

A COMPARISON OF INTENSITIES OF INDIUM
AND THALLIUM SENSITIZED FLUORESCENCE

by

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INTRODUCTION

In this paper the relative intensities of transitions in indium and thallium were considered in sensitized fluorescence. Since these metals were corresponding elements in different but adjacent rows in the periodic table; they would have been expected to behave spectroscopically in a similar manner. These two elements were investigated to determine if that was the case. The accepted selection rules of sensitized fluorescence were applied to explain the intensities of the various indium lines.

From the work by Donat (3) it was found that indium, as well as thallium exhibited sensitized fluorescence when excited by collision with excited mercury atoms. Donat used the experimental methods of Cario and Franck. Winans et al. (13) confirmed Donat's work with indium and found three additional indium sensitized fluorescence lines.

Many investigators, Cario and Franck (2), Loria (8), and Winans (12), have studied the sensitized fluorescence of thallium. In recent work by Swanson (10) evidence was given of temperature dependence of the sensitized fluorescence intensities.

One can define sensitized fluorescence in the following fashion. If two different gases A and B are confined in a vessel and if atom A is excited and then collides with atom B, giving up its excitation energy to atom B, then atom B can be in an excited state. Atom B loses its excitation energy by various transitions. The radiation due to these transitions are measured on the sensitized fluorescence lines.

Postulates concerning sensitized fluorescent intensities are as follows:

1. That a mixture of two monoatomic gases A and B, illuminated by

light which only A absorbs, emits fluorescence light from B. Further, that the intensity from B is greatest when the excitation energy of A is equal to or greater than that of B.

2. That the intensity of B depends upon energy difference between excited atom A and excited atom B. The intensity is greater for small energy difference as was shown by Beutler and Josephy (1).

3. That the intensities of lines of sensitized fluorescence follow the rule of Wigner that those transitions are most probable for which the change in spin angular momentum for one atom is equal and opposite to that of the other atom.

4. That for collisions between atoms A and B, the probability for a transfer of excitation energy is greater if the total angular momentum, $J(= J_A + J_B)$ remains constant during the collision (13).

It was the objective of this work to further investigate transition probabilities and to compare these probabilities for two similar atoms, thallium and indium.

EXPERIMENTAL APPARATUS AND PROCEDURE

Preparation of Spectral Tubes

The indium and thallium tubes were prepared in the same manner. The vacuum system used consisted of a Welsch Duoseal fore pump and two series connected Wisconsin type, air cooled, mercury diffusion pumps. The system was trapped at appropriate points with liquid air and P_2O_5 traps to remove water vapor and other condensable vapors. A Pirani gauge and an ionization gauge were used to provide pressure measurements on the high vacuum side of the system.

The experimental tubes, constructed as a unit in a series of three, were placed on the vacuum system, and an auxiliary oven was placed around them. They were outgassed for two days at 1000°C to drive off any gases absorbed on or which might have diffused into the quartz. The vacuum system was then opened, and the end tube was filled with either indium or thallium. This metal was outgassed for several days and was then distributed through the three tubes by vacuum distillation. In a similar fashion a few grams of mercury were introduced into each of the three tubes. The tubes were then sealed and removed from the vacuum system.

Optical System

The experimental tubes were placed in an oven which contained windows to allow the light to enter and leave the oven. The optical system consisted of a germicidal mercury lamp which emitted predominately 2537A mercury light. The light from this source was focused on the tube by two quartz lenses through the quartz windows of the oven. The emergent fluorescent light was passed through a Bausch and Lomb quartz grating monochromator. The optimum conditions of intensity and resolution were obtained with the slits of the monochromator set at .4 mm.

Detection Apparatus

The detection apparatus was similar to that used by Swanson (10) in earlier work. It consisted of an 1P28 photomultiplier tube at the exit slit of the monochromator. The voltage of the various stages was supplied by a stabilized high voltage supply and was controlled by a group of dropping resistors. These resistors consisted of a network of ten 22,900

ohm variable resistors in parallel with ten, 20,000 ohm resistors. The various stages of the tube were operated at 80 volts except that the voltage between the last dynode and anode was 100 volts. The output of the photo-multiplier tube was passed through a 3 megohm resistance to supply an output voltage.

The output of the photomultiplier tube was amplified by a twin-T-amplifier set to the frequency of the mercury source which was operated on 60 cycle alternating current. Thus, the impulse was sent through the amplifier and the intensity of the various lines was exhibited as a voltage reading on an R.C.A. audiovoltmeter. As an additional precaution, the line voltage for the electronic detection apparatus and the source was controlled by Raytheon voltage regulator.

Focusing Procedure

The procedure for focusing of the fluorescence lines was that used by Swanson (10). The position of focus was chosen so that the Hg resonant line, 2537A, was as strong as possible under the same conditions that the scattered light line, 3119A, of mercury was weak. Thus it was attempted to obtain the highest intensity ratio possible for the 2537A to 3119A mercury lines. Also the 3519-29A thallium line, which was the strongest fluorescent thallium lines, was kept at its optimum intensity. Maximum intensity of thallium lines with minimum intensity of scattered light was obtained in this manner.

In the case of indium, the same procedure was followed, with the intensity of the 3256A sensitized fluorescence line of indium maximized. Again, there was an attempt made to keep the intensity ratio of the 2537A

to 3119A mercury line as large as possible. Thus, the optimum focusing conditions were obtained.

Temperature Control

In the work by Swanson (10) it was found that a definite relation was observed between intensities of the sensitized fluorescence lines and the mercury and thallium temperatures. In order to obtain these conditions, differential heating was necessary. This was accomplished by constructing the experimental tube so that it extended from the high temperature part of the oven. The temperature of the mercury which condensed into this region was controlled by an auxiliary oven. The vapor pressure of the thallium bead was controlled by the temperature of the main oven. These temperatures were measured by the use of thermocouples.

In the case of indium, it was found that higher temperatures were necessary to obtain sensitized fluorescence. Thus the metal lined ovens used by Swanson (10) were inadequate, and a new oven was developed. Large window areas were also found to be advantageous due to the lower intensity of the indium fluorescence. This oven was made out of two ceramic heating element cones in which a window of one by 1 1/2 inches was cut. The ceramic material was shaped so that the tube extended through one end and a transite plug was placed in the other end to hold the tube in position. The two sections of ceramic were fitted together and held by a transite frame. This minimized the coating of the tubes by metal oxides which was troublesome in the case of the metal lined oven.

In order to overcome the problem of the ovens burning out, 23 gauge Nichrome V wire was used. Fingerprints were removed from the wire and the

wire was isolated from transite and asbestos, as they caused the wire to corrode. A commercial refractory insulation was placed around the wires. The wires were also washed in alcohol after they were mounted on the ceramic frame.

After assembly, the tube was held in place in the oven at the back end by a transite plug and in the front end by a ceramic collar. Two sets of windows were placed in the oven with a separate heating coil between them to reduce the effect of heat loss through these large windows.

The oven was covered on the outside with a layer of asbestos paste for added insulation. It might be mentioned that no transite was to be found inside the oven except for a small end plug which held the back end of the tube in place. It was noted that any transite in contact with the tube caused a fogging of the quartz. These improvements to the oven eliminated most of the early troubles.

Spectrographic Methods

Photographic plates of the sensitized fluorescence spectrum of indium were taken during the preliminary stages of the experiment. For this work, a medium quartz Bausch and Lomb spectrograph was used. The same 2537A mercury light source was used to excite the mercury vapor, and this light was focused on the front edge of the experimental tube. The resulting fluorescent light was focused on the slit of the spectrograph by a 10 cm. quartz lens. Images of the fine droplets of metal which condensed on the front wall of the tube were focused on the slit of the spectrograph. This assured that the fluorescent light was coming from the front edge of the tube, for this was the area where most of the fluorescent light was known

to originate. Plates of indium sensitized fluorescence were obtained.

EXPERIMENTAL RESULTS

In the preliminary work, a number of spectrographic exposures of indium sensitized fluorescence were taken. These were taken because of the weak intensities of the indium lines and because of scattered mercury lines which the monochromator could not resolve from several of the indium lines. Thus two photographic spectra were shown in the results. These gave some indication of the intensities of the indium lines compared to those of scattered mercury lines. These spectra were taken at a constant indium temperature and at the mercury temperature in the region where maximum intensities were to be expected. Tesla discharge spectra of indium and mercury are also presented for comparative purposes. The important lines of mercury and the fluorescent lines of indium were marked on these plates.

