ABSORPTION SPECTRA OF CERTAIN DYES
IN THE
VISIBLE AND ULTRAVIOLET

Thesis for Degree of M. S.

Melvin Arthur Leach

1927.

INTRODUCTION

An absorption spectrum is the spectrum of light that has passed thru a medium capable of absorbing a portion of the rays. It is characterized by dark spaces, bands, or lines. There are absorption spectra of organic and inorganic chemical compounds. This inquiry treats of the absorption spectra of that class of organic compounds called dyes.

ABSORPTION OF LIGHT

There are three types of absorption; namely, line, general, and selective. When light from an incandescent solid is allowed to pass thru a gas at a lower temperature the gas absorbs certain definite wave lengths, This causes dark lines to appear in the spectrum where bright lines would have been if the gas had been the source of light. This is known as line absorption. The absorption of light by lamp black and thin layers of glass illustrates the second type of absorption. In this type there seems to be a certain amount of absorption regardless of the wave length of the incident light, and bodies that exhibit general absorption give a continuous spectrum when heated to incandescence. Some substances exhibit marked absorption in one or more parts of the visible spectrum. Thus the spectrum of light transmitted thru a solution of a blue dye will often show an absorption band in the orange while a solution of an orange dye will quite likely show an absorption band in the blue. These need not be the only bands present for some dyes like indigo may exhibit several bands. This ability to select and absorb certain groups of wave lengths is known as selective absorption.

Absorption is a powerful agent in the production of colors in natural bodies. When white light passes thru any substance some of its components are wholly or partially absorbed and if the material absorbs some of the simple colors more strongly than others the emergent light will be colored and this we call the color of the body. Many of our dyes appear one color when viewed by reflected light and quite a different color when viewed by transmitted light. For example, if a thin film of indigo is rubbed on a glass plate, it will present a rose color when looked at and a blue when looked thru. The light reaching the eye by reflection consists of two parts one the portion that has been refused admission and the other scattered in the ordinary manner after penetrating the substance a little below the surface and suffering absorption. This mixture determines the color as seen by reflection and gives the body surface color often different from its body color.

The character of the absorption exerted by any substance within the visible range can be observed by receiving the transmitted light on the slit of a spectroscope and noting the dark regions in the spectrum. Since this method is limited in its range and is not accurate, a quartz spectrograph which gives the absorption spectra in the ultraviolet as well as the visible and makes the record photographically is used instead. The light as it passes thru the spectroscope is bent from its path and the shorter wave lengths suffer the most bending. In this way, the incident light is separated into its component parts and the process of separation is called dispersion.

There is a close relation between dispersion and absorption. It is found as an absorption band is approached from the side of the longer wave lengths the index of refraction is greatly increased and as an absorption band is approached from the side of the shorter wave lengths the index of refraction is greatly decreased. Hence by noting the change in the index of refraction with a change in wave lengths we can tell approximately the location of an absorption band.

Whenever radiant energy is absorbed by a substance it is transformed into some other form of energy. The commonest transformation is that in which the luminous radiations are spent in warming the body, the absorption of light increasing the kinetic energy of the molecules. Certain substances, however, possess the peculiar propperty of emitting light when illuminated, without any appreciable rise in temperature. The emitted light is usually of a different color from that of the absorbed radiation, and the emission may continue for some time after the illuminating light is cut off. If the emission ceases as soon as the exciting radiations are cut off from the substance, the phenomena is called fluorescence; if it continues for an appreciable time, the term phosphorescence is applied. Fluorescence is shown by liquids and gases, while phosphorescence is shown by solids.

Absorptive power is the ratio of the amount of radiation of a given wave length which is absorbed to the total amount received, provided no rays pass thru the substance. The law which governs the rate of decay of light intensity in passing thru any medium may be readily obtained. If I_0 represents the intensity of the light which enters the surface, I_1 the intensity after passing one centimeter, I_2 the intensity after passing thru two centimeters, and so on: then we should expect that whatever fraction of I_0 is absorbed in the first centimeter, the same fraction of I_1 will be absorbed in the second. That is, if an amount aI_0 is absorbed in the first centimeter aI_1 is absorbed in the second, and so on. We have then

$$I_1 = I_0 (1 - a)$$
$$I_2 = I_1 (1 - a) = I_0 (1 - a)^2$$
$$I_3 = I_2 (1 - a) = I_0 (1 - a)^3$$

and so on, so that if I is the intensity after passing thru a thickness "t" in centimeters, $I - I_0 (1-a)^t$

We might call (a), which is the proportion absorbed in one centimeter, the coefficient of absorption of the medium. It would, however, not then apply to the case of a body for which the whole light is absorbed in less than one centimeter. It is better then to define the coefficient of absorption as a quantity "K" such that (K/N) of the light is absorbed in 1/Nth part of a centimeter where "N" is a large number. The formula then becomes $I = I_0 e^{-kt}$ where "e" is the base of the Naperian system of logarithms and "K" is a constant which is practically the same as "a" for bodies which do not absorb very rapidly.

In case of solutions, if the absorption of the solvent is negligible, the effect of increasing the concentration of the absorbing solute is the same as that of increasing the thickness in the same ratio. This is known as Beer's law. There are cases in which this law fails.

A law which has not been known to fail is credited to Lambert. It is as follows: "Each layer of equal thickness absorbs an equal fraction of the light which traverses it." If we consider layers of the thickness of a single molecule, we can say that each molecule absorbs an equal fraction of the light which passes it.

What causes absorption of light? What is the mechanism by which the work is done?

Preston says that the vibrations of the ether are taken up by the matter molecules and these in turn vibrate and become centers of disturbance. The matter molecules are intimately bound up with the ether and the energy of the ether vibration is converted into energy of motion in the matter molecules. If we consider any system of matter molecules it will be easily inferred that some ether vibrations will be much more powerfully absorbed than others, viz. those most competent to excite that vibration which the matter molecules execute freely. It is well known that a series of slight taps may excite a considerable oscillation in a pendulum, the condition being that the taps be timed to the period of swing of the pendulum. The same point is illustrated in the resonance of organ pipes which are excited by vibrations of their own free period. Hence it follows that of the multitude of waves in a pencil of white light those which will be most freely absorbed by any substance will be those which synchronize in period with the free vibrations of the matter molecules. The molecules absorb waves of their own period of vibration, and these again are the waves which the molecules will excite when they become centers of disturbance.

Consequently, it is to be expected that different kinds of matter should absorb waves of different periods, or rays of different refrangibility; that they should thus exercise selective absorption.

According to Baly, the most important fact that must be taken into consideration is the great influence that the solvent has upon the absorption of various substances. A consideration of this influence of the solvent will show that some account must be taken of the residual affinities of the two, solvent and substance dissolved. If the chemical properties of substances be considered it will be quite evident that every atom or group of atoms in a compound must possess residual affinity to a greater or a less extent. Since the possession of residual affinity tends to endow a compound with the power of forming additional compounds with other substances it may be said that the existence of residual affinity is accompanied by the existence of force lines in the surrounding ether. Every atom or group of atoms must be the center of a field of force in the ether, the strength of which depends upon the amount of the residual affinity present in each case. The independent existence of these various fields of force round about one molecule is manifestly impossible, such a condition must be metastable. There must ensue a certain amount of condensing together of the force lines accompanied by the escape of energy. The resulting condensed system must have a decreased chemical reactivity compared with the original meta-stable condition. In fact, if the system be entirely closed it will have no chemical reactivity at all, and it is only when the closed system is unlocked that it can show any chemical reactivity. It does not necessarily follow that altho the condensing together of the force lines must occur, the resulting system is entirely closed. The system may still possess some small residue of reactivity which however in any case will be very much smaller than that of the meta-stable uncondensed form.

In order that a compound exert its true reactivity it must be unlocked by some external means. One way of opening up such a condensed system would be to supply free energy to it. It is a well known fact that certain reactions are catalyzed by the action of light as, for example, the union of hydrogen and chlorine. Before the hydrogen and chlorine molecules can react upon one another, it is necessary that their closed systems be opened up, and it would seem that this opening up can be affected by means of the influence of the light rays. The light rays must therefore be doing work against chemical forces. This at once gives a rational explanation of the absorption of light by substances.

Namely, that the light is doing work against the chemical forces which tend to produce the closed systems, and that the necessary free energy is supplied in this way.

