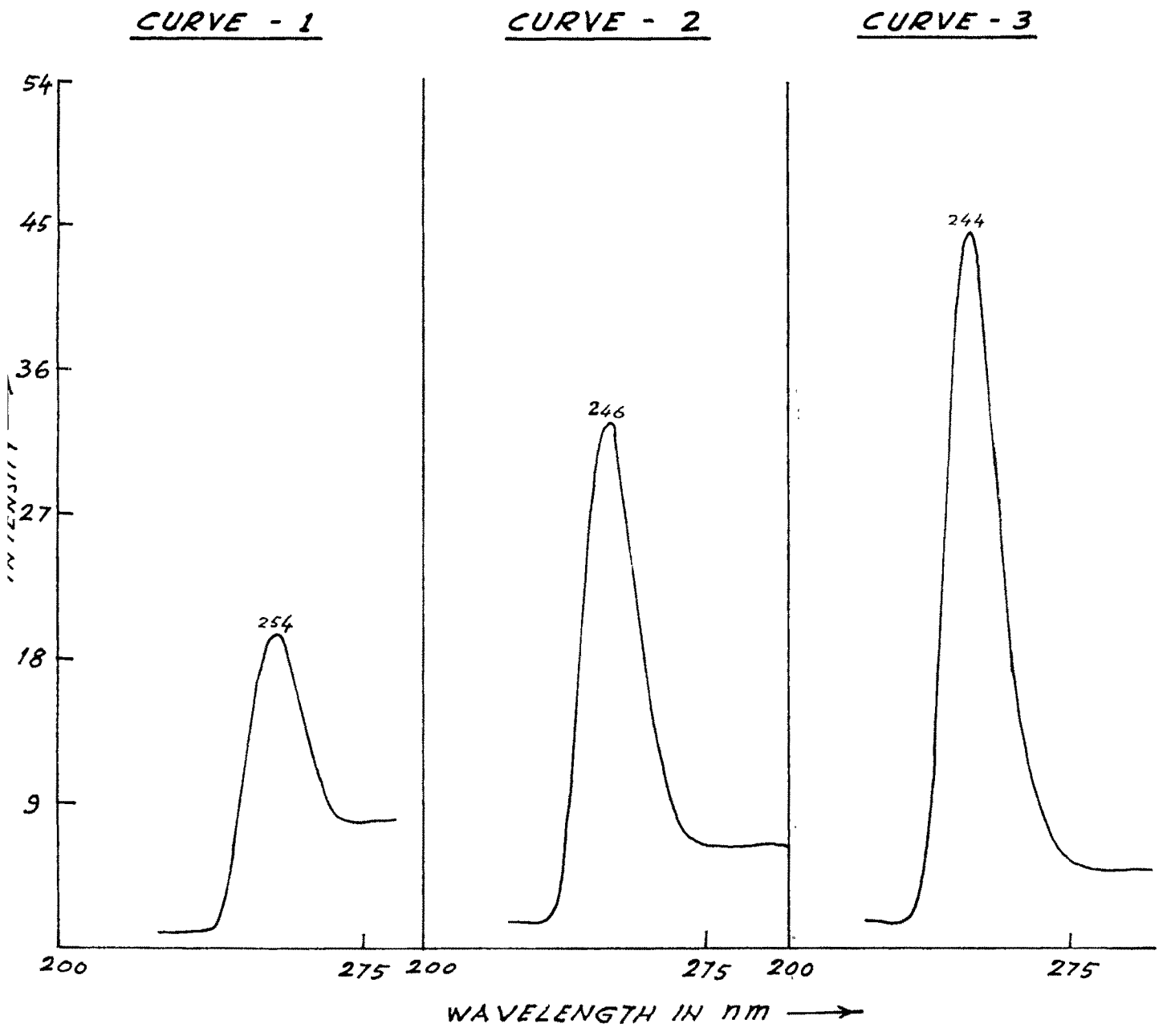

CURVE - 1
CURVE - 2
CURVE - 3
54
45
36
27
18
9
INTENSITY
254
246
244
200
275
200
275
200
275
WAVELENGTH IN nm

FIG. 55

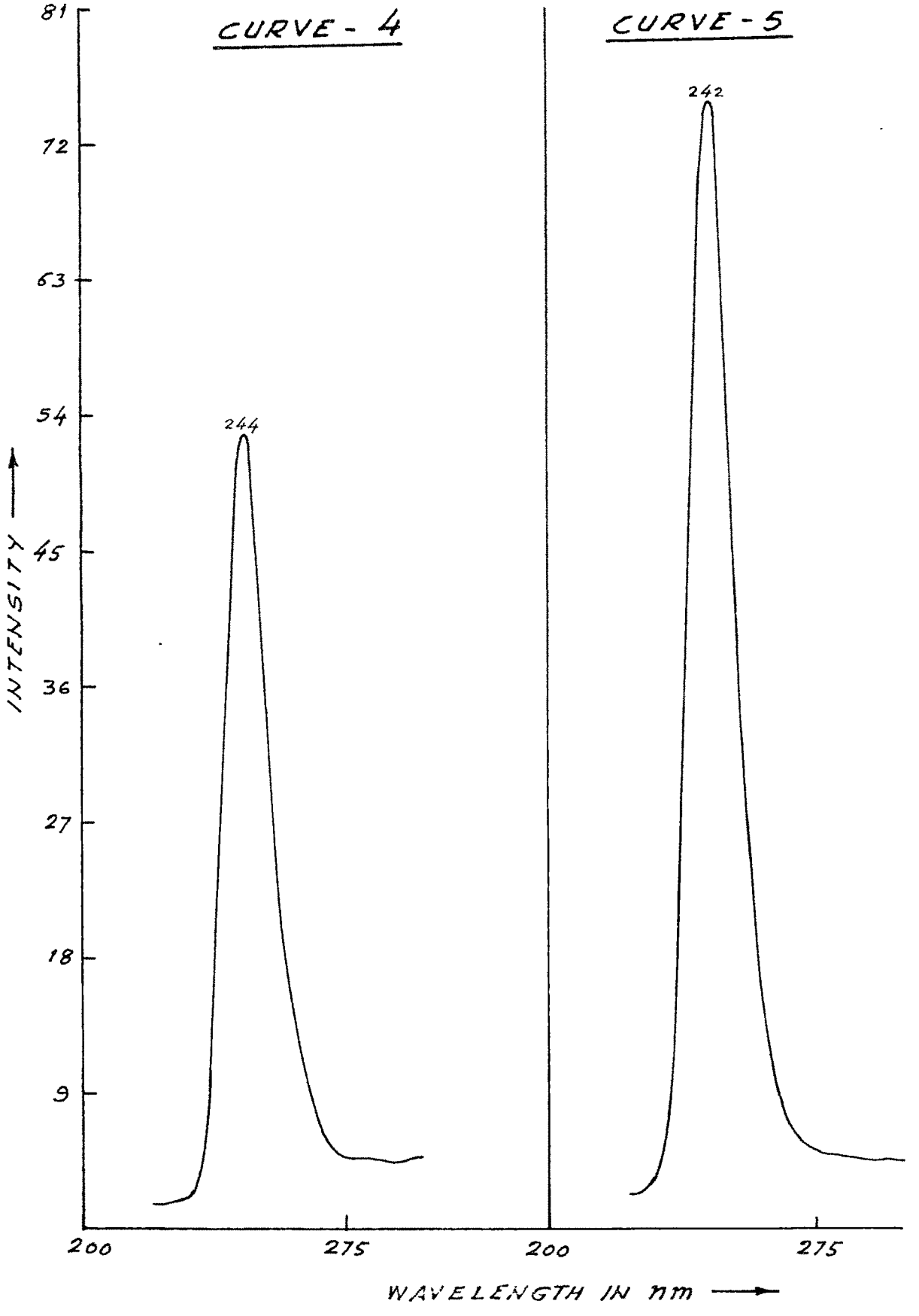

CURVE - 4
CURVE - 5
244
242
81
72
63
54
45
36
27
18
9
INTENSITY
200
275
200
275
WAVELENGTH IN nm

FIG. 55

Fig. 56 : Fluorescence intensity of aqueous TlCl-solution at various TlCl concentration.

Curve : 1 - Saturated TlCl solution
Curve : 2 - Dilution of the saturated TlCl-solution with water in the proportion of ... 1:1
Curve : 3 - " " " ... 1:2
Curve : 4 - " " " ... 1:3
Curve : 5 - " " " ... 1:5