In these results, graphs of the relative intensities (intensities of the lines as indicated by voltmeter readings which are proportional to the actual intensities) of indium and thallium sensitized fluorescence lines were included. These graphs, Plates III, IV, V, VI, VII, and VIII, were obtained for constant thallium and indium temperatures by plotting the relative intensities of thallium or indium lines against the mercury temperature. Data were obtained also for the relative intensities of the lines at a constant mercury temperature with the thallium or indium temperature varied. These results will not be considered in our discussion, but two representative curves were shown in the data on Plates XI, and XII, for the sake of completeness.

In making the comparison of thallium intensities to those of indium,

it was decided to use three representative pieces of data on both thallium and indium. These three different sets of data were chosen, the first in the 700°C temperature range of thallium and indium, the second in the 800°C range, and the third in the 900°C range.

Temperatures were chosen for the representative data on thallium as readings at 745°C, 845°C, and 930°C. The graphs obtained from this data appear in Plates III, V, and VII. These graphs exhibit a definite temperature dependence of the sensitized fluorescence on mercury and thallium temperatures. In order to compare these graphs with those on indium, the indium graphs of temperatures at 755°C, 820°C and 901°C are shown. These appear on Plates IV, VI, and VIII respectively.

Plates I and II are two of the spectra taken. Plate I was taken with an exposure time of 21 hours. This plate shows two mercury spectra with exposure times of two and three minutes and a tesla discharge spectrum of the tube with an exposure time of five minutes. These are labeled in the plate. Plate II shows a test run for sensitized fluorescence with an exposure time of 18 hours. There are two tesla discharge spectra of exposure time of five and ten minutes and also two mercury spectra of exposures of two and 3 1/2 minutes.

Also included in these data is a table showing the wavelengths of the various measured indium lines and the wave length of various scattered mercury lines around these indium lines. This table is useful in the discussion of the results in order to account for the observed indium intensities.

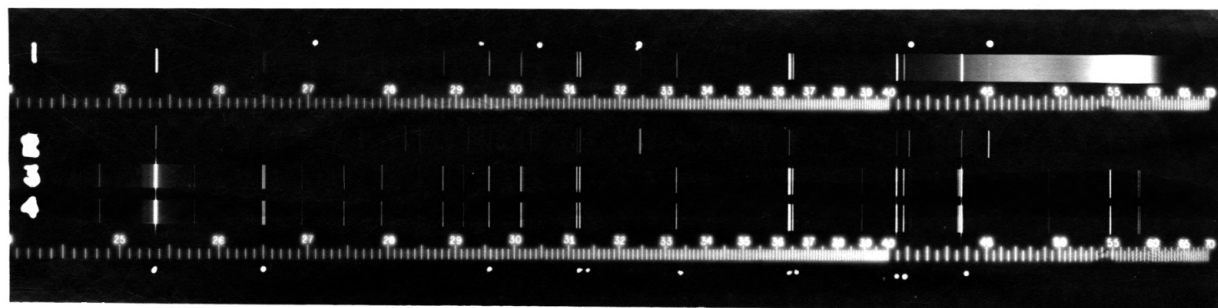
EXPLANATION OF PLATE I

Indium Sensitized fluorescence and tesla discharge spectra

Indium and mercury temperatures were 850°C and 120° respectively.

1. Spectrum of sensitized fluorescence of indium.
2. Tesla discharge spectrum of indium.
3. Spectrum of mercury.
4. Spectrum of mercury.

PLATE I



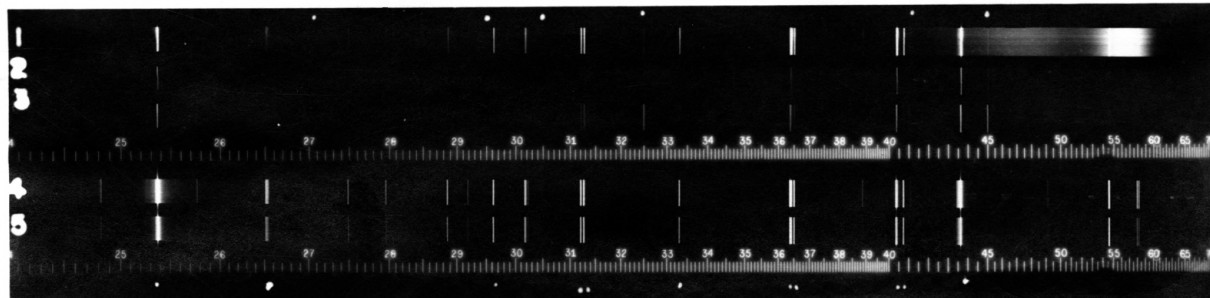
EXPLANATION OF PLATE II

Indium sensitized fluorescence and tesla discharge spectra.

Indium and mercury temperatures were 875°C and 130°C respectively.

1. Spectrum of sensitized fluorescence of indium.
2. Tesla discharge spectrum of indium.
3. Tesla discharge spectrum of indium.
4. Spectrum of mercury.
5. Spectrum of mercury.

PLATE II



EXPLANATION OF PLATE III

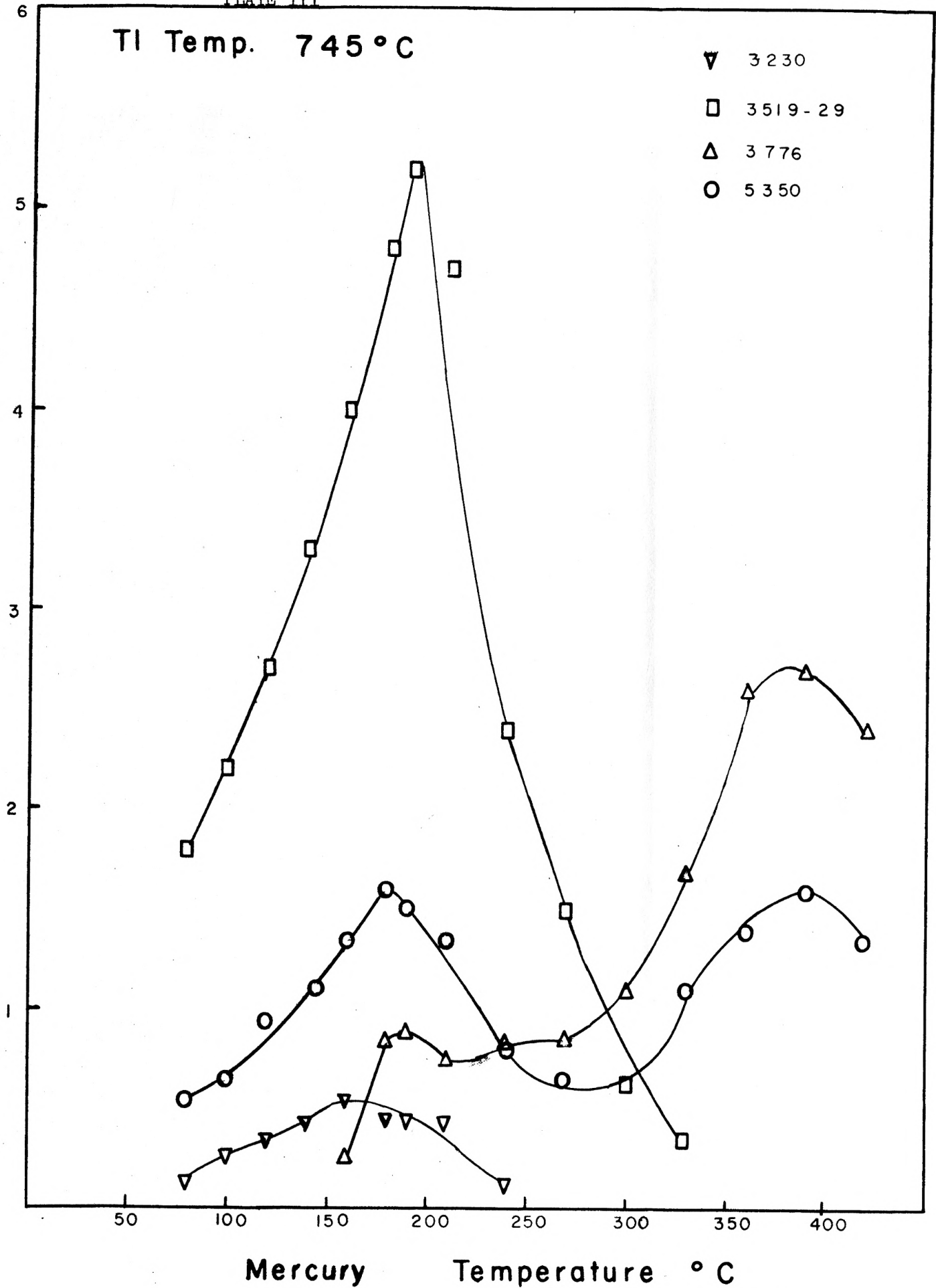
Sensitized fluorescence of thallium

Relative intensity of thallium lines as a function of mercury temperature with a fixed thallium temperature.