The mutual influence of two centers of residual affinity causes a shift of the absorption maximum towards the longer wave lengths. The amount of the mutual influence which takes place, and the resulting absorption are functions of the new system of solvent and solute which is produced. The failure of Kundt's rule is therefore not surprising, for the shift in the absorption bands is not necessarily a function of the optical properties of the solvent, but is a function of the relation between the residual affinity of the solvent and that of the solute. It also follows that Beer's law must fail to hold in certain cases where there is a marked mutual influence between solvent and solute. If, for example, at a given concentration this influence is not the maximum possible for a pair of substances, then this influence will change when the solution is further diluted. The result will be that the absorption exerted by the two solutions can not be comparable as required by Beer's law. The great difference between the absorption exerted by many substances in various states can be explained by this theory.

Substances such as aniline exert no selective absorption when in the liquid condition but do so in the state of vapor and in solution. The differences Hartley and Purvis have noticed between the absorption of compounds in the vapor state and in solution is naturally due to the fact that in the latter case the solvent has partially opened the condensed field of the aniline, and it is this combined system that is exerting the absorption, while in the former case the light is acting on the aniline molecules alone. On the other hand, Purvis discovery that a very thin film of liquid aniline exerts no selective absorption shows that under these circumstances the force fields are entirely closed, and cannot be opened by the light.

According to Stark's view there exists at the surface of the atom a limited number of separable electrons which play the part of valency electrons, that is, they serve to bind together the chemical atoms in a molecule by the electrical forces exerted. A valency electron may be completely separated from its atom and become attached to a second atom. The first atom in this way assumes a positive, the second a negative charge, and we thus obtain a positive and a negative atom-ion. Stark supposes that band spectra are characteristic of the valency electrons, and that the carrier of a band spectrum is a single atom or a molecule composed of several atoms. He divides the band spectra of a substance into two classes which he calls short wave and long wave bands. In the short wave bands, formed by absorption, the intensity diminishes in passing from shorter to longer wave lengths, but in the long wave bands, the intensity diminishes in passing from longer to shorter wave lengths. Stark believes that the short wave and the long wave bands of a valency electron are dynamically coupled together in such a way that the absorption of light with the frequency of a short wave band is necessarily accompanied by a simultaneous absorption of light with the frequency of a long wave band. When light is absorbed in a short wave absorption band which is shaded towards the red, fluorescence and photo-electric effect appear; but neither occur during the absorption of light in a long wave band which is shaded towards the ultraviolet.

The Thomson-Einstein theory of absorption claims that light is transmitted and absorbed only in definite sized packets, or quanta. These quanta are dependent for their size upon the frequency of vibration and always equal "h N" in which "h" is Planck's constant of action and "N" is the frequency of the incident light. If a molecule is in the proper condition to receive one of these bundles of energy, absorption takes place; if not, reflection or transmission is the result. Whether a molecule is in the proper condition to receive a certain quantum of light depends to a great extent upon the size (h N) of the quantum, some quanta being more readily taken in than others. This accounts for selective absorption.

Among the most recent theories of band spectra and hence for selective absorption is the following which was taken from an article by Smith, Boord, Adams and Pease in the American Chemical Society Journal, May 1927. This article states that according to the quantum theory of band spectra each line of such a spectrum results from the simultaneous accurrence in a molecule of quantum jumps of three distinct types. Each of the three types of quantum numbers- electronic, molecular vibrational, and molecular rotational- may have initially any one of a variety of values which may change either by a positive or by a negative integer. Consider the energy which is absorbed when a molecule passes from a less to a more excited state. Let E' devote the total energy of the molecule in its more excited state and E" its total energy in the less excited state. Each of these energies E' and E" is a function of a set of electronic quantum numbers (e_1, e_2, e_3 -----) a quantum number "n" associated with the vibration of the nuclei and a quantum number "m" associated with the rotation of the nuclei about some axis in the molecule. Assume that the total energy can be divided into three parts which depend solely on "m", "n" and the e's respectively. Let E_e be the electronic energy depending only on the e's; E_n, the vibrational energy depending only on "n"; and E_m , the rotational energy depending only on "m". Then $E = f\ (e_1, e_2 ----- n,\ m) = E_e + E_n + E_m$ where $E_e = f\ (e_1, e_2 ----- o,\ o)$; $E_n = f\ (e_1, e_2 ----- n,\ o) - E_e$, and $E_m = f\ (e_1, e_2 ----- n,\ m) - E_n$. Since $h\ N = E' - E''$ the frequency of any line which is absorbed by the vapor is $N = \frac{E' - E''}{h} = (1/h)\ (E_e' + E_n' + E_m'\ ) - 1/h\ (E_e'' + E_n'' + E_m''\ )$ and $N = (1/h)\ (\Delta\ E) = (\Delta\ Ee + \Delta E_n + \Delta E_m\ )$. In general $N = N_e + N_n + N_m$; $N_e > N_n > N_m$. The values of both N_n and N_m may be either positive or negative. In the near infra-red region of the spectrum, band spectra are characterized by the omission of the term N_e . In the far infra-red, both the terms N_e and N_n are absent. In line spectra the term N_e alone is present. All the lines on a band spectra are collectively designated as a band system. Each individual band in a band system is determined by a pair of values (N_1 N_2)

The structure of each band in a band system is determined by changes in "m". The changes $M_1 \longrightarrow M_2$ are limited in accordance with the correspondence principle by the rules $(m_2 - m_1) = \pm 1$, or 0. Hence N m is usually relatively small. The origin of a band may be defined as frequency $N = N_e + N_n$, corresponding to $N_m = 0$; similarly, the origin of a band system may be defined as the frequency N_e, corresponding to $N_n = 0$ and $N_m = 0$.

The article states further that the three prominent band systems which occur in benzene also occur in cyclohexene, ethyl ether, methyl normal amyl ether, and ethylene chlorohydrin. It seems that this result should be interpreted as meaning that the electronic frequency number and the vibrational frequency number are not influenced by the composition and structure of these organic molecules. Hence, it becomes of importance to inquire concerning the atoms or groups of atoms from which these bands may arise and yet remain unchanged in these compounds. There are in the compounds under consideration only two common linkages, the carbon-hydrogen linkage and the carbon-carbon linkage. It seems probable that one or the other of the linkages gives rise to these systems of bands. In a large number of organic liquids containing the carbon-hydrogen linkage there are a number of absorption bands in the near infrared region of the spectrum. These bands have been attributed by Ellis to the carbon-hydrogen linkage. By calculating the position of the bands in the infrared region from data obtained in the ultraviolet, using Henri's formula, the agreement between observed and calculated values seems to be close enough to justify the conclusion that the bands in the ultraviolet are due to carbon-hydrogen linkage, if those in the infrared are due to that cause.

WHAT HAS BEEN DONE
and
WHAT I HOPE TO ACCOMPLISH

A considerable amount of work has been done upon the absorption spectra of organic compounds in the visible region by various experimenters among whom may be mentioned Ostwald in support of the electrolytic dissociation hypothesis. Vogel and others have studied the absorption spectra with the hope of finding some connection between the constitution of a body and its absorption spectrum. Hartley in his investigations upon ultraviolet absorption spectra has discovered certain most important facts concerning chemical constitution and absorption spectra. Dr. Uhler working under the direction of R. W. Wood made photographic records of the absorption spectra of more than one hundred aniline dyes. A quartz cell containing a wedge shaped layer of liquid was placed in contact with the slit of a large grating spectroscope. The photographs showing the position and forms of the absorption bands in the visible and ultraviolet have been published in the form of an atlas by Uhler and Wood. K. S. Gibson and his associates published in the United States Bureau of Standards Science Paper

Number 440 the results of a very careful examination of the spectral transmissive properties of seven permitted food dyes in the visible, ultraviolet and near infra-red. Among still later writers, W. C. Holmes in 1924 determined the influence of constitutional variation in dyes upon their relative absorption in aqueous and alcoholic solutions; W. R. Brode, in 1925, determined the effect of solvents on the absorption spectrum of a single azo dye; and R. W. French in 1926, determined the effect of variations in concentration of dyes in solution upon their quantitative determination spectrophotometrically.

A vast amount of good work has been done by various experimenters but a still greater amount of work may need to be done before we understand; first, the relation between the absorption of light by a substance and its physical condition; second, the relation between the absorption of light by a substance and its chemical constitution; third, the mechanism by which absorption of light takes place.