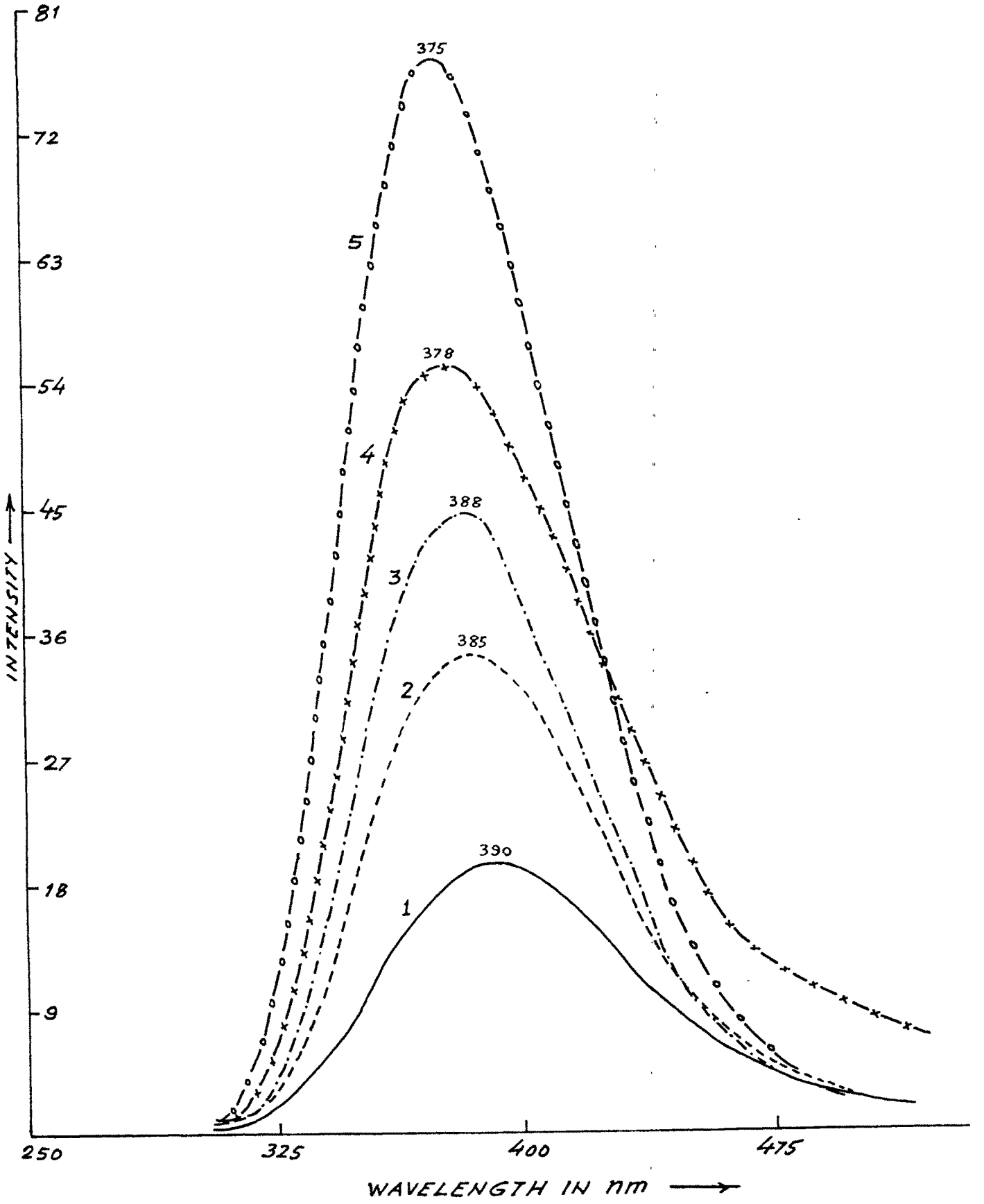

81
72
63
54
45
36
27
18
9
INTENSITY
375
378
388
385
390
5
4
3
2
1
250
325
400
475
WAVELENGTH IN nm

FIG. 56

Fig. 57 : Excitation of aqueous TlCl-solution as a function of TlCl concentration.

Curve : 1 - Dilution of the saturated TlCl-solution with water in the proportion of ... 1:10

Curve : 2 - " " " ... 1:20

Curve : 3 - " " " ... 1:30

Curve : 4 - " " " ... 1:40

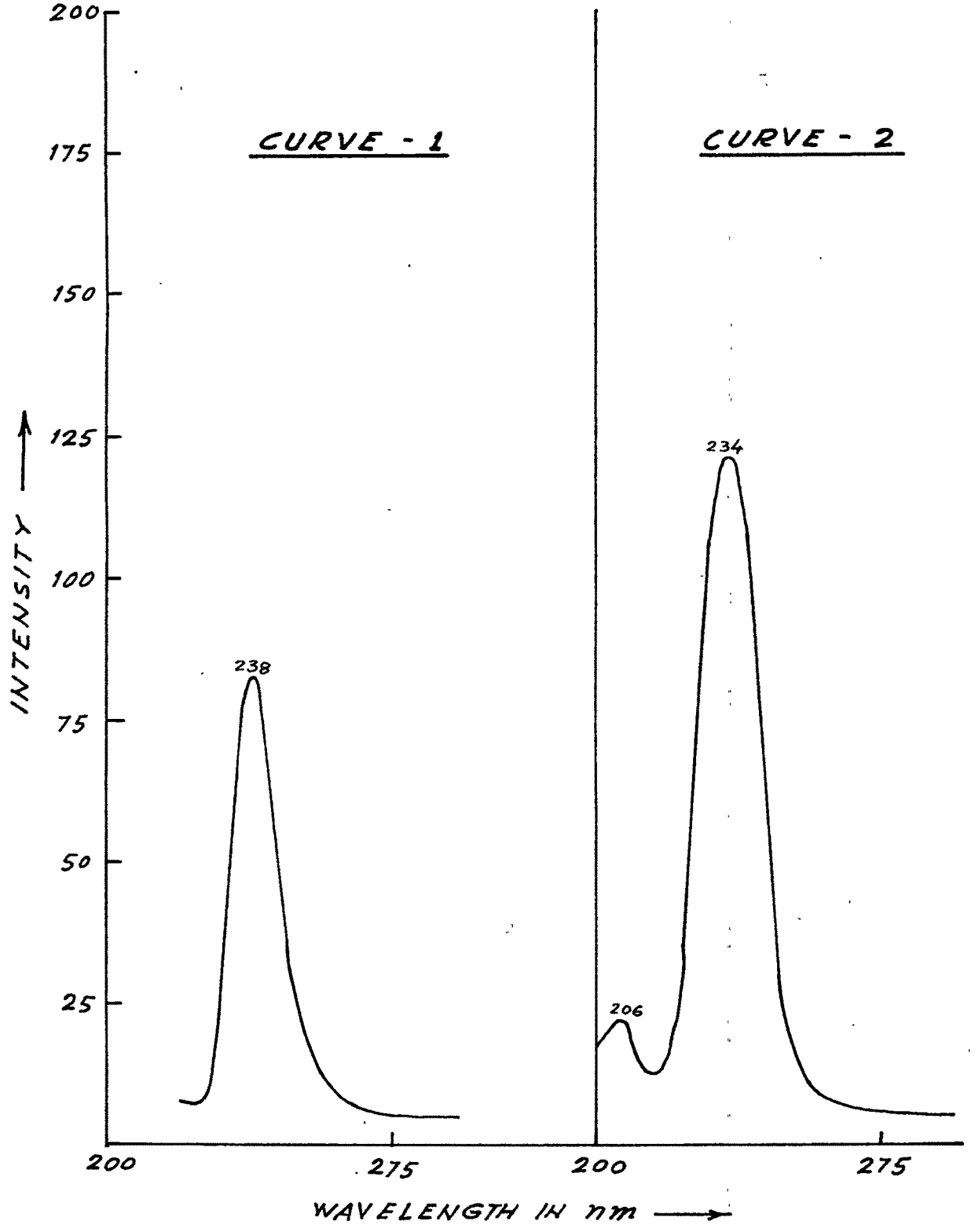

200
175
150
125
100
75
50
25
INTENSITY
CURVE - 1
CURVE - 2
238
234
206
200
275
200
275
WAVELENGTH IN nm

FIG. 57

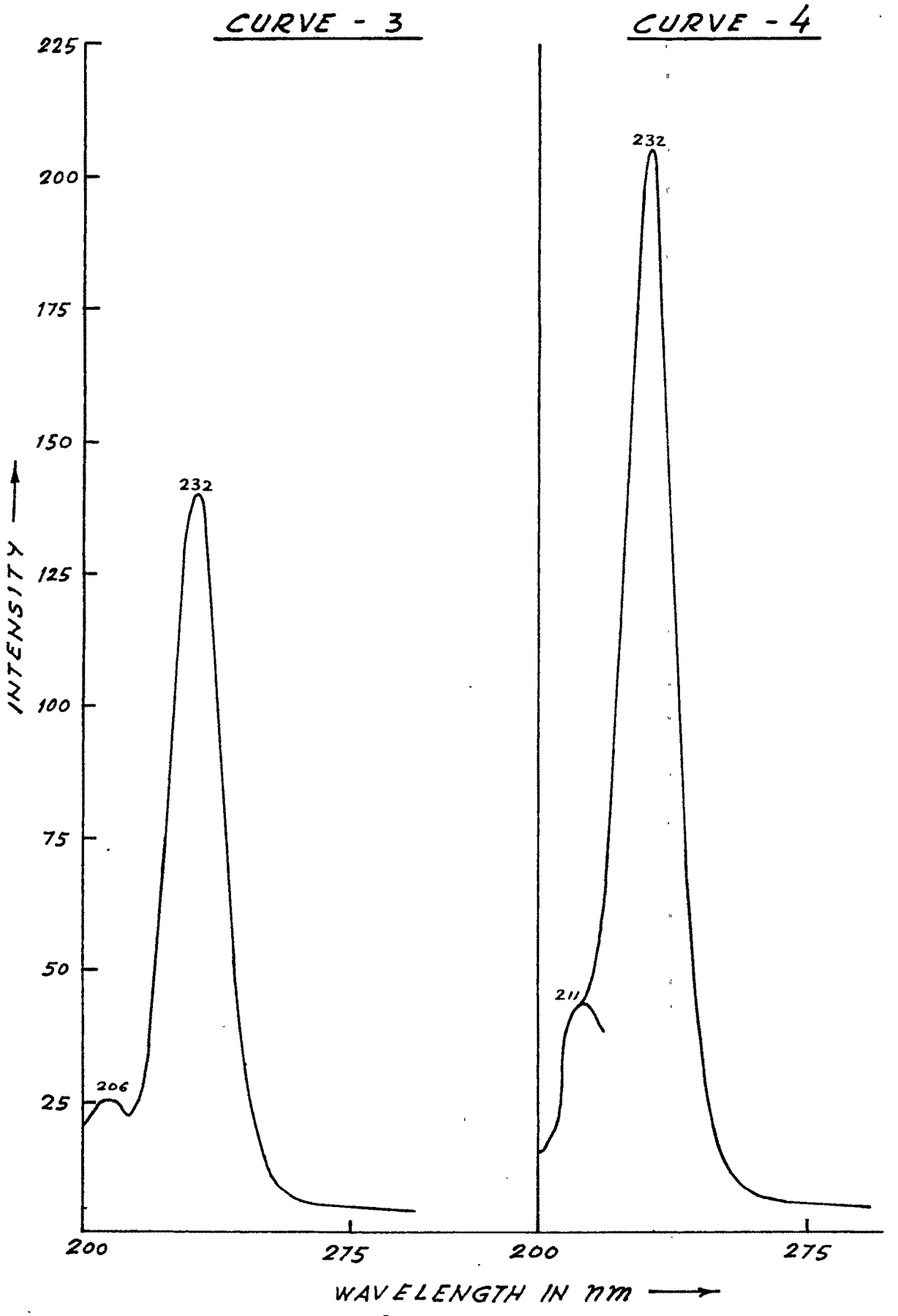

CURVE - 3
CURVE - 4
225
200
175
150
125
100
75
50
25
INTENSITY
232
206
232
211
200
275
200
275
WAVELENGTH IN nm

FIG. 57

Fig. 58 : Fluorescence intensity of aqueous TlCl-solution at various TlCl concentration.