Tl Temp. 745 °C

- ▽ 3 230
- 3 519-29
- △ 3 776
- 5 350

Relative Intensity



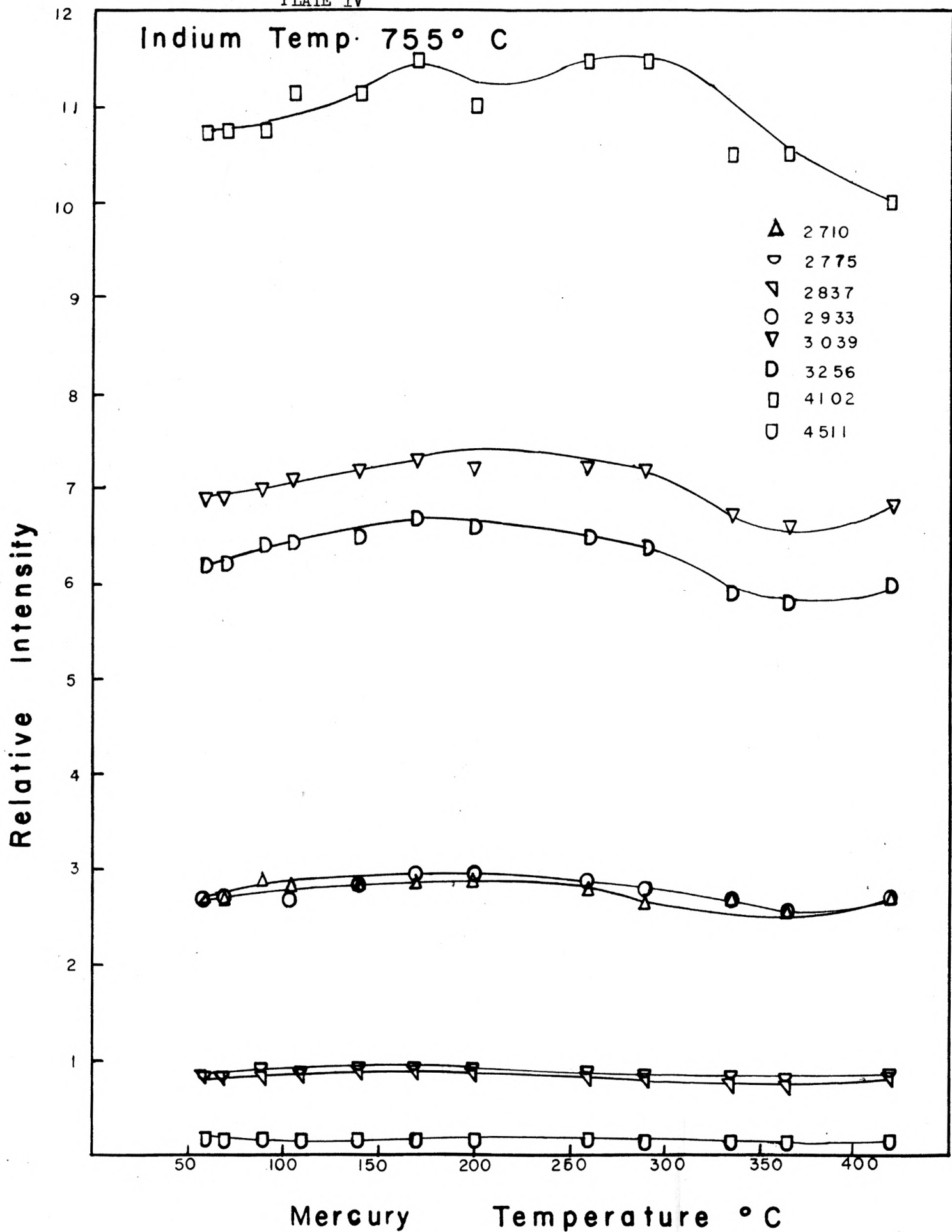
Mercury Temperature °C

EXPLANATION OF PLATE IV

Sensitized fluorescence of indium

Relative intensity of indium lines as a function of mercury
temperature with a fixed indium temperature.

Indium Temp. 755° C



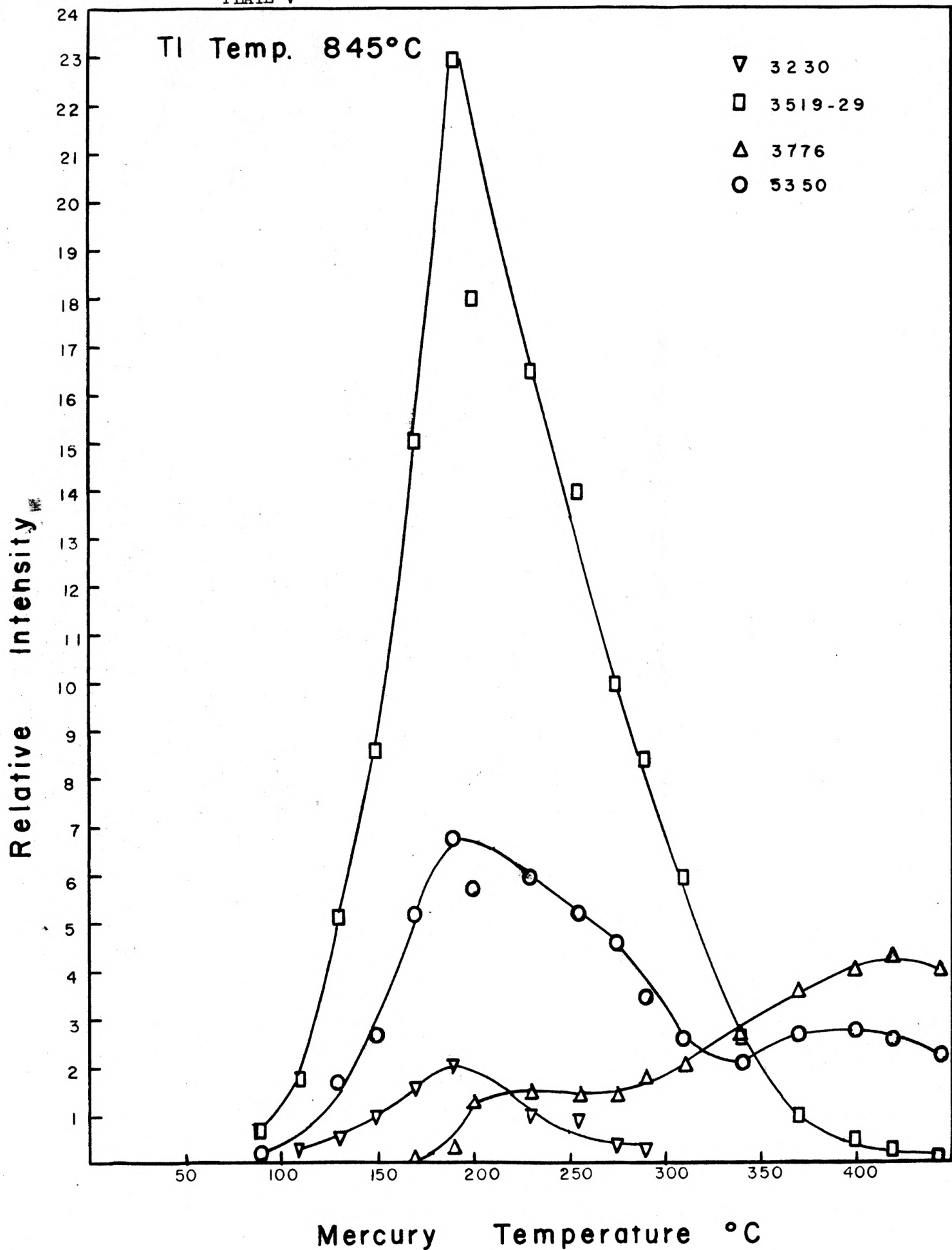
EXPLANATION OF PLATE V

Sensitized fluorescence of thallium

Relative intensity of thallium lines as a function of mercury temperature with a fixed thallium temperature.