In hopes of determining the relation between the absorption of light by a substance and its physical condition, I have examined by means of a small quartz spectrograph, a Hilger wave length spectrometer, and a large

Gaertner Quartz Spectrograph, the absorption of light by a variety of dyes in the visible and ultraviolet regions. Much of my work has been a checking of the work of others, and in only one particular do I claim anything absolutely new, and that is in the method of determining the absorption of light by a dry dye.

EXPERIMENTAL WORK

The apparatus used in the South Physics Laboratory at Michigan State College is shown in Plate I. Plate II shows a photograph of the apparatus represented in section on Plate I. The rheostats and meters are not shown on either plate.

The light used was obtained from an electric arc between metal electrodes. Copper electrodes were used for a comparison spectrum because copper gives a spectrum with a fair number of quite well placed lines whose wave length could be readily obtained. Iron electrodes were used for light to be passed thru the solutions and other absorbing media because iron has so many lines in its spectrum that it forms an almost continuous spectrum which is needed for absorption work. The current used was furnished by a 220 volt direct current source which was controlled by two large rheostats not shown in the plates.

Since the spectrograms were to include the ultraviolet as well as the visible range of frequencies, it was necessary to use quartz lenses. These were nearly three inches in diameter and about six inches focal length. L_1 (See Plate I) was used to make the rays which entered the absorbing media parallel and L_2 was used to focus the rays on the slit of the spectrograph.

The screen "S" was used to prevent light from the arc, except that which passed thru the hole, from reaching the spectrograph.

The absorption cell (Plate I "T") consists of two glass tubes which fit loosely one inside the other. Both of these tubes have a flange at one end which is ground flat and square to the axis; upon this flange is cemented a quartz plate in each case as shown at Q_1 and Q_2. "B" is a bulb tube sealed to the side of the outer tube and serves to take up the solution when the thickness of the layer is decreased by pushing in the inner tube. At "R" a broad india rubber band is slipped over the junction in order to keep it water tight. The dimensions of the outer tube are 15 cm long and 2.2. cm in diameter. The outer tube has a millimeter scale etched upon it; this scale is so ruled that its zero division coincides with the inner side of the quartz plate "Q_1" , and thus the reading of the inner side of the plate "Q_2" upon the scale gives the thickness of the solution.

The quartz spectrograph, of which "C" is the collimator tube, "P" the quartz prism, Cm the camera, and "F" the film holder, was made by the Gaertner Scientific Corporation, and has four possible adjustments. The slit "S1" could be closed or opened very small amounts by means of a fine threaded screw.

The collimator lens L_3 could be shifted to secure proper definition of image of the slit and the camera tube "Cm" could be changed in its angle with the prism. The film holder "F" could be raised or lowered and held firmly at any desired height within the range of its movement.

The apparatus used at The Dow Chemical Company, Midland, Michigan, thru the kindness of Dr. Herbert Dow, President of that Company, was similar to that shown in Plate I with the following exceptions. For one group of experiments a Hilger Wave Length Spectrometer of the constant deviation type was used instead of the small quartz spectrograph. A photograph of this instrument is shown in Plate III, fig. 1. The design of this instrument is based on the now well known principle of the Constant Deviation prism (See Plate III, fig. 2) which may be considered as made up of two 30 degree prisms and one right angled prism from the hypotenuse of which the light is internally reflected as shown. The telescope and collimator are both rigidly fixed, since to pass thru the spectrum it is only necessary to rotate the prism. The table on which the prism stands is rotated by means of a fine steel screw, the print of which pushes against a projecting arm on the prism table. To the screw is fixed a drum of duralumin (See Plate III fig. 3) on which the wave length of the line or print under observation is read off direct as indicated by the index which runs in a helical slot. The Hilger instrument is limited in its use to the visible spectrum.

For another group of experiments, a large quartz spectrograph was put in place of the small one. This instrument (Shown on Plate IV fig. 1) was of the Littrow Auto-Collimating Type and gave a spectrum from 210 Mu Mu to 790 Mu Mu about 600 mm long. The light enters by the slit and is reflected by a small quartz prism along the camera tube where it is collimated by the quartz lens; it then enters a 30 degree quartz prism whose back surface is covered with tin foil amalgam; such rays as traverse the prism at minimum deviation strike the back surface at right angles and are reflected to retrace their own path, the lens forming an image on the photographic plate. This arrangement is equivalent in every important respect to a two-lens spectrograph with a 60 degree Cornu prism of the same length of face. The quartz prism has a face 98 x 57 mm; the lens has an aperture 70 mm and focal length of 1700 mm. Prism and lens are mounted on a slide which can be shifted to focus by rack and pinion motion. The prism table can be rotated to photograph different parts of the spectrum. Both the shift and the rotation are made entirely automatically by turning a lever on the outside of the instrument. The instrument is so designed that three different positions of the prism will photograph the entire range from 210 Mu Mu to 790 Mu Mu in three exposures. Each of these is taken in an individual film holder with focal curve carefully worked out against which the film is pressed by means of clamps. The size of film used is $2\frac{1}{2}$ inches by 10 inches and it may be set to successive exposures by means of a rack and pinion adjustment.

All that is required for taking photographs is (a) Setting the slide carrying lens and prism to one of the three positions as indicated by a scale on the outside of the instrument and turning the lever to adjust both position of slide and rotation of prism automatically. (b) Choosing the film holder corresponding to this position. (c) Making the exposure.

For still other experiments, not only the large spectrograph was substituted for the small one, but the following substitutions were made for the absorption cell; First, a pyrex tube about one half inch internal diameter and about 18 inches long was put in its place. The tube was wrapped with alternate layers of insulated copper wire and asbestos.

The asbestos was held in place by sodium silicate. Second, a board with about fifteen narrow slots perpendicular to its edge and having coated quartz plates in several of the slots was substituted for the absorption cell (See Plate IV fig. 2.)

The dyes used were obtained by Prof. Morell from the following sources: Putnam dyes, Monroe Drug. Co. Quincy, Ill.; Diamond package dyes, Wells and Richardson Co. Inc. Burlington, Vt.; DuPont dyes, E. I. DuPont DeNemours and Co. Wilmington, Del.; Dow indigo, Dow Chemical Co. Midland, Michigan. The aqueous solutions of the dyes were made by carefully weighing on a chemical balance one gram of the dye and dissolving it in 100 c.c. of distilled water. Then 10 c.c. of this solution was diluted to 100 c.c. with distilled water thus making a solution that contained .1 g. of dye in 100 c.c. of water, or .001 g/c.c. If this solution was too dense it was diluted again until by trial it was found to be of proper optical density. The indigos not being soluble in water were first sulphonated. For example, a one gram sample of the dye was placed in 40 c.c. of concentrated sulphuric acid and heated for two hours at a constant temperature of 55 degrees centigrade. The resulting solution was diluted by distilled water as statedabove. The vapors were produced by placing a thin layer of the dry dye in a pyrex glass tube, around which was wound a coil of insulated copper wire, and turning on the current until a suitable vapor density was obtained. The solid films were obtained by rubbing the dry dye on quartz plates by means of a cloth until a very thin coating was formed on the plate.

To determine the absorbing qualities of any sample in solution, vapor, or solid form it was necessary to let light pass thru varying depths of the samples and then thru the spectroscope to the film where it left its peculiar imprint upon adjacent portions of the same film. In the case of the solid form, where the dye was in a very thin coating upon quartz plates, the light from an iron arc was allowed to pass thru a number of plates and then thru the spectrograph to the film in the film holder. When sufficient exposure of the film in a given position had been made the light was shut off from the slit, the film was moved to expose an adjacent portion to the light and, after lessening the number of plates in the path of the beam, another exposure was made. This process was continued until an exposure was made with no plates in the path of the light. Two more exposures, one on each side of the previously exposed portion, were made using a copper arc.

This completed one negative and formed a spectrogram. Prints of some of these negatives are shown in Plates V to XI inclusive.