Curve : 1 - Dilution of the saturated TlCl-solution with water in the proportion of ... 1:10

Curve : 2 - " " " ... 1:20

Curve : 3 - " " " ... 1:30

Curve : 4 - " " " ... 1:40

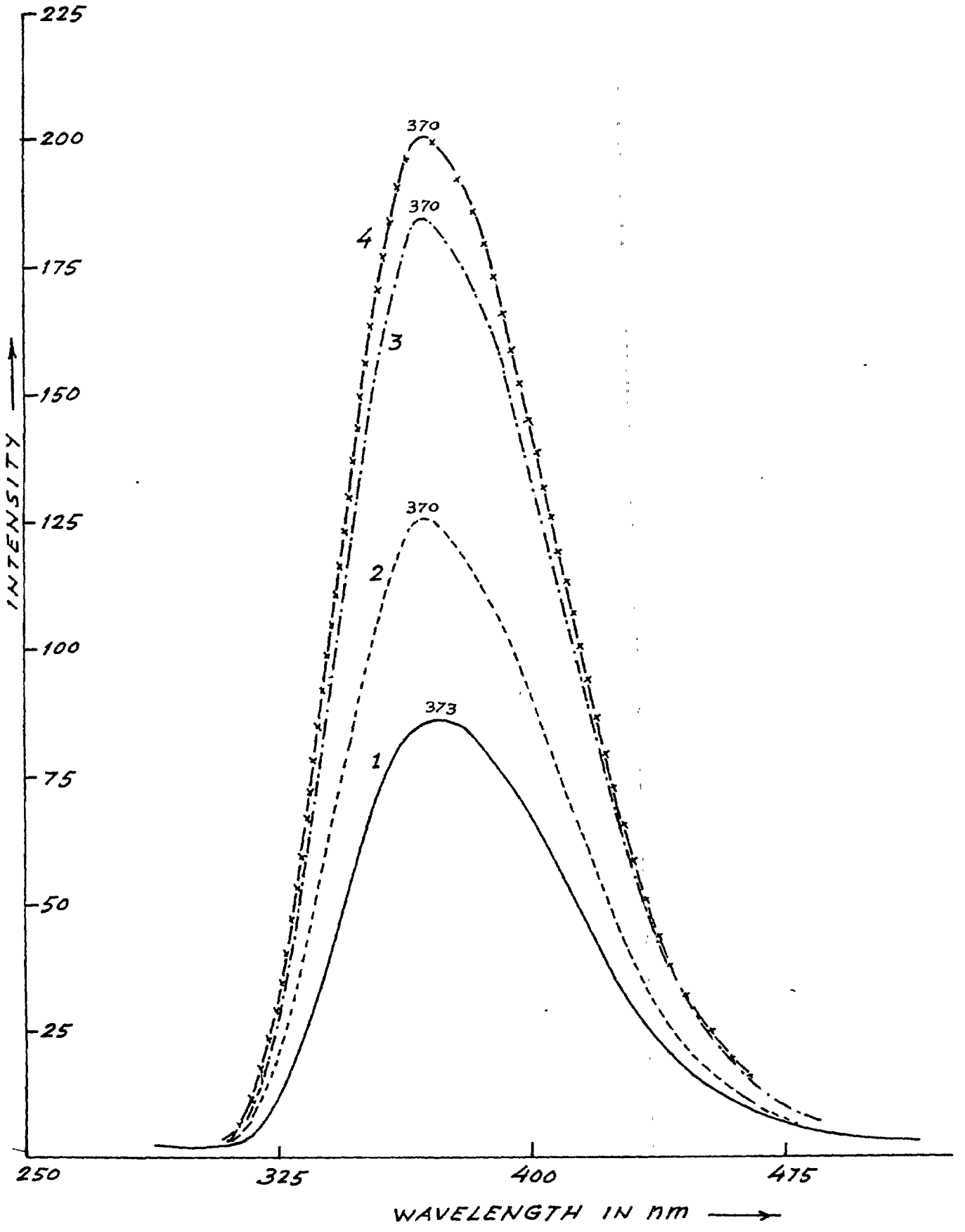

225
200
175
150
125
100
75
50
25
INTENSITY
370
370
370
373
4
3
2
1
250
325
400
475
WAVELENGTH IN mm

FIG. 58

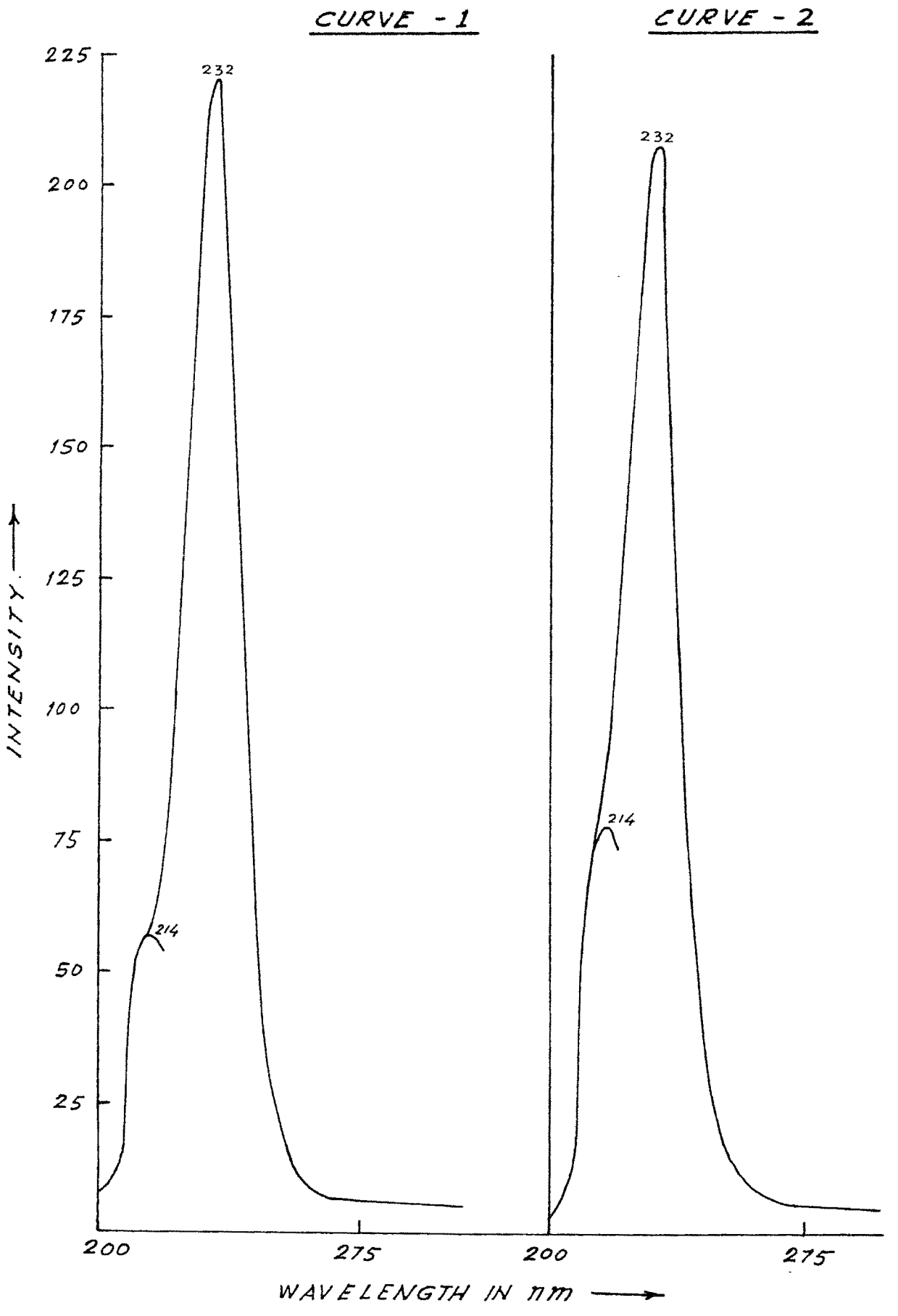
Fig. 59 : Excitation of aqueous TlCl-solution as a function of TlCl concentration.

Curve : 1 - Dilution of the saturated TlCl-solution with water in the proportion of ... 1:50

Curve : 2 - " " " ... 1:70

Curve : 3 - " " " ... 1:90

Curve : 4 - " " " ... 1:600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CURVE - 2
225
200
175
150
125
100
75
50
25
INTENSITY
232
232
214
214
200
275
200
275
WAVELENGTH IN nm

FIG. 59

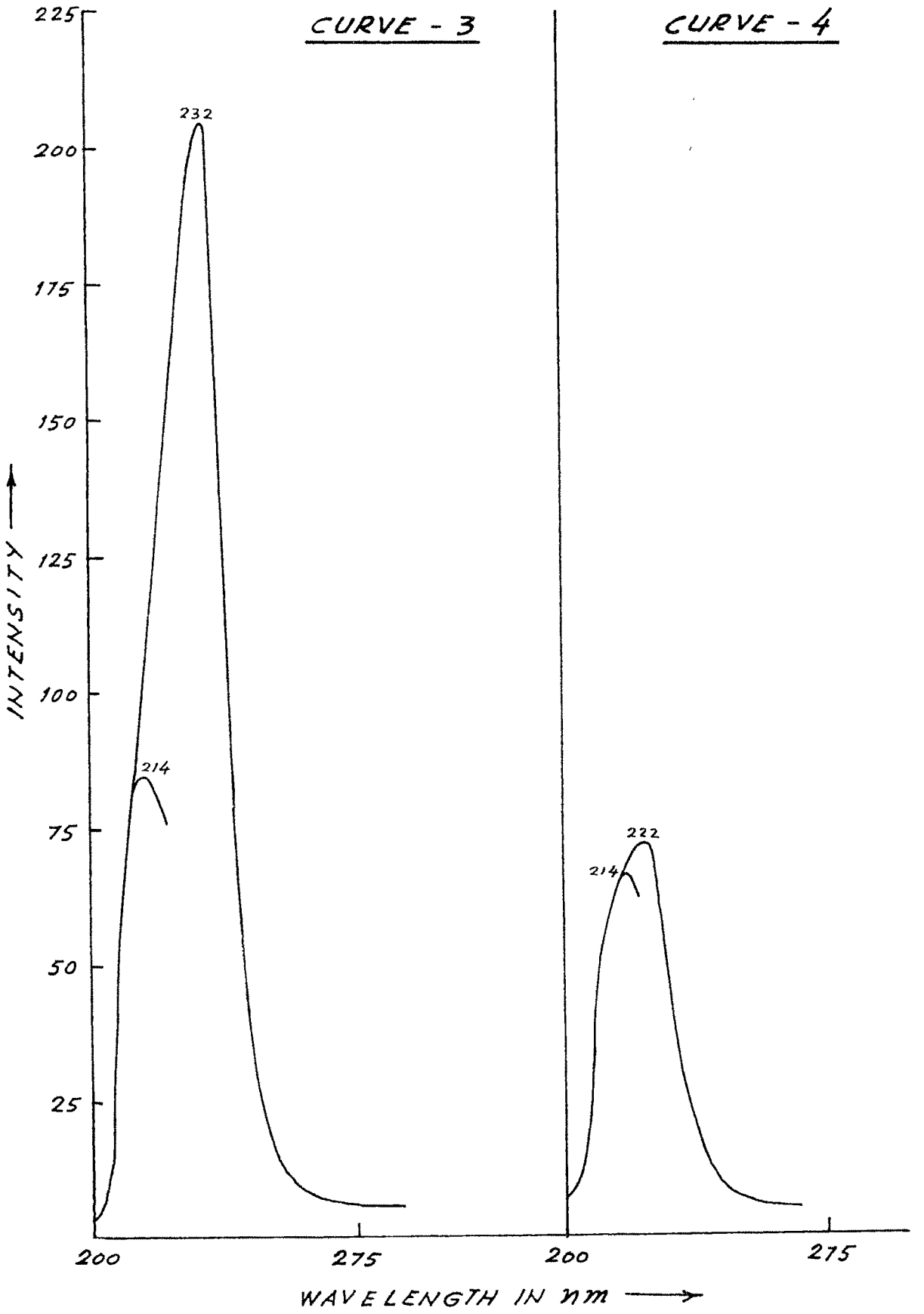
CURVE - 3
CURVE - 4
225
200
175
150
125
100
75
50
25
INTENSITY
232
214
222
214
200
275
200
275
WAVELENGTH IN nm