Tl Temp. 845°C

- ▽ 3230
- 3519-29
- △ 3776
- 5350



EXPLANATION OF PLATE VI

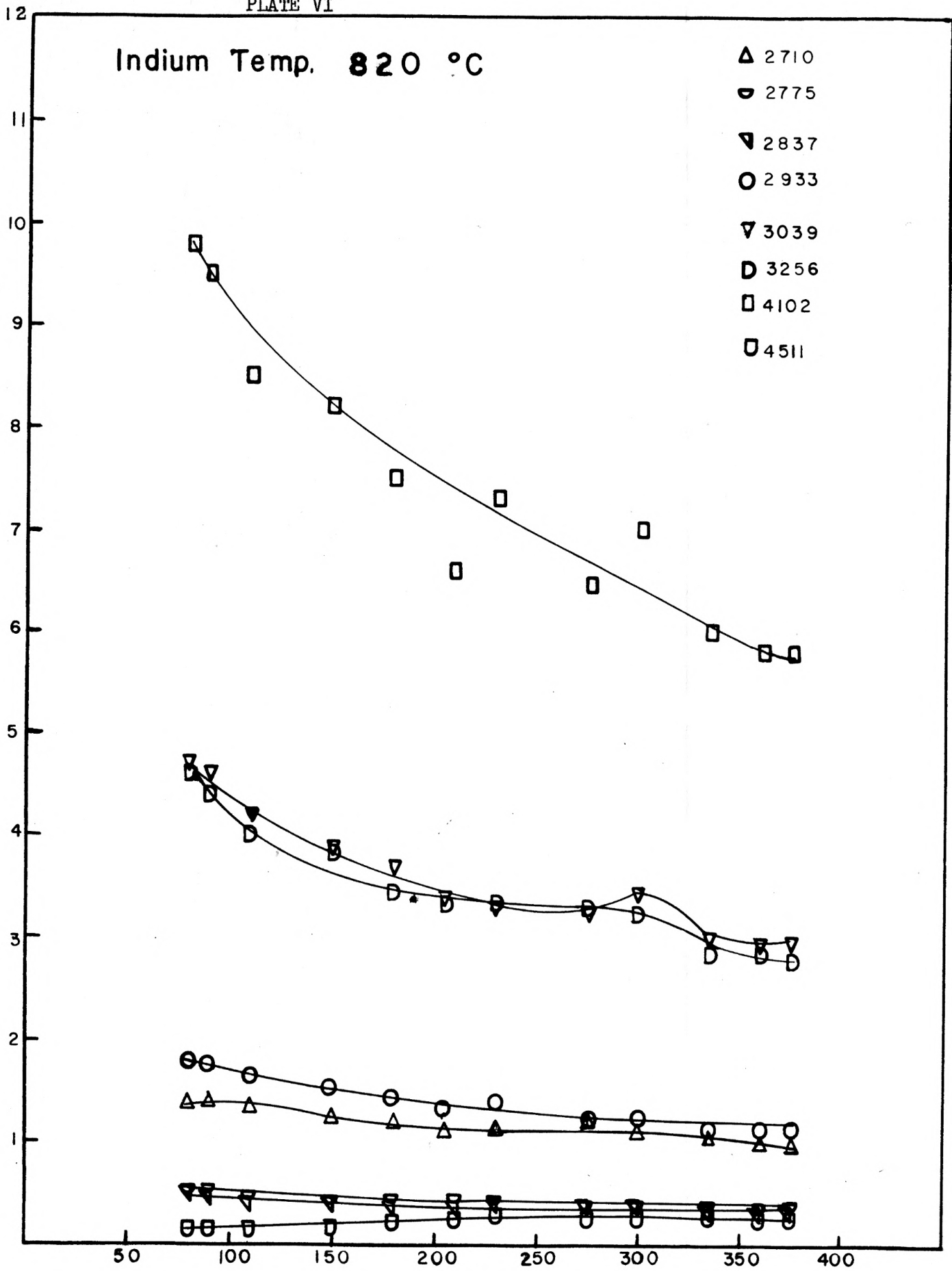
Sensitized fluorescence of indium

Relative intensity of indium lines as a function of mercury temperature with a fixed indium temperature.

Indium Temp. 820 °C

- △ 2710
- ◐ 2775
- ▽ 2837
- 2933
- ▽ 3039
- ◐ 3256
- ◻ 4102
- ◻ 4511

Relative Intensity



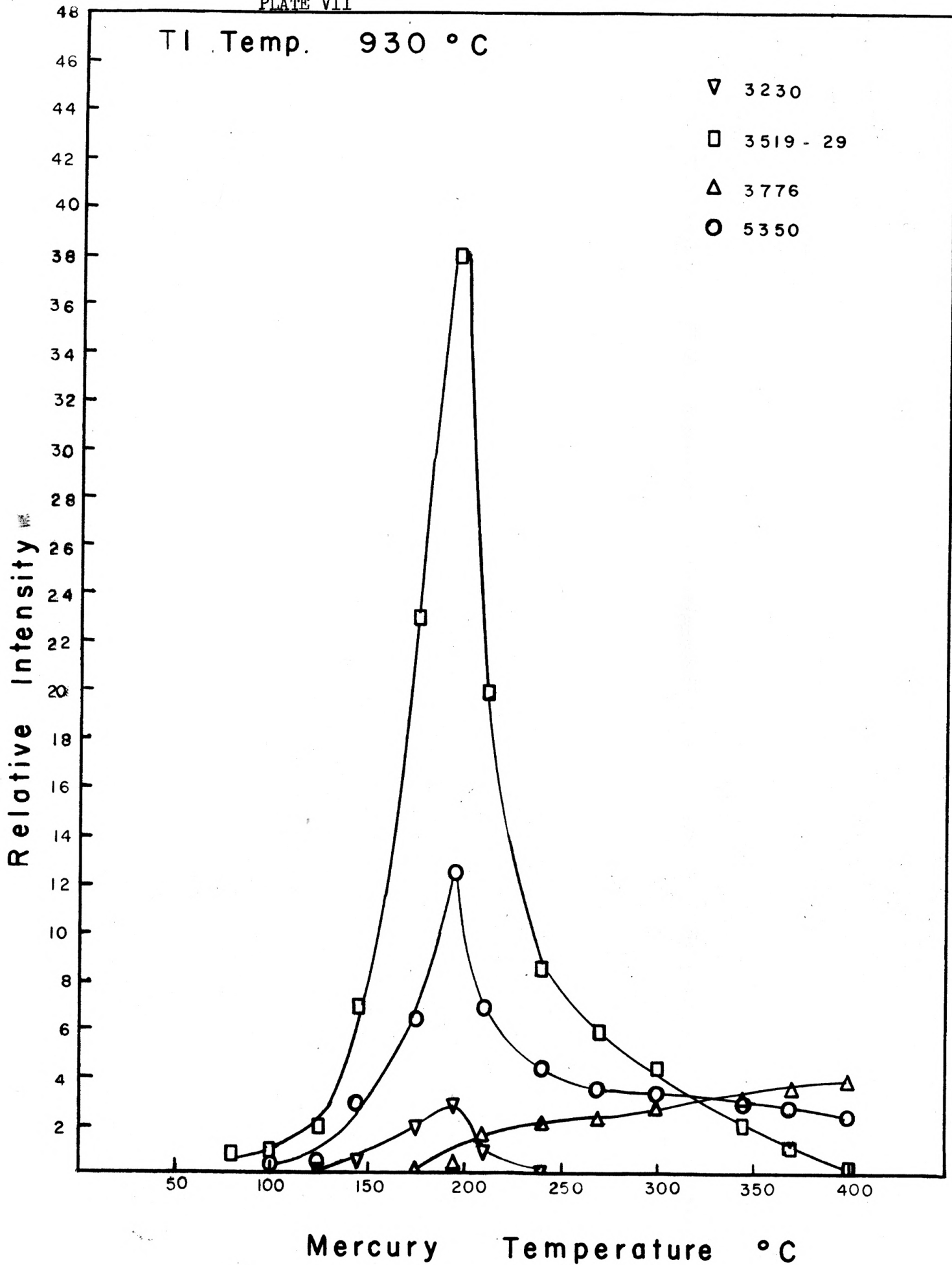
Mercury Temperature °C

EXPLANATION OF PLATE VII

Sensitized fluorescence of thallium

Relative intensity of thallium lines as a function of mercury temperature with a fixed thallium temperature.