DISCUSSION OF RESULTS and CONCLUSION

The plates are arranged in numerical order at the back of this thesis and the right hand end of each print represents that portion of the spectrum which extends toward the red. In case of Plate VIIand Plate VIII, Fig. 2 and Fig. 3 respectively, belong at the left of Fig. 1; Fig. 1, respresenting the visible portion of the spectrum; Fig. 2, the near ultraviolet; and Fig. 3, the far ultraviolet. There is a slight overlapping of range covered by Fig. 1, Fig. 2, and Fig. 3, Plates VII and VIII, which can be determined by consulting the comparison spectrum at the edge of each print. Plates IX, X and XI have the prints arranged so that they are in register, that is a given wave length on one print is directly opposite the same wave length on the adjacent print. The purpose of this arrangement is to enable one to determine quite readily the effect upon an absorption band of a change in form or a change in temperature.

The absorption bands are outlined on the prints by means of white dots. In some cases, these white dots do not appear to represent the edge of an absorption band.

This is because some of the fainter portions of the negative were lost in printing, black dots being used on the negative to represent the boundaries of bands.

In all cases, the bands were formed by allowing the light from an iron arc to pass thru the absorbing media. Plates V to VIII inclusive, also IX Fig. 1, IX Fig. 2, X Fig. 1, and XI Fig. 1 show the result of using various depths of dye solutions. Plate IX Fig. 3 shows the result of using various optical densities of the dye vapor, and Plate X Fig. 2 also Plate XI Fig. 2 show the result of using the dry dye as a solid film upon a varying number of quartz plates.

A comparison of Fig. 1 and Fig. 2 Plate V will show the need of using panchromatic films to record the absorption at the red end of the spectrum. Fig. 1 shows a print of a spectrogram made with a process film, while Fig. 2 shows (other conditions remaining exactly the same) the print obtained by using a panchromatic film. The process film not being sensitive to red gives no record of its transmission and its print (See right hand side of Fig. 1) shows only the left edge of the absorption band leaving one to infer that the absorption continues into the infra-red. The panchromatic film gives a nicely formed band with its maximum absorption, which is represented by the peak of the band, at a wave length of about 5200 Angström units. An orange Diamond Package Dye concentration .0001 g/c.c. was used for Fig. 1 and Fig. 2 Plate V.

A glance at Fig. 3 and Fig. 4 Plate V shows that the absorption in Fig. 4 is much the greater. This is due to a greater concentration, the strength of the Putnam yellow dye being .001 g/c.c. in Fig. 3 and .01 g/c.c. in Fig. 4.

The solutions from which Fig. 5 and Fig. 6 were obtained appeared the same shade of blue to the naked eye, the first mentioned being a Putnam royal blue, concentration .0001 g/c.c.; and the second a sulphonated indigo, concentration .00001 g/c.c. The peak of the absorption band in the visible region is in each case near wave length 5800 Angström units, but the absorption in the case of the royal blue is much greater including both the yellow and green regions while the indigo absorbs only the yellow. The absorption of the indigo in the ultraviolet is indicated by two large bands while the royal blue has three narrow ones.

The little white dots on the comparison spectrum at the top of Fig. 5 were used to locate certain lines when taking comparator readings for the determination of wave lengths by means of Hartmann's formula.

For the comparator readings and computed wave lengths see Table I at the back of thesis. Table II shows comparator readings and computed wave lengths for Plate VI.

Plate VI shows three radically different absorption bands in the visible region. The Putnam dark blue shown in Fig. 1 gives an absorption band which extends from a wave length of about 4750 A. U. to a wave length of about 6150 A. U. and has its maximum at about λ5650. The Putnam olive green shown in Fig. 2 has two absorption bands with maxima near λ6600 and λ 6000 respectively also streng absorption in the blue and violet. Fig. 3 shows a small band in the green. This is a Putnam scarlet dye and Plate VII shows the same dye in a little stronger solution as taken on the large quartz spectrograph. Again absorption is shown in the green and by following the order Fig. 1, Fig. 2, and Fig. 3, one will see several bands as he passes on thru the ultraviolet.

Plate VIII represents the absorption of a Dupont sulphonated indigo in the visible and ultraviolet. A dome shaped band near the right hand side of Fig. 1 extends from λ 5480 to λ6420 and has its peak or maximum absorption at about λ6040. A band in the near ultraviolet (Fig. 1 left side) has its peak at λ 3224, a band in the ultraviolet (Fig. 2) has its peak at λ2883, and a band in the far ultraviolet (Fig. 3) has its peak at λ 2492.

In Plate IX, Fig. 1 shows the absorption of a solution of Dow indigo at a temperature of 27 degrees centigrade, Fig. 2 shows the absorption of the same solution at a temperature of 60 degrees centigrade, and Fig. 3 shows the absorption of the same dye in vapor form. The prints are from spectrograms taken in the first position on the large spectrograph; hence, show only the visible and near ultraviolet.

A dye known as Pontamine Fast Orange S was used in making the spectrograms whose prints are shown in Plate X. Both prints are of the visible region, Fig. 1 showing the solution and Fig. 2 the dry dye. Plate XI shows the same dye in the same forms as Plate X but the spectrograms were taken in the ultraviolet instead of the visible portion of the spectrum.

The sensitiveness of the films and the character of the light used must be known when making a study of selective absorption by photographic methods, otherwise misleading impressions may be obtained. Solutions must be free from bubbles and precipitates and of proper concentration in order to form good absorption bands.

The number, size, location and shape of the absorption bands often show differences in colored solutions that would not be perceived by the eye. If the edge of an absorption band is a straight line at right angles to the length of the picture, it means that the position of this side of the band will not appreciably change with wide variations in the concentration. The right hand side of the principal band shown in Fig. 2, Fig. 4, Fig. 5, and Fig. 6 of Plate V represents this condition; and if this condition holds for all the bands of a given substance, which are within or near the confines of the visible spectrum, the color of the light transmitted by the solution will be the same no matter how much the concentration is varied. This is illustrated by Fig. 5 Plate V. On the other hand, if the edge of a band makes an oblique angle with the side of a spectrogram, it means that the color of the solution as seen by transmitted light changes with the concentration or with the depth of the liquid in the path of the light. The orange dye represented in Fig. 1 Plate X showed this in a pronounced way, for it appeared yellow in a dilute solution and red in a concentrated solution; furthermore, a thin layer of the solution appeared yellow while a thicker layer appeared orange.

My contribution is closely associated with the facts shown in Plates IX, X, and XI. The absorption band in Fig. 2 Plate IX has its peak about 50 Angström units farther towards the violet than Fig. 1; due apparently, to the temperature of the solution in Fig. 2 being 60 degrees centigrade instead of 27 degrees centigrade as in Fig. 1; and Fig. 3 Plate IX shows the peak of this same band moved about 700 Angström units towards the violet; due, in some way, to the heat energy necessary to put the dye in the vapor form. In Fig. 2 Plate X, the peak of the absorption band is about 300 Angström units farther towards the red end of the spectrum than the peak of the same band in Fig. 1. The solid form of the dye was used for Fig. 2 and its aqueous solution was used for Fig. 1, both being at room temperature; therefore, something besides difference of temperature must account for this shift. As a further check, spectrograms of the same solution and same dry dye were made in the ultraviolet to see whether the shift, if any, was in the same direction as before. A comparison of Fig. 1 and Fig. 2 Plate XI shows that every band in Fig. 2 is a little farther towards the red end of the spectrum than its corresponding band in Fig. 1. This seems to prove that each and every absorption band in the spectrogram of the solid dye, both in the visible and ultraviolet, is farther towards the red end of the spectrum than its corresponding band in the aqueous solution.

Why should the absorption found in the spectrograms of the aqueous solutions be displaced towards the violet end of the spectrum in case of the vapor, and towards the red end of the spectrum in case of the solid?

I venture the following explanation. Since heat tends to drive molecules apart and to give them greater freedom of motion, the more rapid light vibrations would be readily absorbed; and the band, in case of the vapor, would be farther towards the violet. In case of the solid, cohesion tends to draw the molecules together and to restrain their motion so that the slower light vibrations would be more readily absorbed and the absorption band would be shifted towards the red.

The facts presented prove that the absorption bands found in the spectrogram of an aqueous solution of a dye are displaced toward the violet end of the spectrum in case of its vapor and toward the red end of the spectrum in case of its solid form. There is, therefore, a definite relationship between the absorption of light by a substance and its physical condition.