FIG. 59

Fig. 60 : Fluorescence intensity of aqueous TlCl-solution at various TlCl concentration.

Curve : 1 - Dilution of the saturated TlCl-solution with water in the proportion of ... 1:50

Curve : 2 - " " " ... 1:70

Curve : 3 - " " " ... 1:90

Curve : 4 - " " " ... 1:600

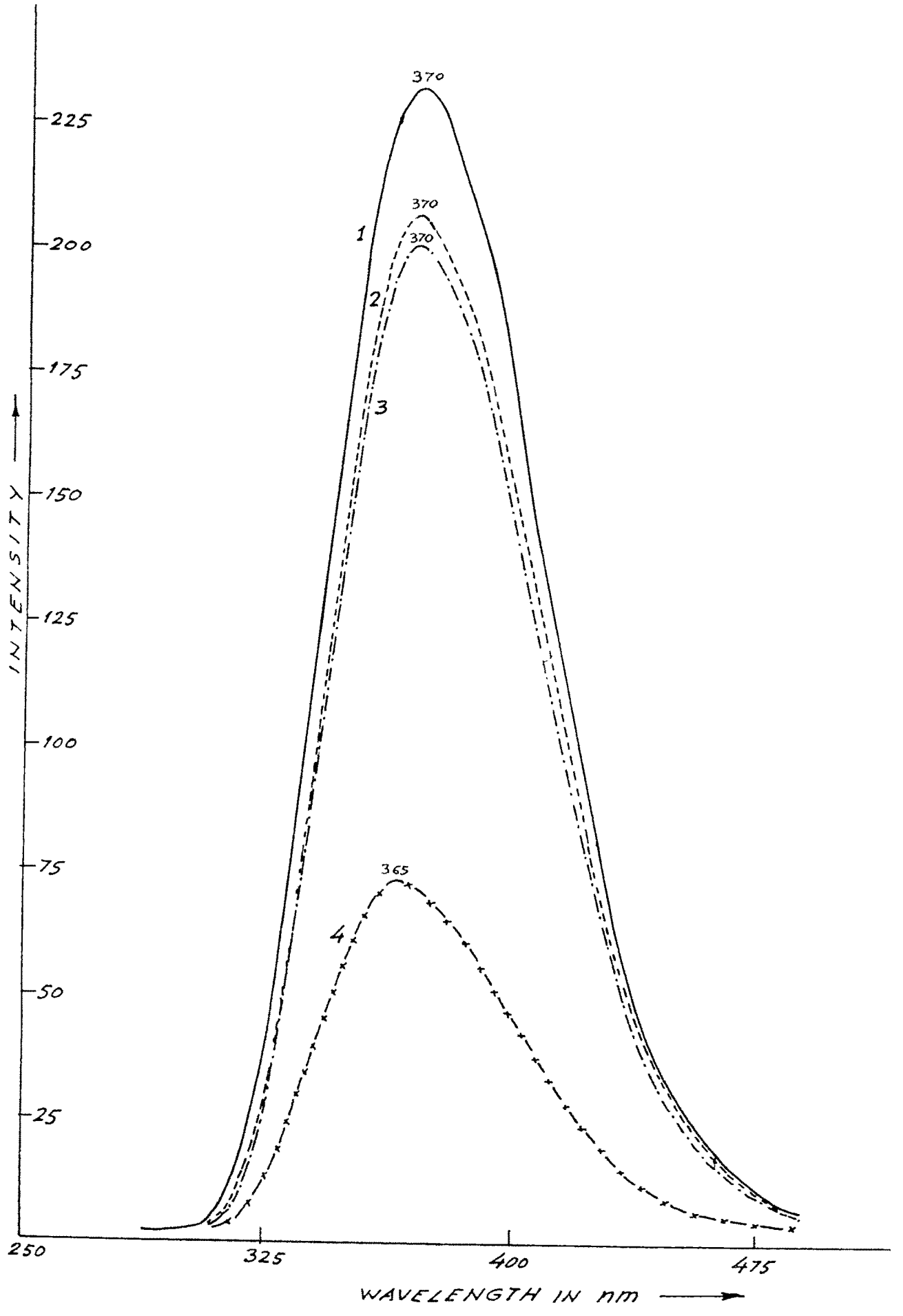
370
370
370
365
1
2
3
4
225
200
175
150
125
100
75
50
25
INTENSITY
250
325
400
475
WAVELENGTH IN nm

FIG. 60

Fig. 61 : Excitation spectra of aqueous saturated NaCl-solution with varying concentrations of TlCl for 425 nm emission.

Curve : 1 - 1.0 mg of TlCl in 20 c.c. of saturated NaCl solution.

Curve : 2 - 3.0 mg " " "

Curve : 3 - 5.0 mg " " "

Curve : 4 - 7.0 mg " " "

Curve : 5 - 9.0 mg " " "

Curve : 6 - 10.0 mg " " "

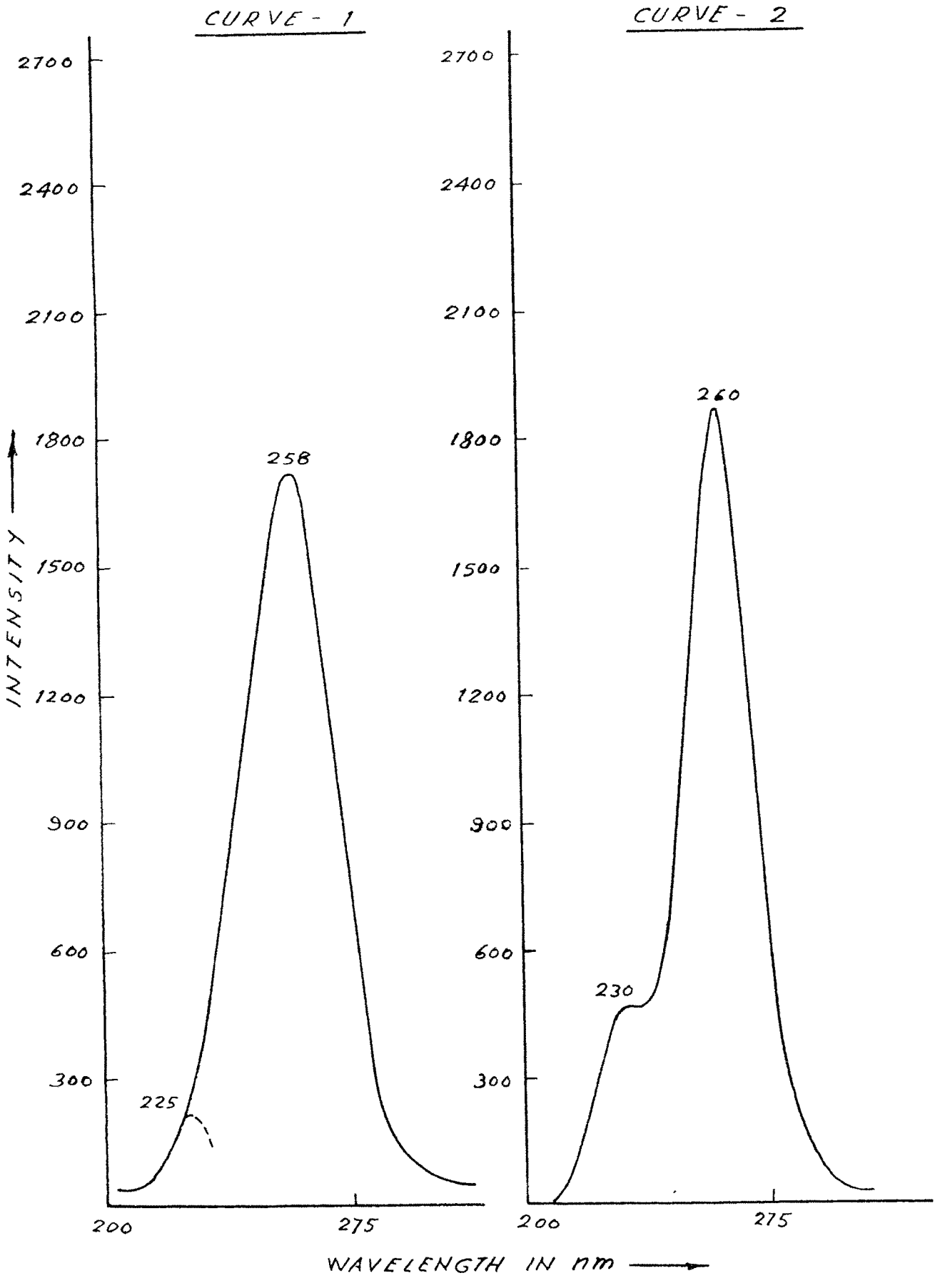
CURVE - 1
CURVE - 2
2700
2400
2100
1800
1500
1200
900
600
300
INTENSITY
258
225
260
230
200
275
200
275
WAVELENGTH IN nm