TI Temp. 930 °C



EXPLANATION OF PLATE VIII

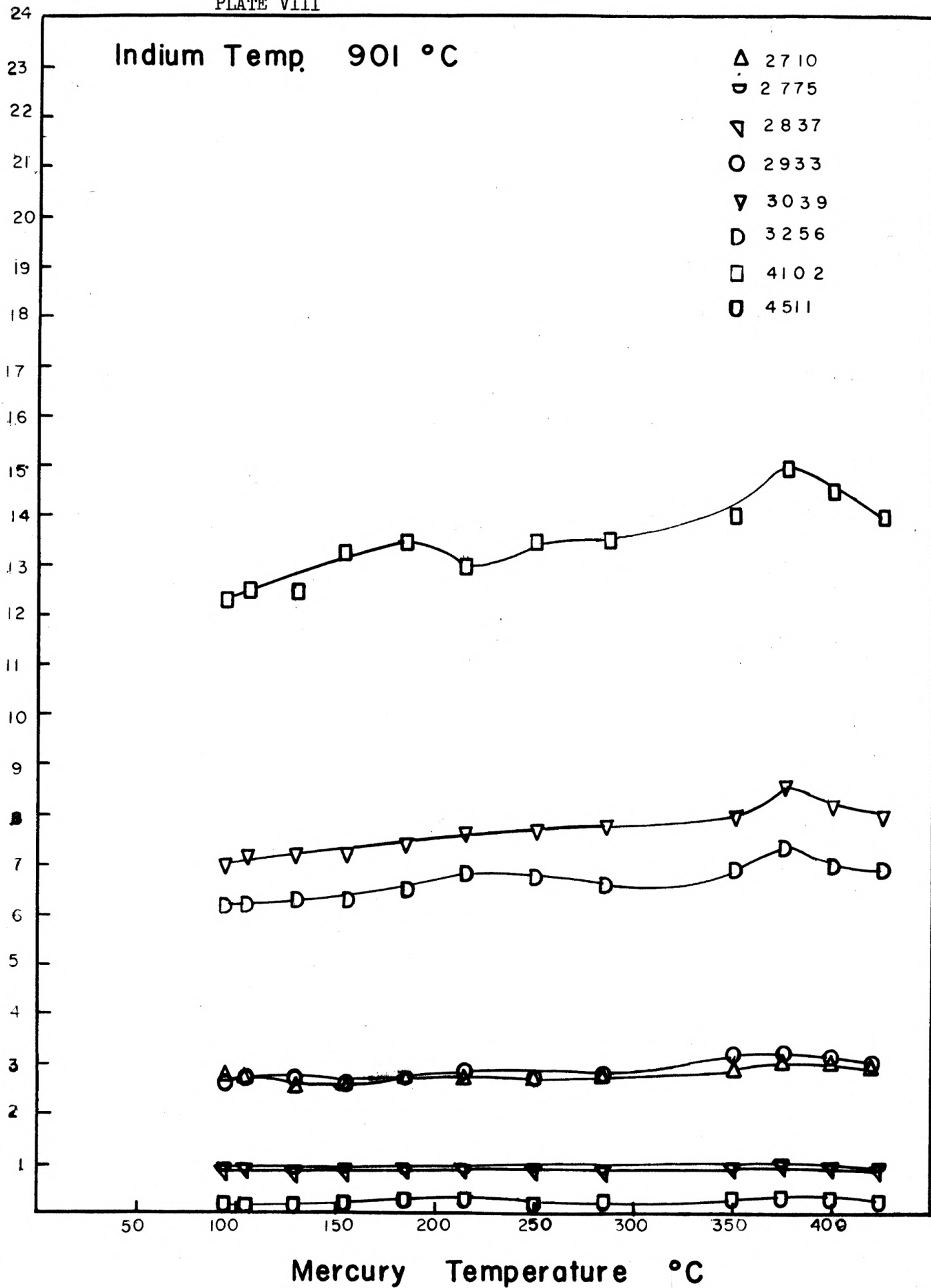
Sensitized fluorescence of indium

Relative intensity of indium lines as a function of mercury temperature with a fixed indium temperature.