BIBLIOGRAPHY

Acly and French
Study of the molecular constitution of certain organic compounds by the absorption of light.
Am. Chem. Soc. J. 49: 847-56 Mr. '27

Allen, H.S.
Photo-electricity pp. 215 and 218

Baly, E. C. C.
Spectroscopy Chapters I-V and XIV

Brode, W. R.
Absorption spectra of benzene-azo benzene
Am. Chem. Soc. J. 48: 1984-8 Jl. '26

Effect of solvents on the absorption spectrum of a simple azo dye.
Jr. Phys. Chem. 30: 56-59 Je. '26

Capper and Marsh
Absorption spectra of condensed nuclear hydrocarbons.
Chem. Soc. J. 128: 724-9 Ap. '26

Ellis J. W.
Band series in infra-red absorption spectra of organic compounds.
Phy. R. 27: 298-313 Mr. '26

French, R. W.
Effect of variations in concentration on dyes in solution upon their quantitative determination spectrophotometrically.
Ind. and Eng. Chem. 18: 298-9 Mr. '26

Gibson and others
Spectral transmissive properties of dyes; seven permitted food dyes, in the visible, ultraviolet and near infra-red.

Holmes, W. C.
Influence of variation in concentration on the absorption spectra of dye solutions.
Ind. and Eng. Chem. 16: 35-40 Ja. '24

Spectrophotometric i~~n~~dentification of dyes
Ind. and Eng. Chem. 17: 59-60, 918-19 Ja.'25

Jones and Strong
The absorption spectra of solutions of comparative rare salts.
Carnegie Inst. of Wash., Pub. 160 pp. 1-25, 87-100

Lowry and Owen
Studies of valency; absorption spectra of halogens and sulphonic derivative of camphor; origin of the ketonic absorption band.
Chem. Soc. J. 129: 606-22 Mr. '26

Merritt, E.
Form of the absorption bands in solutions of organic dyes and a relation between absorption and fluorescence.
Phy. R. Oct. 1927 pp. 694

Millikan, R. A.
The Electron Chapters V and X

Mullikan, R. S.
Electronic states and band spectrum structure in diatomic molecules; statement of the postulates, interpretation of Cu H, CH, and CH and CO band types.
Phy. R. 28: 481-506 S' 26

Nicholson, J. W.
General nature of band spectra.
Philos. May 6th ser. 50: 650-62 S.'25

Palkin and Wales
Azo dyes from alkaloids of ipecac root and their identification by means of the spectroscope.
Am. Chem. Soc. J. 47: 2005-10 Jl. '25

Preston, Thomas
The Theory of Light, pp. 379-397

Purvis, J. E.
Influence of different nuclei on the absorption spectra of substances.
Chem. Soc. J. 127: 2771-6 D.'25

Rice, F. O.
Effect of solvent on the ultraviolet absorption spectrum of a pure substance.
Am. Chem. Soc. J. 42: 727-35 Ap. '20

Riegel and Reinhart
Ultraviolet absorption of a series of eight organic substances of the gamma-pyridine type in water solution.
Am. Chem. Soc. J. 48: 1334-45 My '26

Smith and others
Ultraviolet absorption spectra of cyclohexene, ethyl ether, methyl normal amyl ether and ethylene chlorohydrin.
Am. Chem. Soc. J. 49: 1335-46 My.'27

Thomson, J. J.
Spectrum analysis and atomic structure
Sci. Am. S. 87: 382-3 Je. 14 '19

Uhler and Wood
Atlas of absorption spectra.
Carnegie Inst. of Wash. Pub. 71

Wales, H.
Absorption spectrum and its relationship to color.
Am. Chem. Soc. J. 45: 2420-30 O'23

Wood R. W.
Physical Optics Chapters XIV, XV and XX

TABLE-I

Film #13, Fig. 5 Plate 5

Comparator Readings	Value of "N" (Rdg.-40,015)	Computed Wave Lengths	Known Wave Lengths
57580	17565	5780 Å	5782 Å
57350	17335	5704	5700
55690	15675	5225	5218
55425	15410	5161	5153
55210	15195 *	5106	5106
53370	13355	4714	
50810	10795	4278	
49235	9220	4063	4063
48910	8895 *	4023	4023
45775	5760	3687	
44010	3995	3532	
41475	1460	3343	
40500	485	3278	3274
40015	0 *	3248	3248
37580	-2435	3108	
35015	-5000	2981	
33360	-6655	2908	
32010	-8005	2854	
30615	-9400	2801	
26570	-13445	2668	
22460	-17555	2555	
20650	-19465	2508	

Note:

* By using these values for "N" and the corresponding wave lengths, in the next column to the right, as standards for in Hartmann's formula,

$$\lambda = \lambda_o + \frac{c}{N - N_o}$$

we can compute the values of three constants. λ_o, C, and N_o. Using the values of these constants, the wave lengths of the remaining lines may be calculated from their comparator readings.

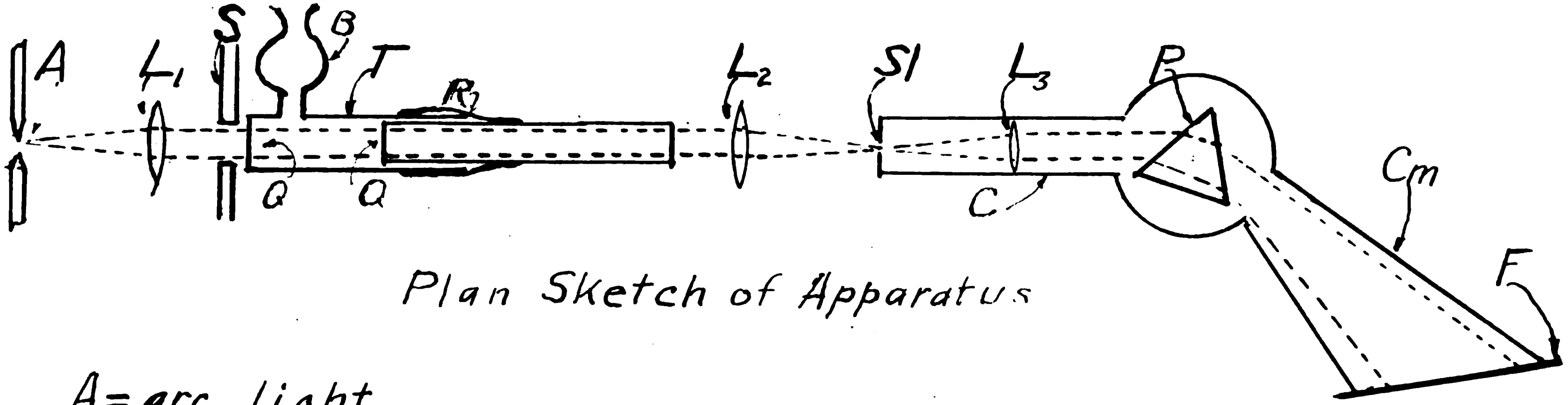
TABLE-II

Spectrogram M 4, Hilger Spectrograph

Comparator Readings	Value of "N" (Rdg.-0.3376)	Computed Wave Lengths	Known Wave Lengths
0.0326	-.3050	5895.1 Å	
0.2040	-.1336	5782.6	5782 Å
0.3376	.0000 *	5700.0	5700
1.1157	.7781	5291.4	
1.2766	.9390	5219.7	5218
1.4321	1.0945	5153.9	5153
1.5503	1.2127 *	5106.0	5106
2.7485	2.4109	4703.4	
2.9390	2.6014	4650.7	
3.1845	2.8469	4586.5	
3.3742	3.0366	4539.4	
3.4120	3.0744	4530.3	
3.5035	3.1659	4508.5	
3.6264	3.2888	4480.1	
3.9223	3.5847	4414.8	
4.0985	3.7609	4377.9	
4.6283	4.2907	4275.4	
5.9500	5.6124 *	4063.0	4063
6.2465	5.9089	4022.3	4023

*-See Note Beneath Table I.