FIG 61

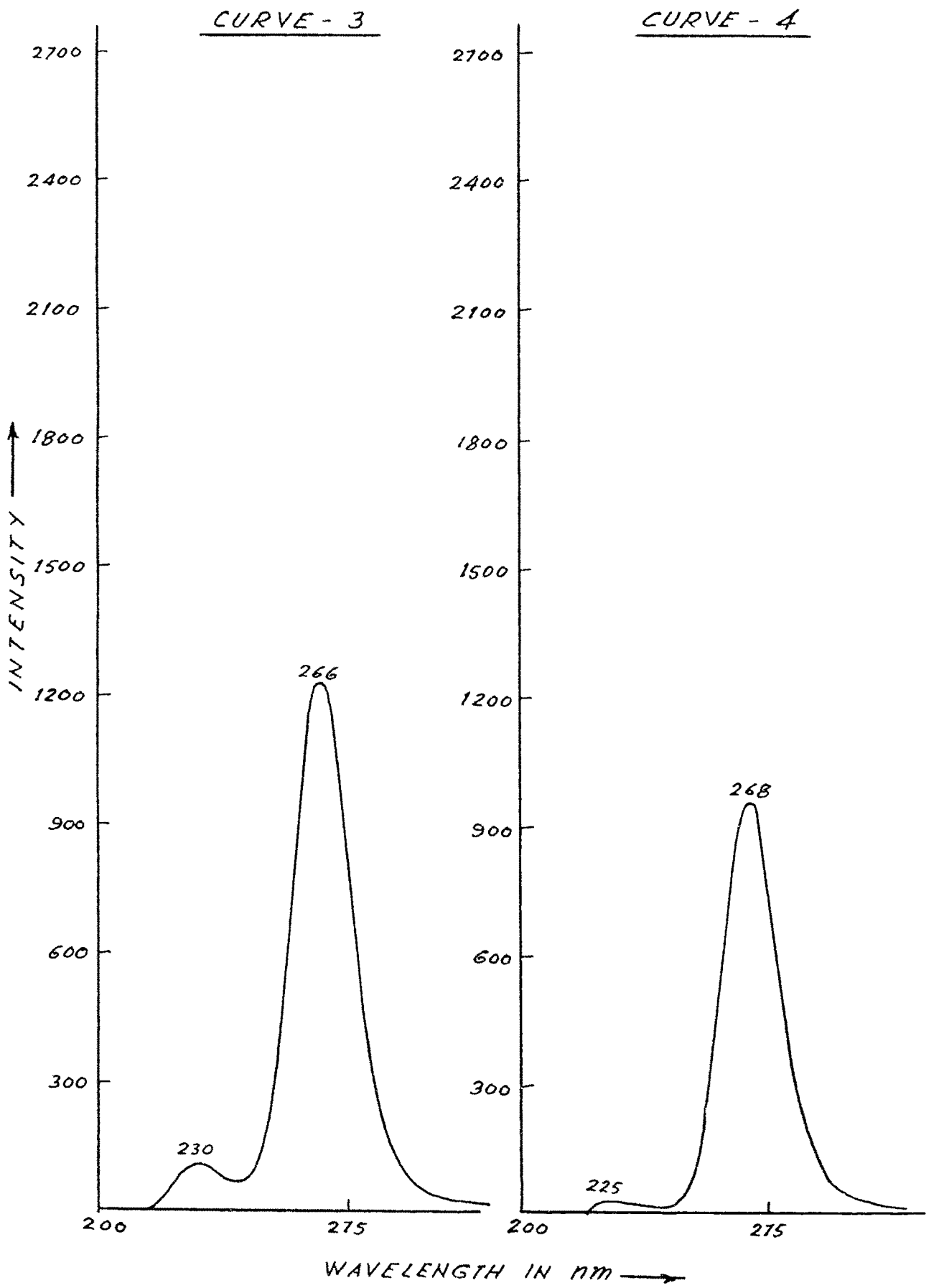
CURVE - 3
CURVE - 4
2700
2400
2100
1800
1500
1200
900
600
300
INTENSITY
266
230
268
225
200
275
WAVELENGTH IN mm

FIG. 61

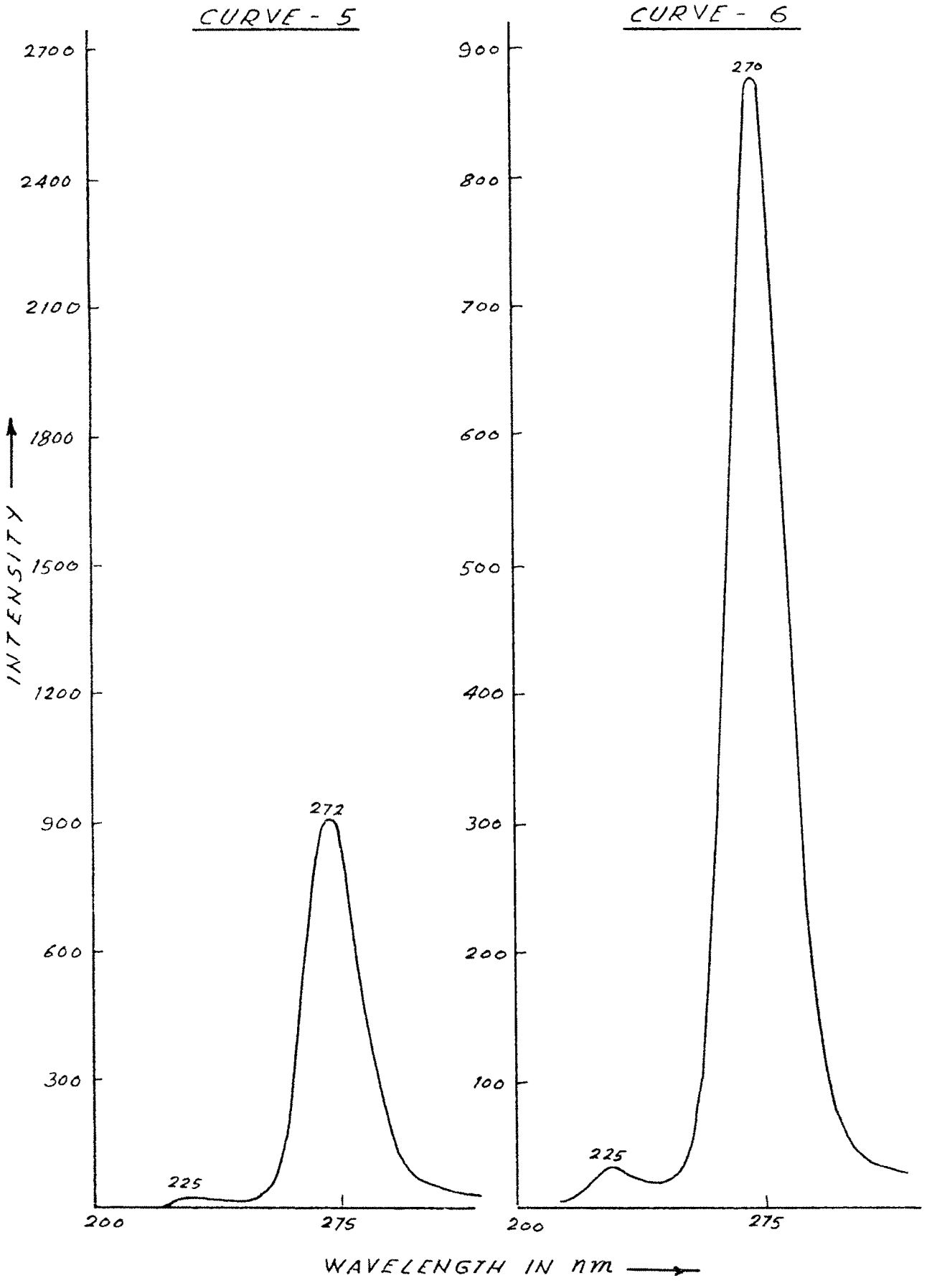
CURVE - 5
CURVE - 6
2700
2400
2100
1800
1500
1200
900
600
300
900
800
700
600
500
400
300
200
100
INTENSITY
272
270
225
225
200
275
200
275
WAVELENGTH IN nm

FIG. 61

Fig. 62 : Emission spectra of saturated NaCl solution with varying concentrations of TlCl upon excitation (higher intensity) at appropriate wavelengths as observed from curves in Fig. 61.

Curve : 1 - 1.0 mg of TlCl in 20 c.c. of saturated NaCl solution; Excitation at 258 nm.