Indium Temp. 901 °C

- △ 2710
- ◐ 2775
- ▽ 2837
- 2933
- ▽ 3039
- D 3256
- 4102
- ◐ 4511

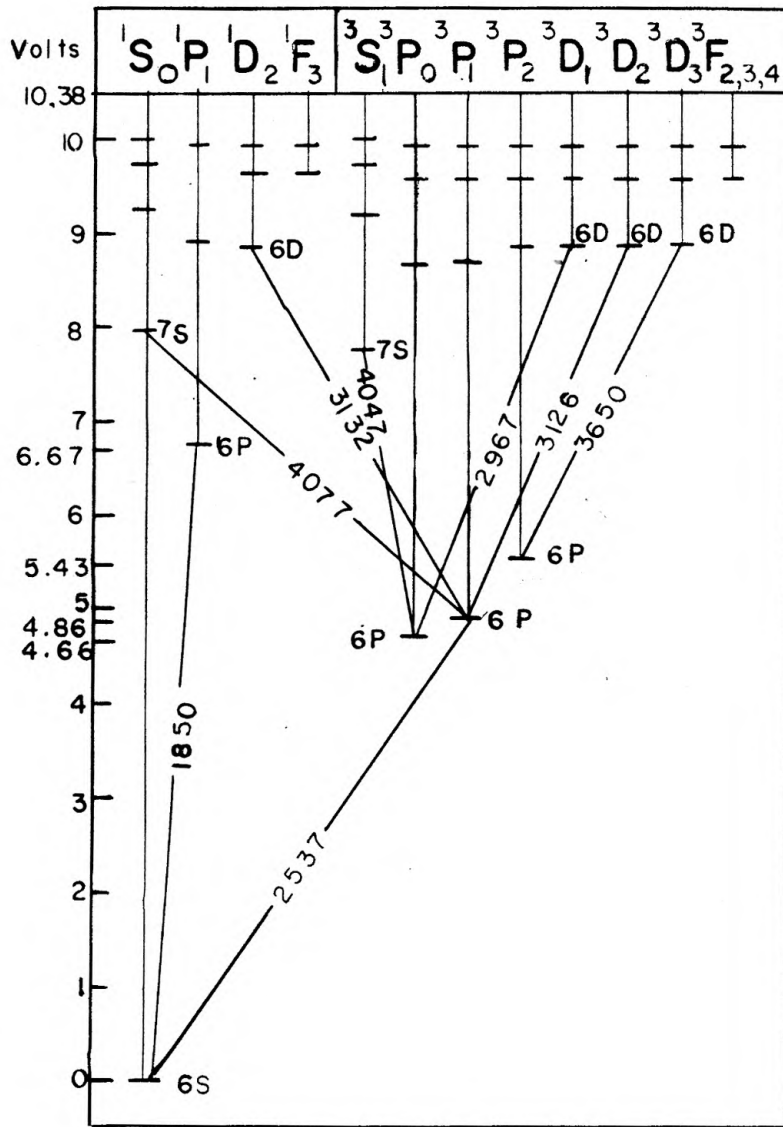
Relative Intensity



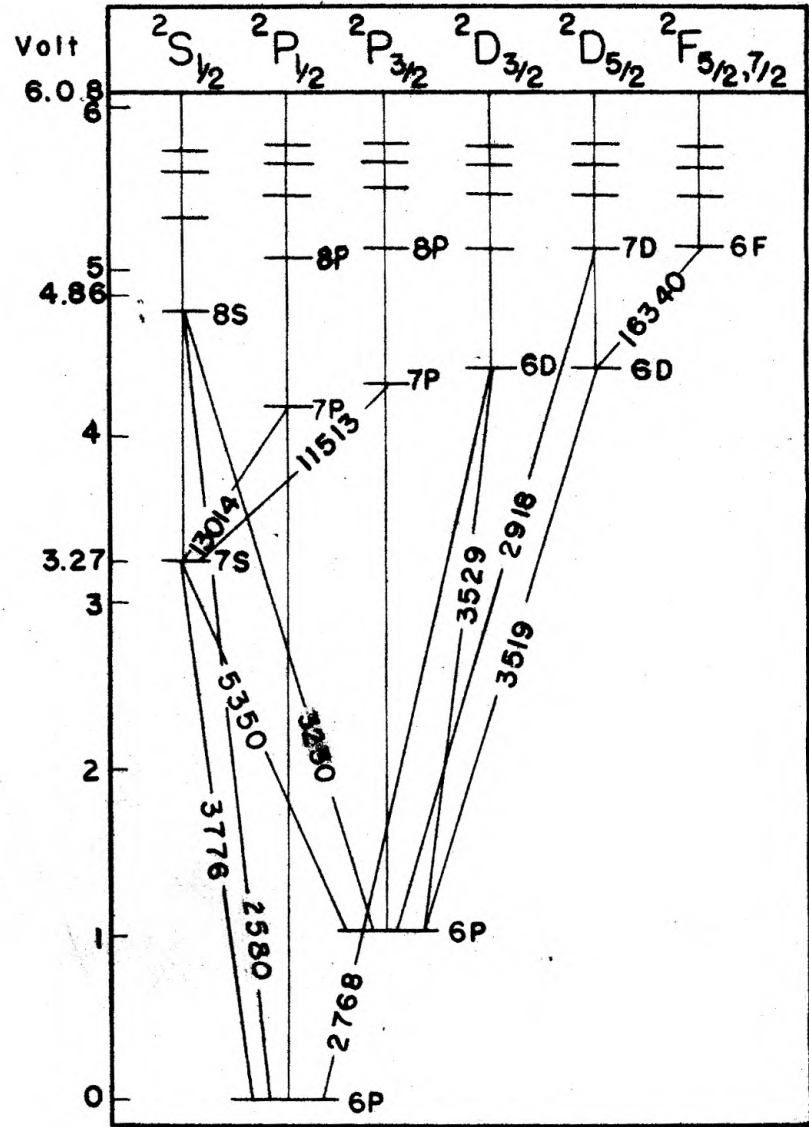
EXPLANATION OF PLATE IX

Energy level diagram of thallium and mercury.

PLATE IX



Mercury

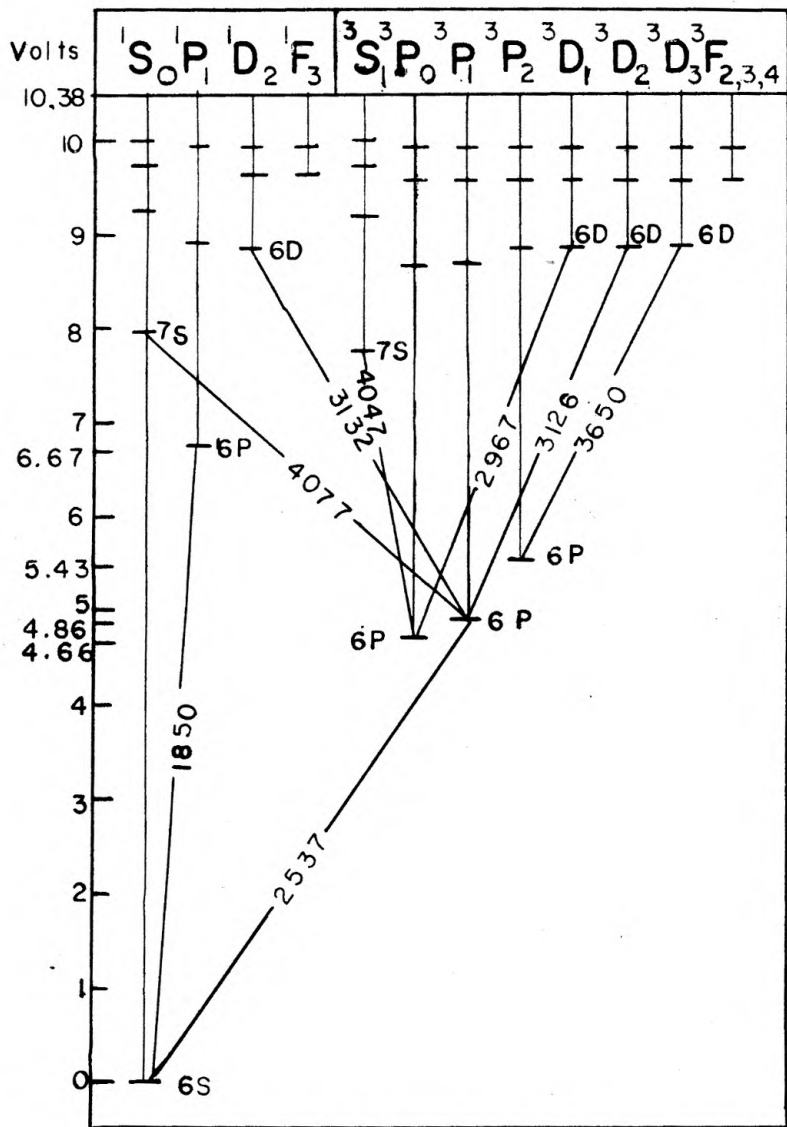


Thallium

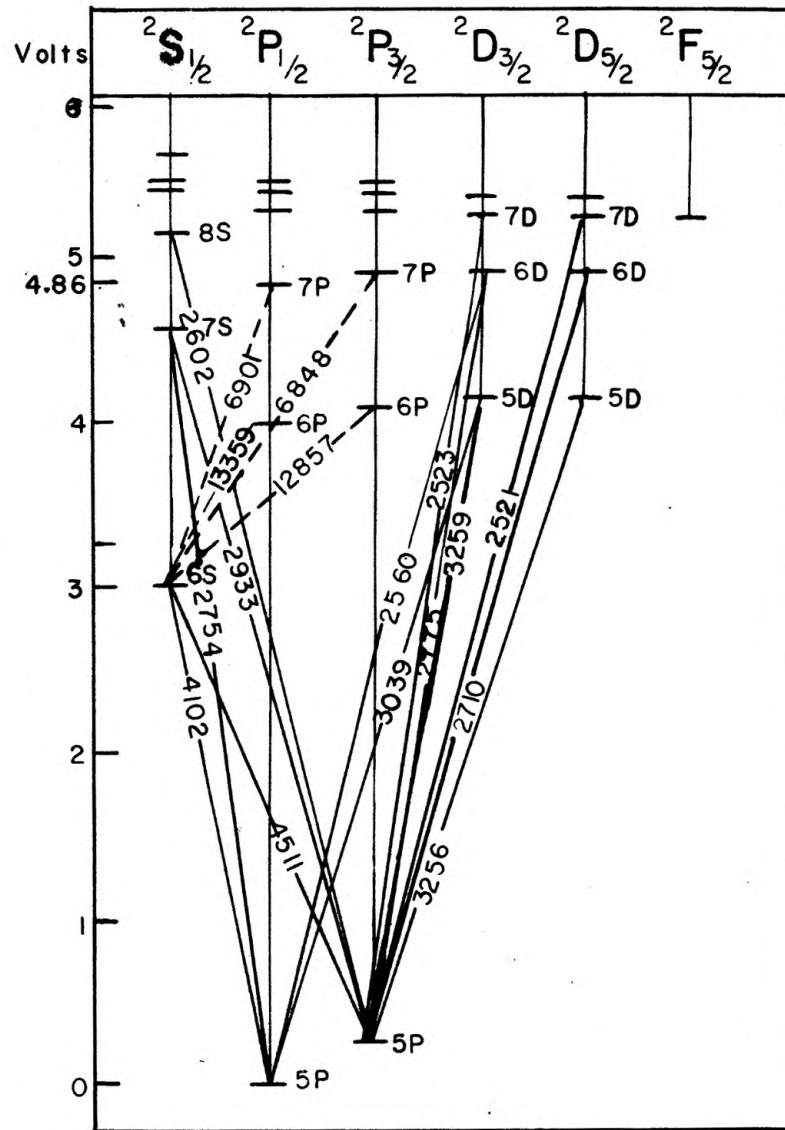
EXPLANATION OF PLATE X

Energy level diagram of indium and mercury.