PLATE I



Plan Sketch of Apparatus

A = arc light
L_1, L_2 = quartz lenses
L_3 = quartz lens in spectrograph
S = screen
T = tube containing the solution
Sl = slit of spectrograph
P = prism of "
Cm = camera of "
F = film holder of camera

PLATE II

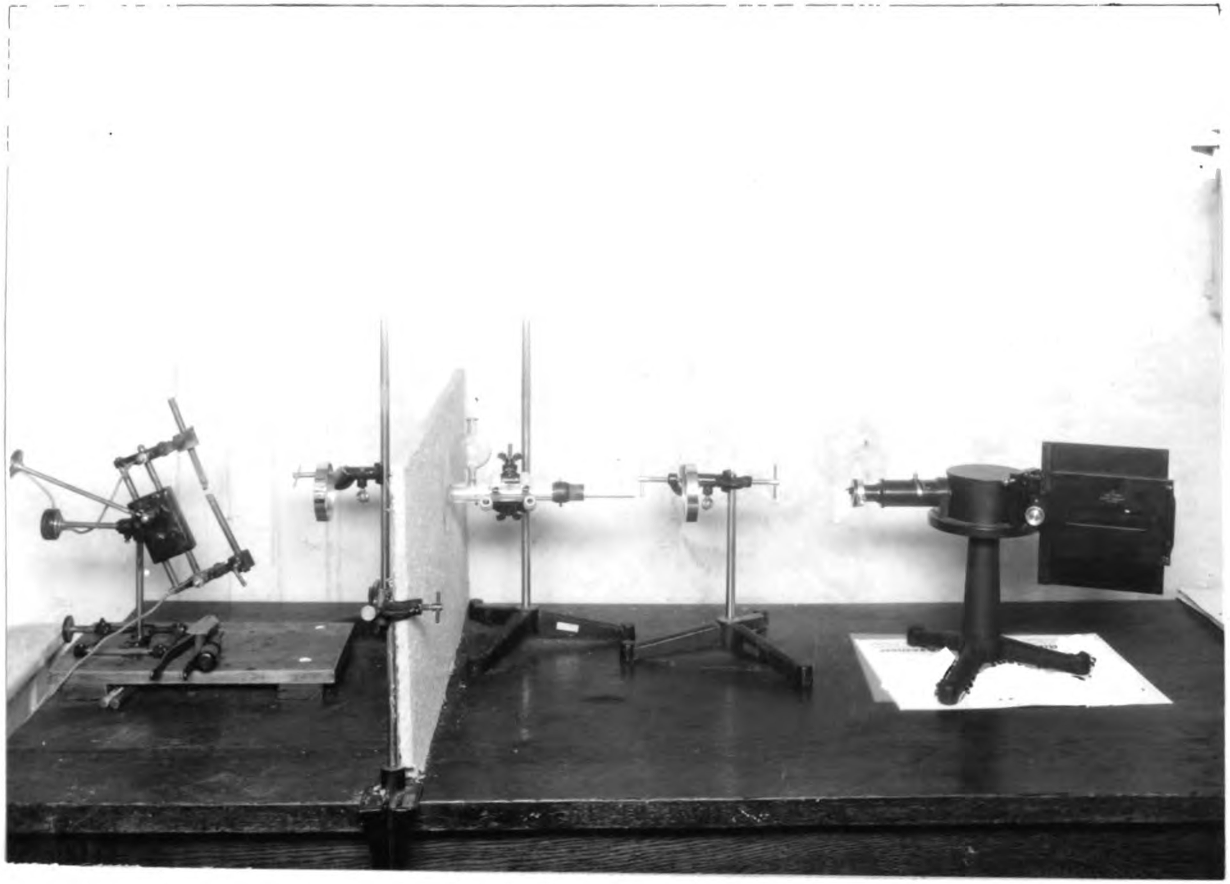


PLATE III

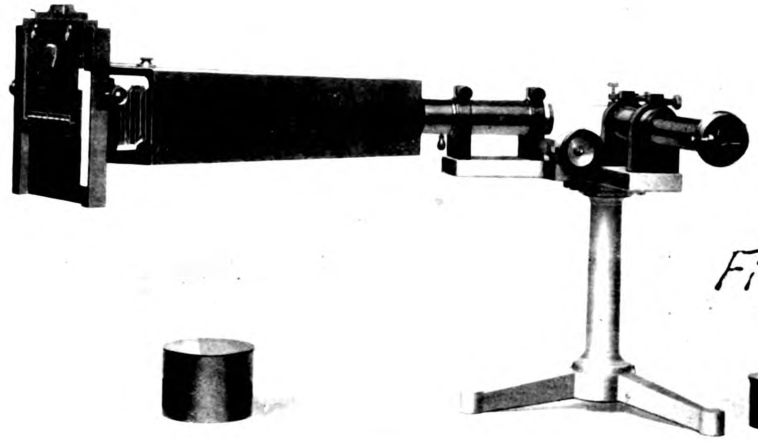


FIG. 5.