Curve : 2 - 3.0 mg " " " " at 260 nm

Curve : 3 - 5.0 mg " " " " at 266 nm

Curve : 4 - 7.0 mg " " " " at 268 nm

Curve : 5 - 9.0 mg " " " " at 272 nm

Curve : 6 - 10.0 mg " " " " at 270 nm

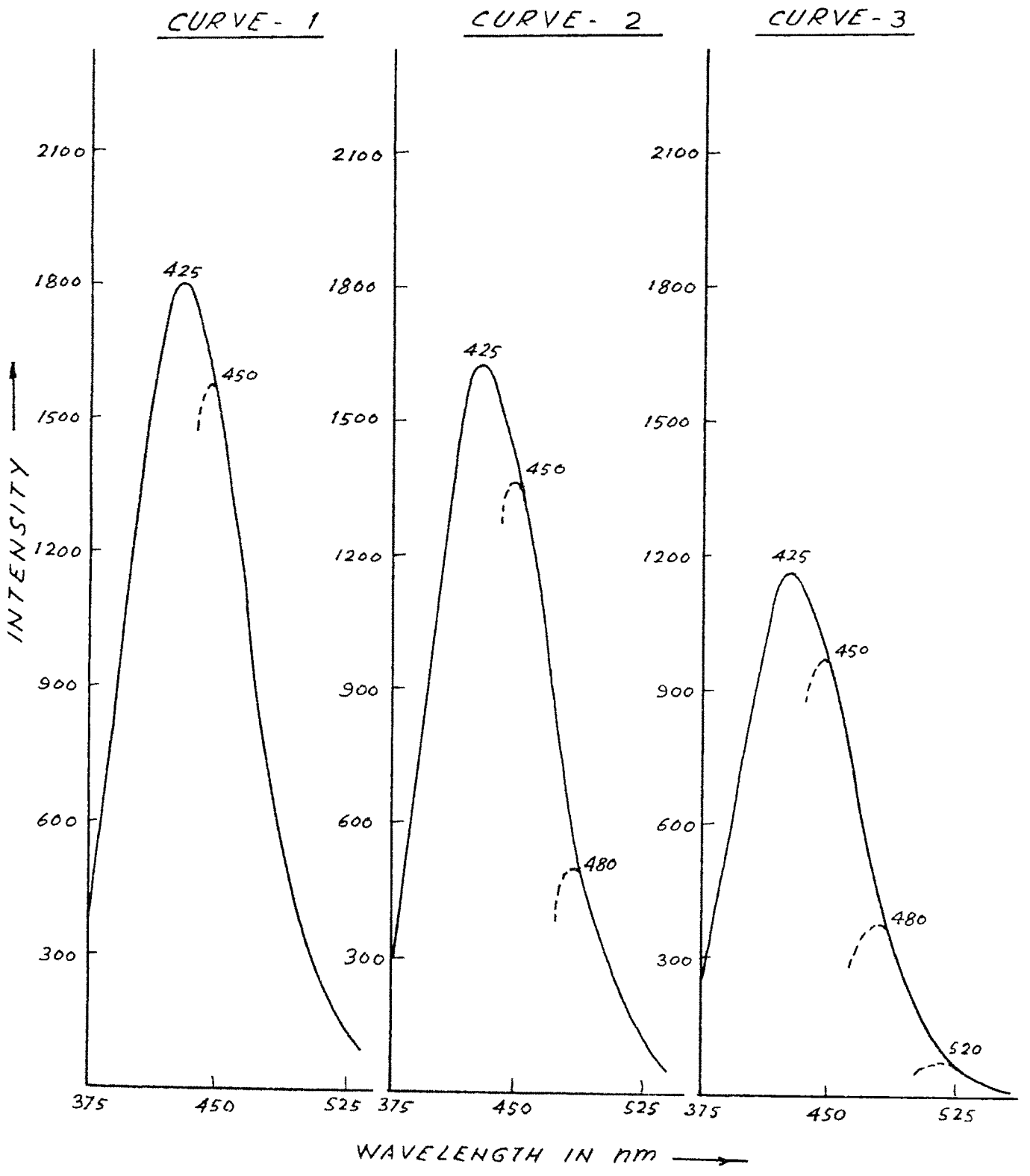
CURVE - 1
CURVE - 2
CURVE - 3
INTENSITY
2100
1800
1500
1200
900
600
300
425
450
480
520
375
450
525
WAVELENGTH IN nm

FIG. 62

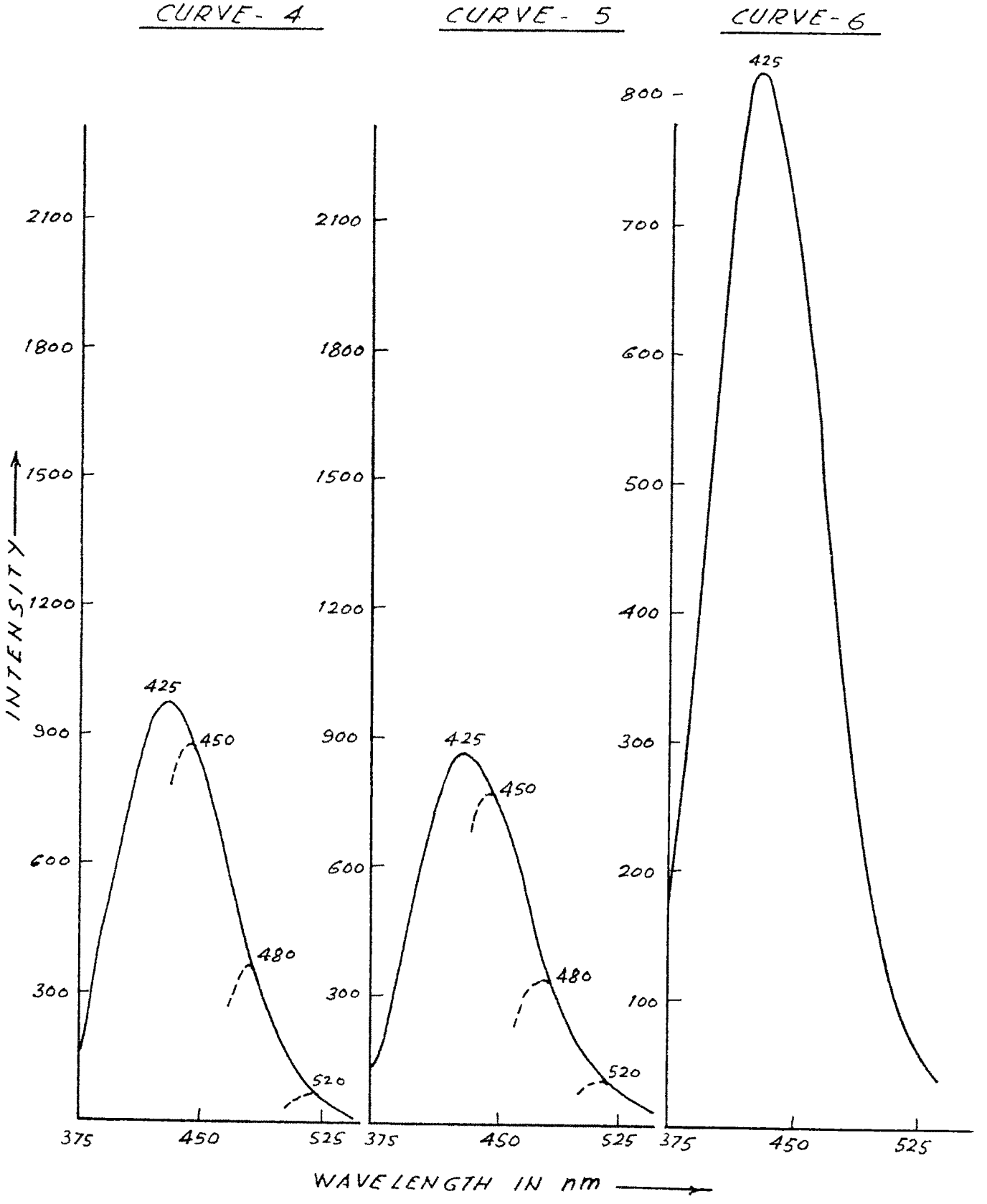
CURVE- 4
CURVE- 5
CURVE- 6
INTENSITY
2100
1800
1500
1200
900
600
300
800
700
600
500
400
300
200
100
425
450
480
520
375
450
525
WAVELENGTH IN nm

FIG. 62

Fig. 63 : Emission spectra of saturated NaCl-solution with varying quantities of TlCl upon excitation (lower intensity) at appropriate wavelengths observed from curves in Fig. 61.

Curve : 1 - 3.0 mg of TlCl in 20 c.c. of saturated NaCl solution.
Curve : 2 - 5.0 mg " "
Curve : 3 - 7.0 mg " "
Curve : 4 - 9.0 mg " "
Curve : 5 - 10.0 mg " "

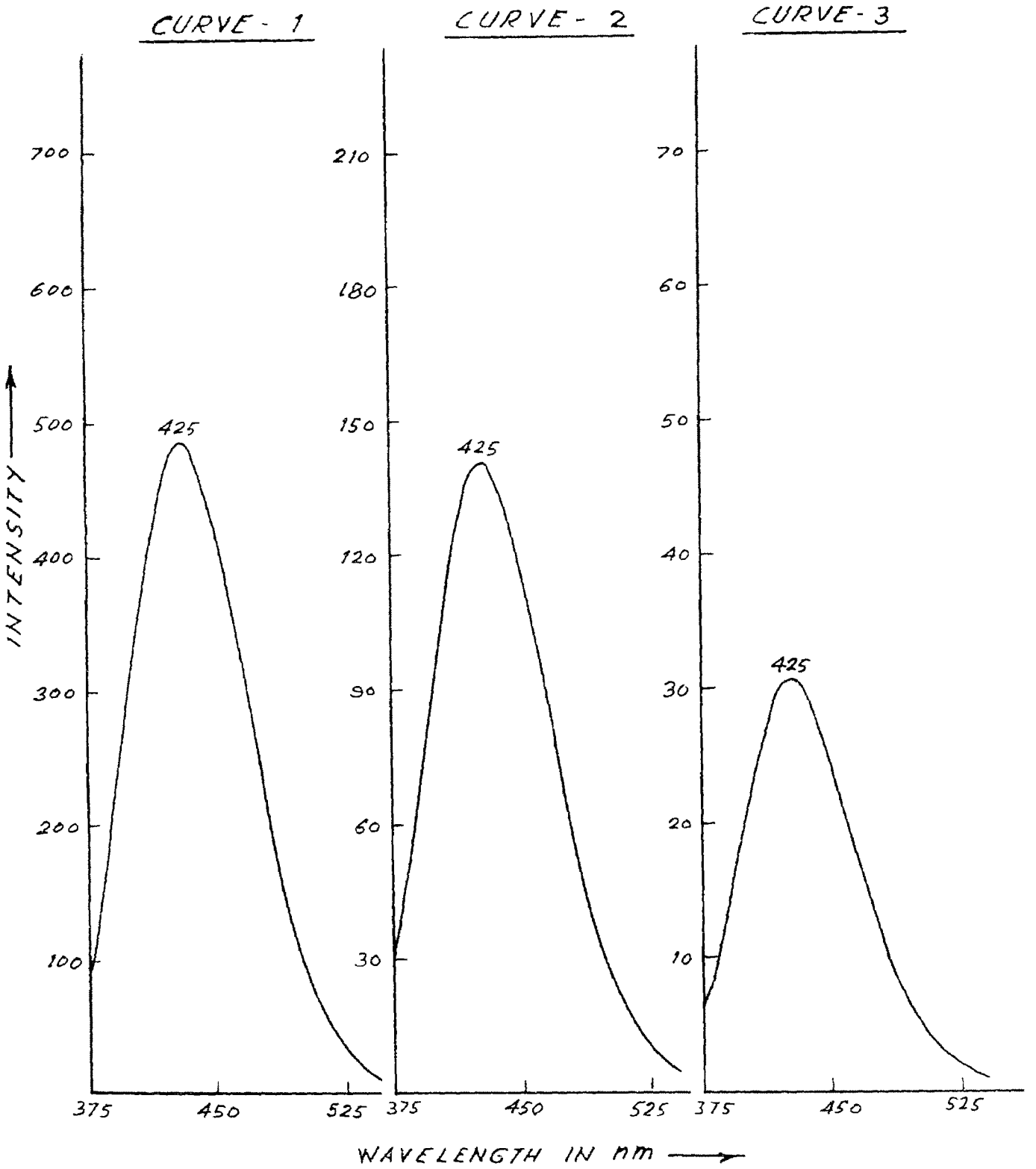
CURVE - 1
CURVE - 2
CURVE - 3
700
600
500
400
300
200
100
210
180
150
120
90
60
30
70
60
50
40
30
20
10
425
425
425
INTENSITY
375
450
525
375
450
525
375
450
525
WAVELENGTH IN mm