PLATE X



Mercury



Indium

EXPLANATION OF PLATE XI

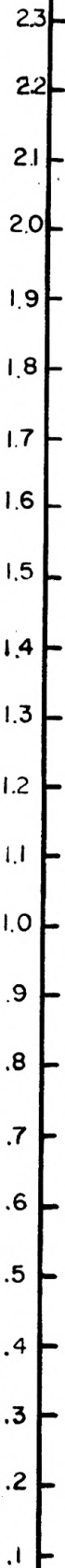
Sensitized fluorescence of indium

Relative intensity of indium lines as a function of indium temperature with a fixed mercury temperature.

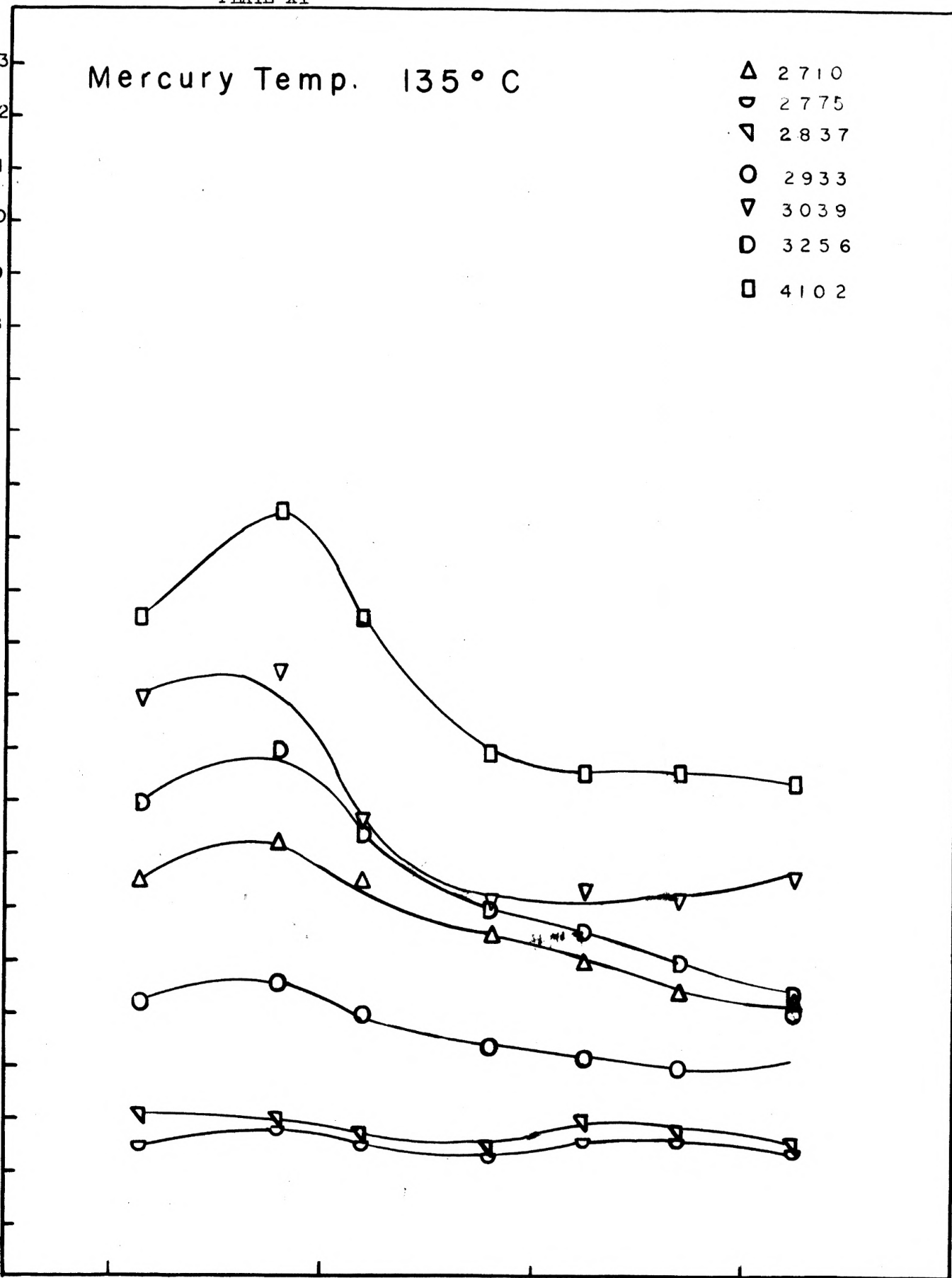
Mercury Temp. 135° C

- △ 2710
- ◐ 2775
- ▽ 2837
- 2933
- ∇ 3039
- D 3256
- 4102

Relative Intensity



Indium Temperature °C



EXPLANATION OF PLATE XII

Sensitized fluorescence of thallium

Relative intensity of thallium lines as a function of thallium temperature with a fixed mercury temperature.

Mercury Temp. 200°C

- ▽ 3230
- 3519 - 29
- △ 3776
- 5350

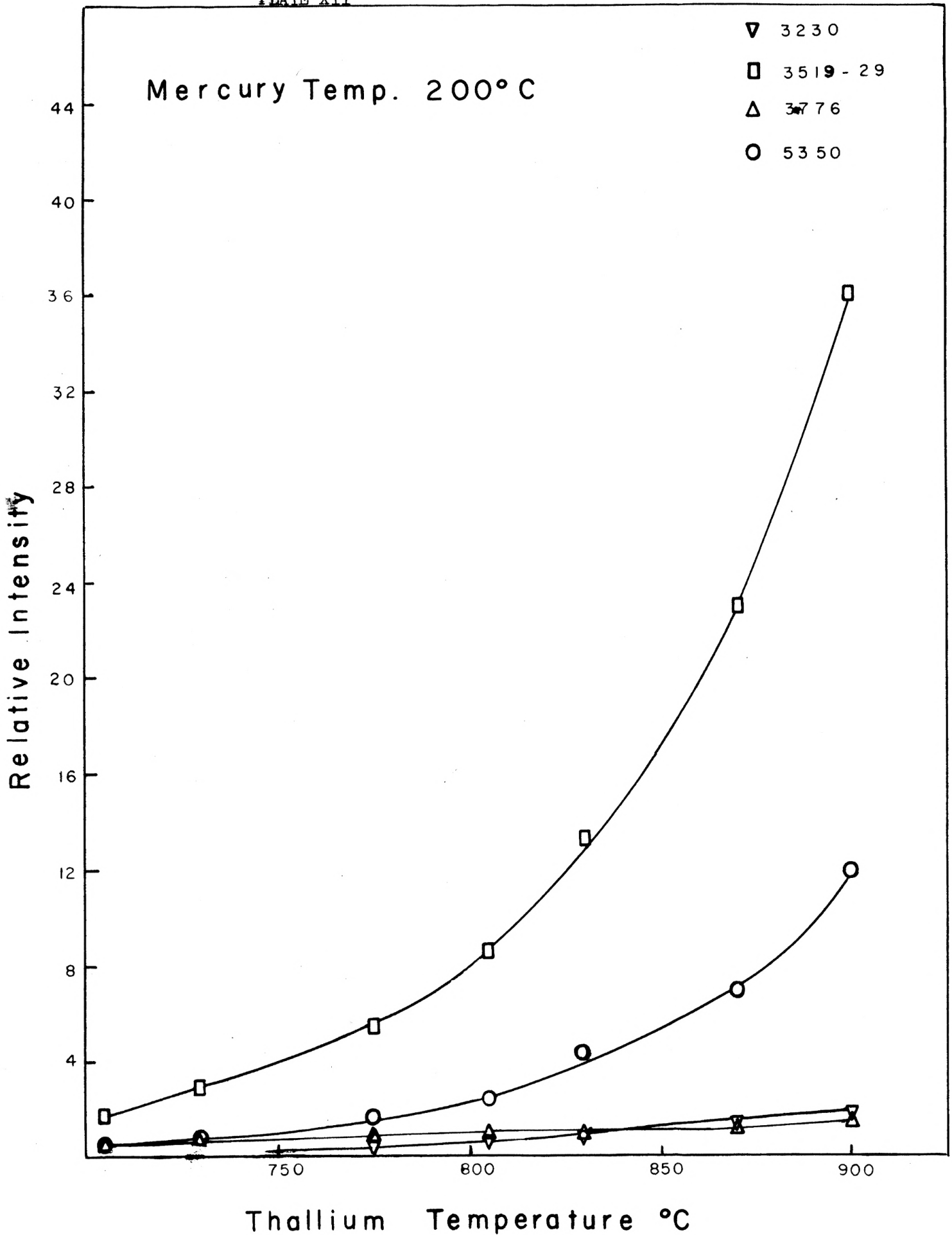


Table 1. Comparison of wave lengths.