Fig1

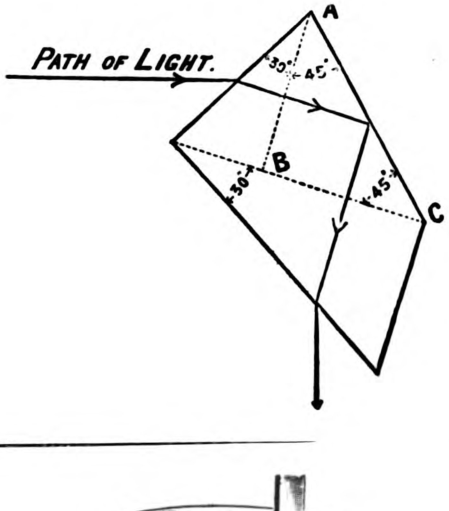


Fig2

Fig3

PLATE IV

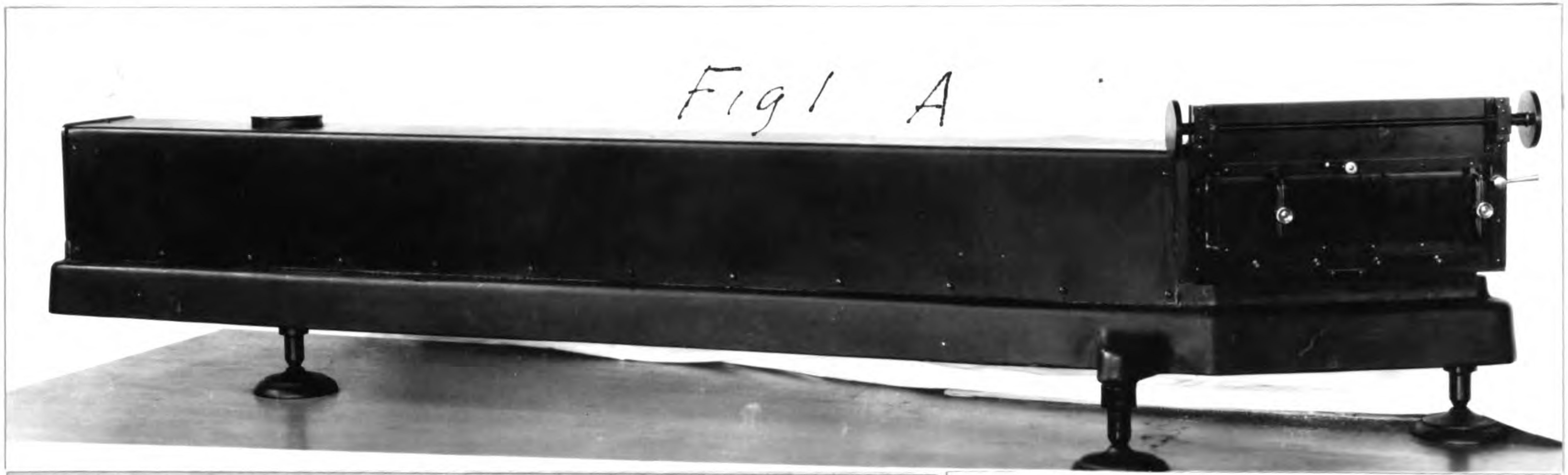


Fig 1 A

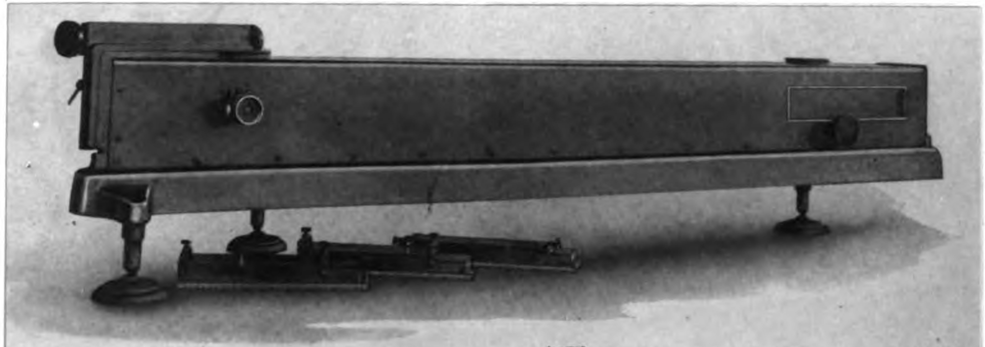


Fig 1 B

QUARTZ SPECTROGRAPH LITTROW AUTO-COLLIMATING TYPE

Fig 2

PLATE V


Fig.1


Fig.2

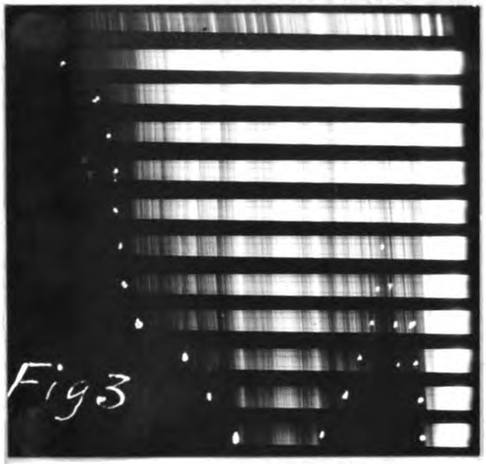


Fig.3


Fig.4

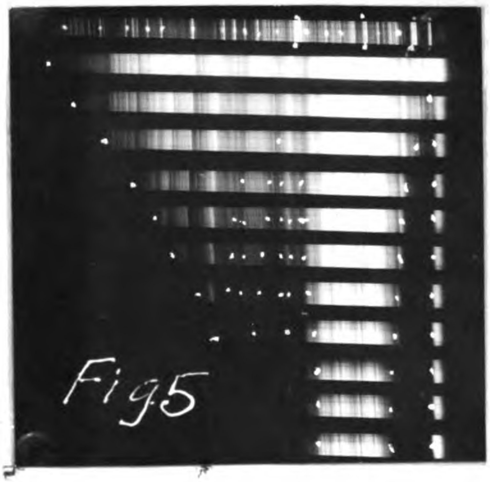


Fig.5

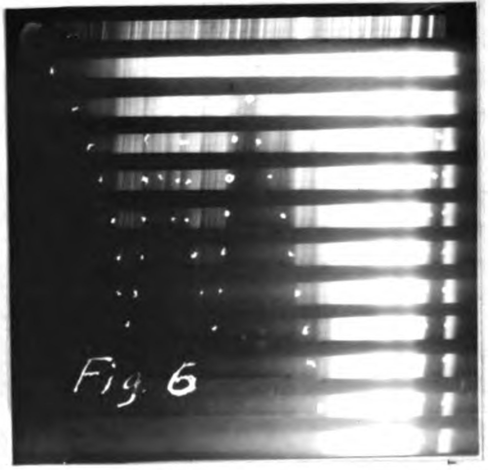


Fig. 6

PLATE VI

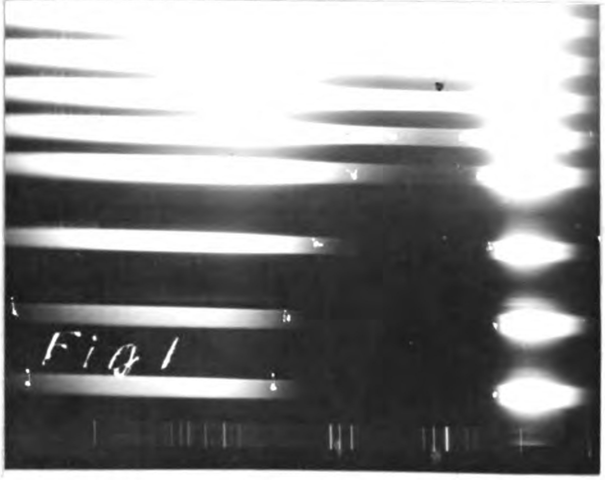


Fig 1

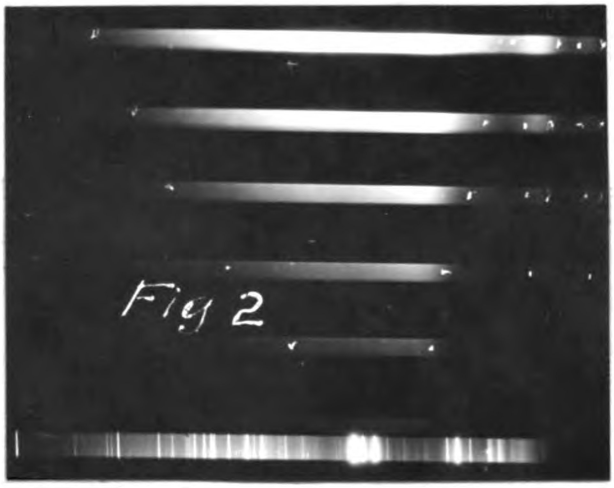


Fig 2

Fig 3.