FIG 63

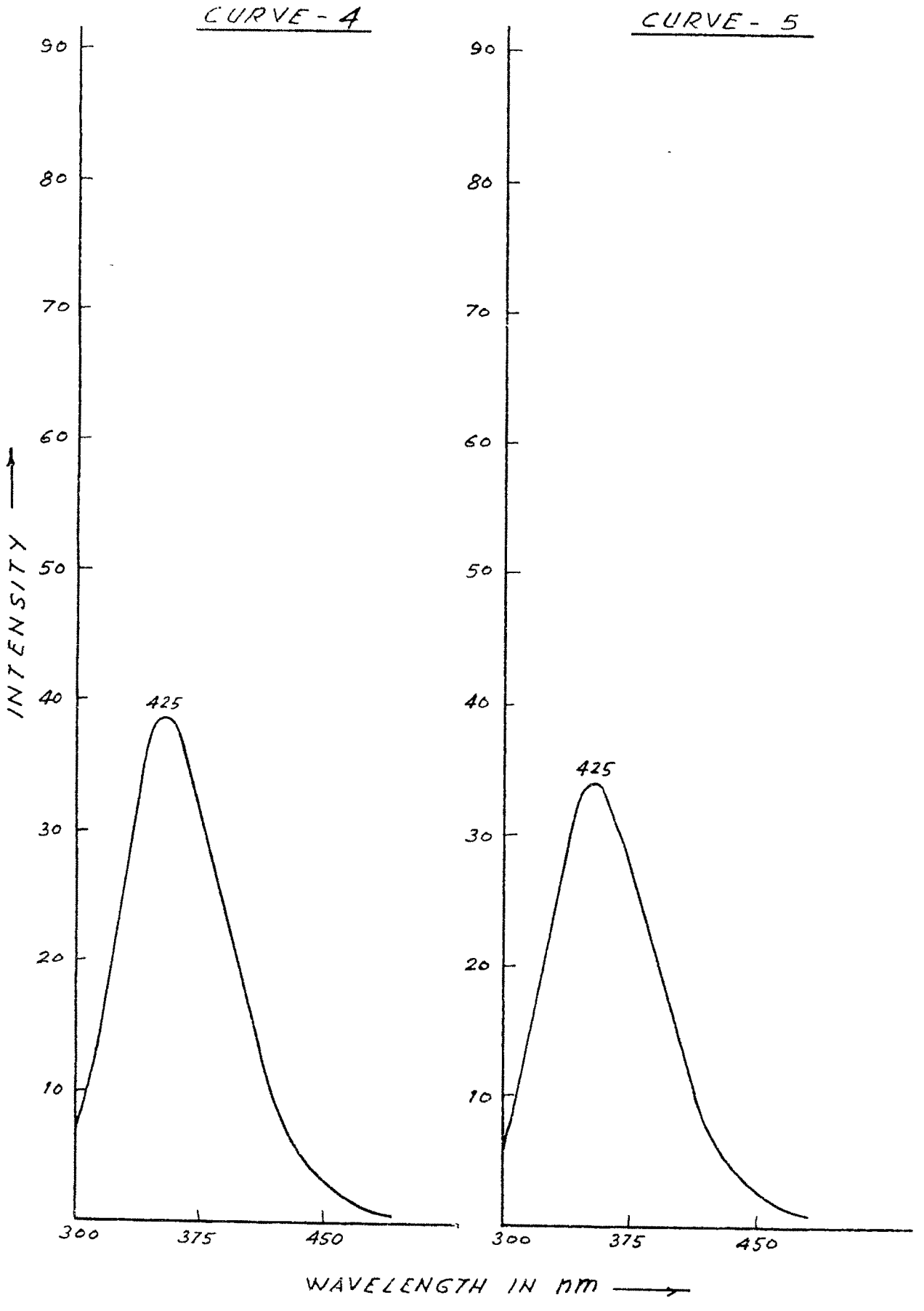
CURVE - 4
CURVE - 5
90
80
70
60
50
40
30
20
10
INTENSITY
425
425
300
375
450
300
375
450
WAVELENGTH IN mm

FIG. 63

(B) DISCUSSION

The Present discussion concerns with the physical models for the luminescence centres associated with the excitation and emission bands of untreated and pretreated NaCl:Tl phosphors differing widely in their thallium content. In the case of alkali halides doped with heavy metal impurities, thallium doped potassium chloride phosphor has been most intensively studied. Other thallium doped alkali halide phosphors studied in sufficient detail are KBr:Tl and KI:Tl. The luminescence study of thallium doped sodium chloride phosphor has not attracted special attention mainly because it is believed that its luminescence characteristics are similar to those observed in thallium doped potassium chloride phosphors. Present investigation indicates that the luminescent properties of NaCl:Tl phosphor are not in all respects identical with those of KCl:Tl phosphor.

It may be mentioned that more frequently the absorption spectra, and not the excitation spectra of the phosphor have been studied. However, it is known that every excitation band must be an absorption band. The intensity distribution in the two spectra can be different because the luminescence yield need not be the same for various absorption mechanisms, and some absorption bands may even be missing from the excitation spectra. The

excitation bands observed in the current investigation, together with the emission bands excited by them, are discussed in certain groups to suit the convenience. As mentioned before, the three emission band groups can be distinguished on the basis of the spectral region in which they appear. The three groups are emission bands in the (i) ultraviolet, (ii) near-ultraviolet and (iii) visible region. First we discuss the excitation process that gives rise to emission in the ultraviolet region.

(i) Excitation Bands Favouring Ultraviolet Emission:

As mentioned earlier in chapter three, the luminescent spectra of alkali halide phosphors containing trace amount of thallium were given a theoretical interpretation by Seitz[1]. His treatment established a model which has been used in the interpretation of the experimental work on many different impurities in the alkali halides. The problem has been approached from the tight binding approximation, that is, it is assumed that the transitions of the ion in the solid are essentially the same as in the gas. Only the energy levels are believed to be shifted as a result of the interaction of the valence electrons with the crystal. The electronic configuration of the ground state of the Tl^+ ion

in the gas is $6s^2$ and the electronic state is $^1S_0$. The first excited state of the free Tl^+ ion has the configuration 6s6p and contains the electronic states $^3P_0$, $^3P_1$, $^3P_2$ and $^1P_1$. When the ion is placed in the crystal, in substitutional position, all these states are raised in energy, the ground state somewhat more than the excited states, by Madelung field. The two strong absorption bands 247 and 195 nm observed in KCl:Tl were identified by Seitz with two most probable transitions $^1S_0$ —— $^3P_1$ and $^1S_0$ —— $^1P_1$ respectively. The task of computing these levels is sufficiently formidable that no detailed treatment of the problem has yet been completed. Despite the difficulties, however, one may still adopt a semiempirical approach to the problem. One such approach was taken by Williams[8,80]. Williams attempted a complete and unified theory of absorption and emission, by computing configuration coordinate curves. He computed Tl^+ wave functions by the Thomas-Fermi method, and assumed that they did not overlap or mix with any other states of the system. He assumed the existence of a single radical configuration coordinate, and computed the energy of the system as a function of the coordinate, taking into account

such important quantities as Madelung energy, repulsive energy, Van der Waals' energy and polarization energy. By computing some quantities, estimating others, and using experimental results where possible, he was able to reproduce certain experimental features of the thallium spectra, in particular, the positions and the widths of the 247 nm absorption and 305 nm emission bands of KCl:Tl. It must be stated that the Williams theory has a number of faults, some of which are discussed by Knox and Dexter[9]. Hence the theory was later modified[62] but it is not still free from objections. It is perhaps best to view Williams' approach as a very valuable, but semiempirical technique.

In the present experiments it is observed that a band in the ultraviolet region with its maximum at 320 nm appears in the emission spectra of the specimens with lower Tl concentration. With the increase of Tl concentration, the intensity of 320 nm emission decreases. The intensity of this band also decreases if the specimen is examined after compression to tablet. In this respect the behaviour of 320 nm emission band is analogous to that of 305 nm emission band observed in KCl:Tl phosphors. The data presented in Figs. 1 through 14 reveal that the 320 nm emission, exhibited by NaCl:Tl phosphor, is favoured by

excitation into 256 nm band. Since Williams' theory has been able to offer satisfactory explanation to the occurrence of 247 nm absorption and 305 nm emission in the spectra of KCl:Tl system, one may reasonably assume that the 256 nm excitation and 320 nm emission in NaCl:Tl arises in isolated substitutional Tl^+ ion in the perfect region of the lattice. The 256 nm excitation can then be due to $^1S_0 \longrightarrow {}^3P_1$ electronic transition within an isolated substitutional Tl^+ ion and the inverse electronic transition $^3P_1 \longrightarrow {}^1S_0$ can be ascribed to the 320 nm emission.

(ii) Excitation Bands Favouring Near-Ultraviolet Emission:

It is clear from Tables 1 and 2 that in the case of NaCl:Tl solid phosphor the emission in the near-ultraviolet region (between 360 - 390 nm) is favoured by two excitation bands the maxima of which range between 225 - 235 nm and 260 - 267 nm. Investigation of the excitation spectra of as-received and pretreated TlCl powder show that in general, the excitation spectrum is broad and diffuse reaching from 210 to 270 nm with poorly resolved maxima (Figs. 51 and 53). The emission spectrum obtained by irradiation of the TlCl specimen, with light of wavelength belonging to any of the

excitation maxima, exhibits band only in the near-ultraviolet region (Figs. 52 and 54). In the case of as-received powder specimen the emission is primarily in the 390 nm band with subsidiary emission in 360 nm band. On the other hand, a tabletted TlCl specimen exhibits emission principally in the 360 nm band. The excitation spectra of TlCl-solution also exhibit a dominant excitation band the position of the maximum of which varies between 220 and 255 nm depending on the concentration of the solution. It shifts to short wavelength side as the concentration of the solution is decreased (Figs. 55, 57 and 59). In the same manner, the TlCl solution exhibits a broad emission band with its peak position lying between 365 and 390 nm when excited by wavelength in the range between 220 and 255 nm. As in the case of excitation spectra, the emission band maximum also moves to short wavelength side with the decrease in the concentration of TlCl-solution (Figs. 56, 58 and 60).