Mercury Wavelength	:	Indium Wavelength
2698.9	:	2710.3
2699.4	:	2713.9
2752.2		
2752.8		
2759.7		2775.4
2820.0		
2847.8		2836.9
2925.4		
2967.3		2932.6
2967.6		2957.0
3021.5		
3023.5		
3025.6		
3027.5		
		3039.4
		3256.1
		3258.6
3341.5		
3351.3		
4046.6		
4077.8		
		4101.8
4108.0		
		4511.3

DISCUSSION OF RESULTS

In the three graphs of thallium sensitized fluorescence for each temperature, there were plotted the relative intensities of four thallium lines. The wavelengths of these lines were 3230, 3519-29, 3776 and 5350A. These corresponded to transitions of $8^2S_{1/2} - 6^2P_{3/2}$, $6^2D_{5/2} - 6^2P_{3/2}$, $6^2D_{3/2} - 6^2P_{3/2}$, $7^2S_{1/2} - 6^2P_{1/2}$, and $7^2S_{1/2} - 6^2P_{3/2}$ respectively. From the thallium data and the graphs, the same general form of the curves were obtained as by Swanson (10). There definitely appeared to be a temperature dependence of the intensities on the mercury and thallium temperatures.

It was the purpose of this experiment to consider the sensitized fluorescence of indium. Thus, data was obtained on eight sensitized fluorescence lines of indium. Four of these lines corresponded to similar transitions in thallium. These were 2933, 3256-59, 4102 and 4511A lines, which corresponded to the 3230, 3519-29, 3776 and 5350A thallium lines respectively. The additional indium lines recorded were the 2710, 2775, 2837 and 3039A.

It was observed that the intensities obtained for all the indium lines were weak compared to those of the thallium lines. Indium lines did not exhibit the temperature dependence as was observed with thallium. These observations are to be explained in the following discussion.

From Table I, it was observed that near every indium fluorescent line, there was a mercury line of approximately the same wavelength except for the 4511 and 3256A indium lines. These scattered mercury lines were intense compared to the weak indium fluorescent lines. Since it was impossible to completely resolve these close lying indium and mercury lines, the mercury lines contributed to the intensity readings. Thus the intensities recorded

for these indium lines were maximum intensity readings except for the 4511 and 3256A lines in that they included scattered light from the source.

Experimentally, this effect was verified as follows: Using photomultiplier techniques, indium lines 4511 and 3256A appeared relatively weak. Spectrographically, however, as seen from Plates I and II, these lines were the most prominent of the indium sensitized fluorescence lines.

Theoretically indium lines 4511 and 4102A should have intensity ratios of approximately two to one. Photomultiplier techniques would indicate the 4102A line as being the more intense of the two. This again illustrated the probability that with the exception of the 4511 and 3256A indium lines, the recorded intensities may be considered only as upper limits of possible intensities.

The difference in response to the mercury temperature variations is of interest and shall now be considered. Swanson (10) in his earlier work, verified experimentally in this paper, has attempted to explain the intensities observed with thallium. His explanation hinged on the justified assumption that the population of the mercury 3P_1 atoms decrease with mercury vapor pressure and the mercury 3P_0 atoms increase with mercury vapor pressure. In addition it was necessary to apply Winan's $\Delta J = 0$ rule in obtaining a satisfactory discussion of the observed variation in intensity in levels which were selectively excited by the two different mercury states.

Another factor which undoubtedly played a part in the intensity of the individual thallium lines was the possibility of reabsorption of all lines whose transition ended on the ground state. Transitions ending on the first metastable level have less probability of absorption due to the smaller population of that state. This was concluded since the thallium metastable

level lies .97 volts above the ground state.

Indium, on the other hand, has its metastable level only .26 volts above the ground state. At indium temperatures above 800°C, the metastable state would be expected to be populated, as well as, the ground state. Through reabsorption processes, all indium sensitized fluorescence lines resulting from transitions to either the $5^2P_{3/2}$ or $5^2P_{1/2}$ level would be expected to be of low intensity due to this absorption as was observed.

The explanation of the lack of temperature variation of indium sensitized fluorescence lines 4511 and 3256A, whose assigned intensities are probably the most nearly correct of those observed, is as follows: This temperature independence of these lines of indium is probably dependent on the same closeness of the ground and first metastable levels of indium. While with thallium all excitation was from the $6^2P_{1/2}$ state to states with j values of 3/2 and 1/2 when excited by mercury 3P_1 and 3P_0 atoms respectively, indium because of its two low lying populated states was not so selective. Excitation to indium states with j values of 3/2 and 5/2 would be most probable by mercury 3P_1 atoms and to 1/2 and 3/2 states by mercury 3P_0 atoms. This caused a doubling of the number of excitation levels. This doubling of excitation levels plus the large number of indium levels, whose excitation energies lie close to the excited mercury levels, apparently led to an ultimate excitation of the indium $6^2S_{1/2}$ and $5^2D_{5/2}$ states which are relatively independent of mercury exciting state. This would have accounted for the independence of these two lines.

This appeared also to be verified by the observations made on the other indium sensitized fluorescent lines, although the observed intensities could only be interpreted as maximal intensities.

CONCLUSIONS

The objective of this experiment was to compare the intensities of corresponding lines of thallium and indium and also to gain further information concerning indium sensitized fluorescence. In comparison of the intensities of the thallium sensitized fluorescence lines with corresponding transitions in indium, it must be concluded that the indium intensities were very much weaker than those of thallium. This was to be observed from the graphs of the indium lines, even though these were considered to be maximum intensities. It also was concluded from the plot of the 4511 and 3256A lines, which were considered to have the most nearly true relative intensities, that there was no temperature dependence for the intensities of the indium lines, as was found for thallium sensitized fluorescence.

These two effects in indium appeared to be largely the result of the closeness of the first metastable state in indium to the ground state. At the temperatures of the observation, both states were populated; and thus any observable selective process in the excitation due to Winan's partial selection rule was nullified. In emission, all transitions observed were to these two lower states and were strongly absorbed accounting for the low intensities.

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It was the objective of this experiment to compare the intensities of corresponding lines of thallium and indium. In the comparison it was observed that the intensities of thallium sensitized fluorescence lines were greater than those of corresponding indium lines. This result was explained by the fact that in indium the metastable level was only .26 volts above the ground state. At high temperatures both of these states were highly populated, and thus all indium sensitized fluorescence lines which ended on these levels were strongly reabsorbed.

It was also observed that indium did not exhibit the temperature dependence, as thallium did. This was explained for the 4511 and 3256A indium lines, whose assigned intensities are probably the most nearly correct of those observed, in the following manner. The temperature independence is probably dependent on the closeness of the metastable and ground states of indium, and on the doubling of excitation levels, and on the large number of levels close to the excited mercury levels. These factors led to an ultimate excitation of the $6^2S_{1/2}$ and $5^2D_{5/2}$ levels which are relatively independent of the mercury exciting state.

It could be concluded from these results that the intensities of indium sensitized fluorescence lines were weaker than those of thallium, and indium did not exhibit a definite temperature dependence.