The results of the excitation and emission spectra for solid NaCl:Tl phosphor, TlCl powder and aqueous TlCl-solution are summarised in Table 3. It is clear from this table that the positions of the maxima of the excitation bands in the above three systems are roughly the same whereas the emission region (360 - 390 nm) for

TABLE 3

Coincidence of the Excitation and Emission Bands of Solid NaCl:Tl Phosphor, TlCl Powder and TlCl-Solution

(Wavelengths in nm)

Sr. No.	Specimen		Maximum of excitation band	Maximum of emission band
	NaCl:Tl powder phosphor prepared from solution.			
1.	10^{-4} m.f.	i)	225 (15)	360 (16)
		ii)	260 (15)	360 (16)
2.	10^{-2} m.f.	i)	228 (19)	378 (20)
		ii)	263 (19)	378 (20)
	NaCl:Tl powder phosphor pressed to tablet.			
3.	10^{-4} m.f.	i)	228 (23)	390 (24)
		ii)	267 (23)	390 (24)
4.	10^{-2} m.f.	i)	235 (27)	392 (28)
		ii)	265 (27)	392 (28)

contd....

TABLE 3

Sr. No.	Specimen		Maximum of excitation band	Maximum of emission band
	NaCl:Tl powder phosphor annealed and quenched from 500°C			
5.	10^{-2} m.f.	i)	233 (31)	364 (32)
		ii)	266 (31)	364 (32)
	NaCl:Tl powder phosphor annealed and quenched from 500°C and then pressed to tablet.			
6.	10^{-2} m.f.	i)	233 (35)	364 (36)
		ii)	267 (35)	375 (36)

contd.....

TABLE 3

Sr. No.	Specimen	Maximum of excitation band	Maximum of emission band
7.	TlCl powder in as-received condition.	Broad excitation band reaching from 210 to 270 nm with poorly resolved maxima (51)	Principal emission band at 385 nm and subsidiary band at 360 nm (52)
8.	TlCl powder pressed to tablet.	" " (53)	Strong emission band at 360 nm (54)
9.	Aqueous TlCl-solution.	Maximum appears between 220 and 255 nm depending on TlCl concentration (55,57,59)	Maximum appears between 365 and 390 nm depending on TlCl concentration (56,58,60)

the three systems exactly coincide. Hence it seems plausible to assume that in all the three systems the excitation and emission originate from internal electronic transitions within the same kind of centre namely, TlCl molecule.

It is important to note that parallelism exists in the behaviour of solid NaCl:Tl phosphor and TlCl-solution in regard to their near-ultraviolet emission. In both the cases the emission maximum shifts from 360 nm to 390 nm as the concentration of TlCl is increased (for solid NaCl:Tl phosphor see Curve : 2 in Figs. 16, 18, 20 and 22). Similarly, in both the cases the intensity of the near-ultraviolet emission band increases at first with the increase in TlCl concentration and after an optimum concentration begins to decrease with further increase in TlCl concentration. Thus, TlCl in NaCl lattice exhibit, with respect to its near-ultraviolet emission, luminescent characteristics similar to those displayed by aqueous TlCl solution. In what follows, the luminescent behaviour of TlCl solution is discussed on the basis of which one can interpret the luminescence

characteristics of the solid NaCl:Tl phosphor in regard to its near-ultraviolet emission.

It is observed from Figs. 56, 58 and 60 that the intensity of the emission of TlCl-solution increases with the decrease of TlCl concentration and reaches a maximum for an 'Optimum Concentration' (1:50 dilution). With further dilution, the intensity of the emission band begins to drop. It is generally considered that in a solution, the degree of dissociation of the molecules into ions decreases with the increase in the concentration of the compound[81]. Thus, different number of TlCl molecules and Tl^+ ions coexist in the solution depending on the concentration of the TlCl-solution. In a saturated TlCl-solution, one would expect the molar concentration of undissociated TlCl molecules to be very much greater than the concentration of the Tl^+ ions formed by the dissociation of the molecules. It is suggested that in a concentrated TlCl-solution the excited TlCl molecule may be strongly perturbed by the interaction with a nearby unexcited TlCl molecule. In such a case, an internal conversion can be made probable which will limit the eventual fluorescence emission of the absorbed energy.

The existence of 'Optimum Concentration' then essentially means that when an excited TlCl molecule is certain distance apart from an unexcited TlCl molecule, the quenching probability of the former by the latter is minimum. Dilution of the TlCl-solution beyond 'Optimum Concentration' leads to further the decrease in the concentration of TlCl molecules and consequential increase in the distance, that is, beyond optimum distance, between an excited and an unexcited TlCl molecule. One may thus say that in a TlCl-solution, the strength and position of the excitation band and of the emission band excited by it is mainly governed by the intermolecular distance. Since extremely dilute TlCl-solution exhibits an emission band around 360 nm whereas a saturated TlCl-solution displays an emission band around 390 nm, it may be concluded that large intermolecular distance favours emission around 360 nm and smaller intermolecular distance favours emission around 390 nm.

In the earlier section it is suggested that in a solid NaCl:Tl phosphor an isolated substitutional Tl^+ ion in the perfect region of the lattice is responsible for ultraviolet emission of the phosphor. It is proposed

that a substitutional Tl^+ ion in the distorted region of the lattice forms one of the components of the centre responsible for near-ultraviolet emission of the phosphor. This hypothesis is borne out by the fact that compression of the NaCl:Tl phosphor to tablet enhances the emission in the near-ultraviolet region whereas suppresses the ultraviolet emission (compare curve : 2 in Figs. 16 and 24; curve : 2 in Figs. 18 and 26 etc.). In the distorted region of the lattice, a Tl^+ ion will not occupy a position of cubic symmetry. This assumption is conducive to a simpler explanation of the near-ultraviolet emission (360 - 390 nm region) of the phosphor. There is a significant possibility that a Tl^+ ion in the distorted region forms a covalent bond with one of the neighbouring Cl^- ion[82]. This would form a TlCl molecule with an axis in the <100> directions. One can now conveniently apply the concepts advanced to explain the luminescent characteristics of the TlCl-solution to interpret the near-ultraviolet emission observed in solid NaCl:Tl phosphor. At lowest TlCl concentration (10^{-4} m.f.) the Tl^+ ions in the distorted regions will be isolated and the resulting isolated TlCl molecules will be responsible for 360 nm emission band of the phosphor (Fig. 16, Curve:2).

With the increase in Tl concentration, the intermolecular distance between TlCl molecules in the distorted regions will decrease and hence the emission maximum would shift to the long-wavelength side and finally for minimum intermolecular distance it would stabilize around 390 nm (Curve : 2, Figs. 18, 20 and 22). One can explain the increase in the intensity of near-ultraviolet emission (till certain optimum Tl concentration is reached) and subsequent decrease in its intensity (with further increase in the Tl concentration) on the basis of the concentration quenching.

(iii) Excitation Bands Favouring Visible Emission:

Data presented so far clearly indicate that excitation of the as-received or pretreated phosphor by absorption of light in the 260 nm region gives rise to emission principally in the near-ultraviolet region alongwith subsidiary emission in the visible region. It is observed that the emission in the visible region becomes significant with the increase of Tl concentration and for a given concentration of Tl the intensity of the emission is enhanced if the phosphor is subjected to thermal and/or mechanical treatment. The detailed study of the excitation spectra for emission in the visible region was carried out for as-received and

variously pretreated specimens. The results obtained are presented in the Figs. 43 through 50 and the same are summarized in Table 4. It is clear from the data that the visible emission arises by absorption of light in the 240 nm and 260 nm region. It may be noted that the excitation maximum for near-ultraviolet emission appears anywhere between 260 and 267 nm whereas excitation maximum for visible emission occurs between 265 nm and 280 nm. Thus, there is an extensive overlap between the excitation band for near-ultraviolet emission and the excitation band for visible emission. It is of significance to note that the thermal and/or mechanical pretreatment of the specimen preferentially shifts the peak position of excitation band for visible emission to long-wavelength side.

Results obtained in the study of the excitation and emission spectra for saturated NaCl-solution containing varying amount of TlCl are given in the Figs. 61,62 and 63 and in the tabular form in Table 5. It is seen that emission of such an aqueous solution is in the visible region, primarily in the 425 nm band. With the increase in TlCl concentration new bands appear at 450, 480 and 520 nm as shoulders on the descending slope of the dominant

TABLE 4

Excitation Bands for Visible Emission Exhibited by As-received and Variously Pretreated Solid NaCl:Tl Phosphor

(Wavelength in nm)

Sr. No.	Specimen	Tl conc. in m.f.	Fig. No.	Excitation band		Emission band for which the excitation is observed
1	NaCl:Tl powder phosphor as-received from solution.	10^{-4}	43	235	265	450
				235	265	480
				-	265	520
2	" "	10^{-2}	44	235	266	450
				235	267	480
				240	268	520
3	NaCl:Tl powder phosphor compressed to tablet	10^{-4}	45	242	272	450
				-	272	480
4	" "	10^{-2}	46	242	269	450
				242	270	480
				242	270	520

contd.....

TABLE 4

Sr. No.	Specimen	Tl conc. in m.f.	Fig. No.	Excitation band		Emission band for which the excitation is observed
5	NaCl:Tl powder phosphor annealed and quenched from 500°C	10^{-2}	47	240	271	450
				242	273	480
				242	276	520
6	NaCl:Tl powder phosphor annealed and quenched from 500°C and then pressed to tablet	10^{-2}	48	240	272	450
				240	280	480
				240	277	520
7	NaCl:Tl melt and quenched phosphor	10^{-2}	49	242	270	450
				242	270	480
				242	271	520
8	NaCl:Tl melt and quenched phosphor pressed to tablet	10^{-2}	50	243	275	450
				245	280	480

TABLE 5

Excitation and Emission Bands Exhibited by Saturated NaCl-Solution Containing Varying Amounts of TlCl

(Wavelengths in nm)

Sr. No.	Specimen	Excitation band/ bands	Emission band/ bands
1	Saturated NaCl-solution + 1 mg TlCl	225 ; 258 (61 ; Curve : 1)	425 ; 450 (62 ; Curve : 1)
2	Saturated NaCl-solution + 3 mg TlCl	230 ; 260 (61 ; Curve : 2)	425 ; 450; 480 (62 ; Curve : 2)
3	Saturated NaCl-solution + 5 mg TlCl	230 : 266 (61 ; Curve : 3)	425 ; 450;480;520 (62 ; Curve : 3)
4	Saturated NaCl-solution + 7 mg TlCl	225 ; 268 (61 ; Curve : 4)	425;450;480;520 (62 ; Curve : 4)
5	Saturated NaCl-solution + 9 mg TlCl	225 ; 272 (61 ; Curve : 5)	425;450;480;520 (62 ; Curve : 5)