PLATE VII

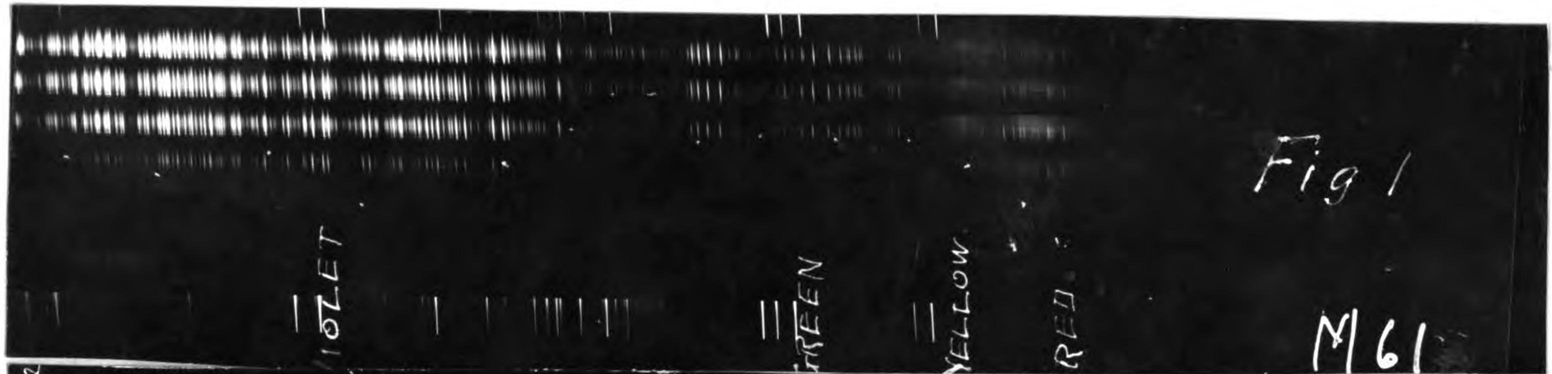


Fig 1

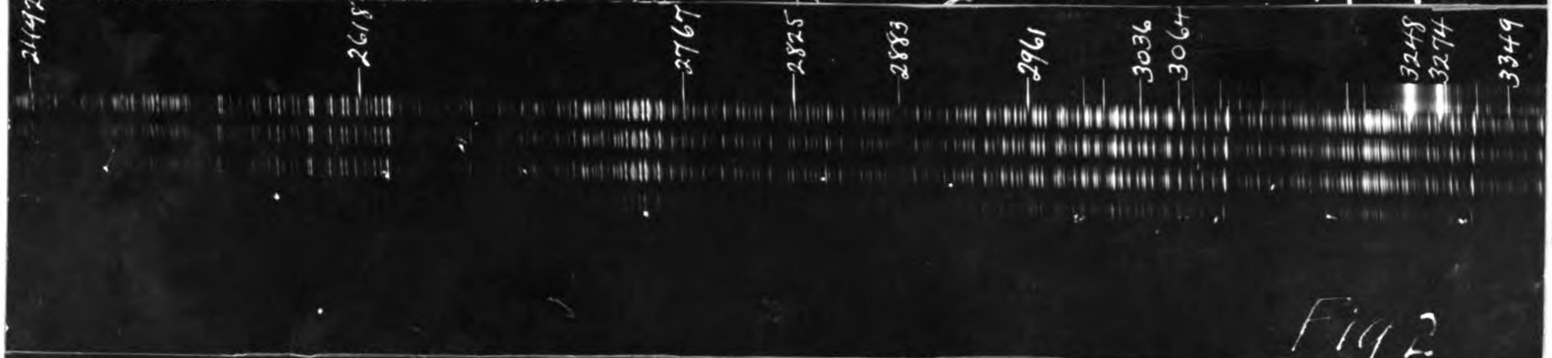


Fig 2

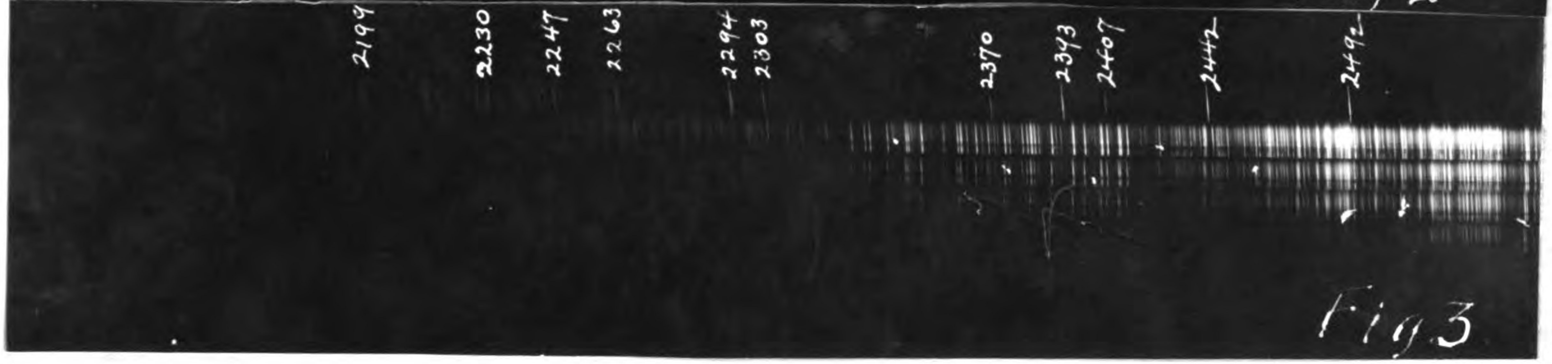


Fig 3

PLATE VIII

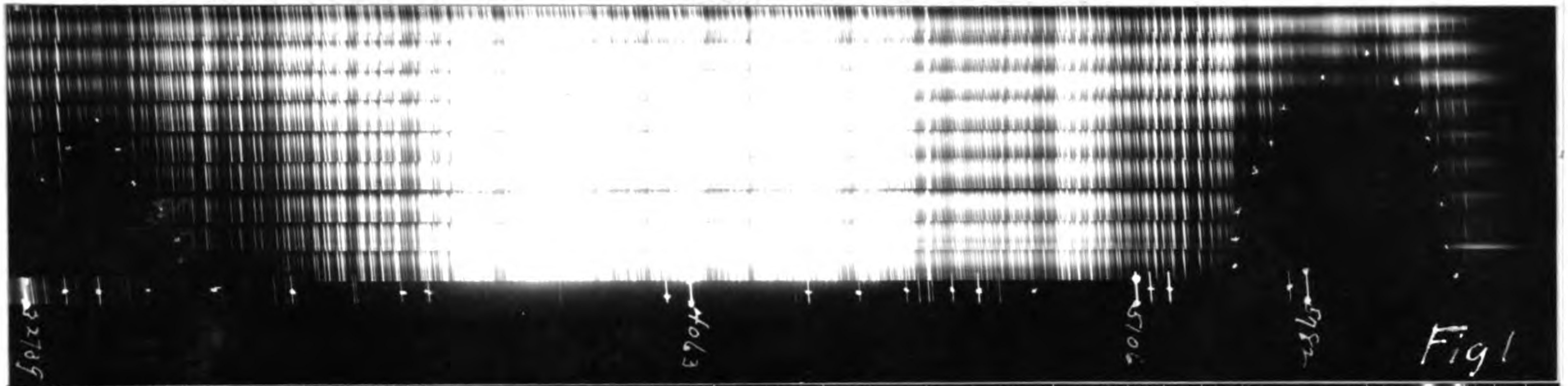


Fig 1

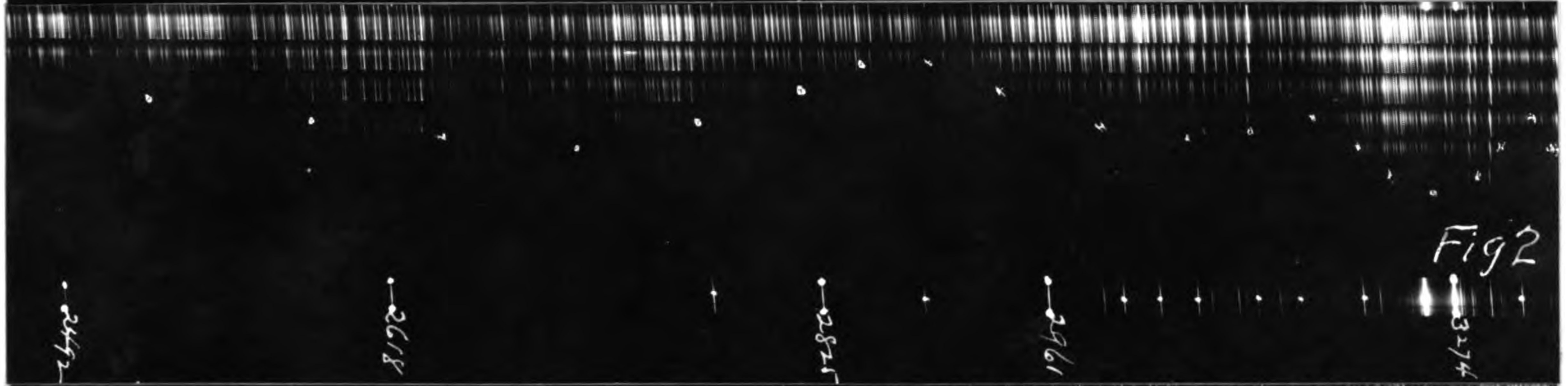


Fig 2

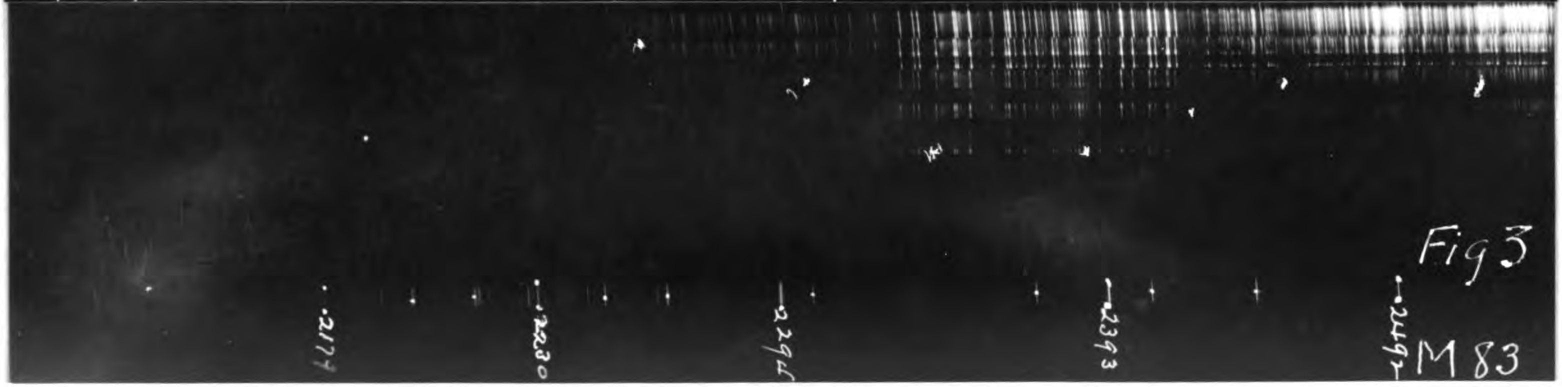


Fig 3
M 83

PLATE IX

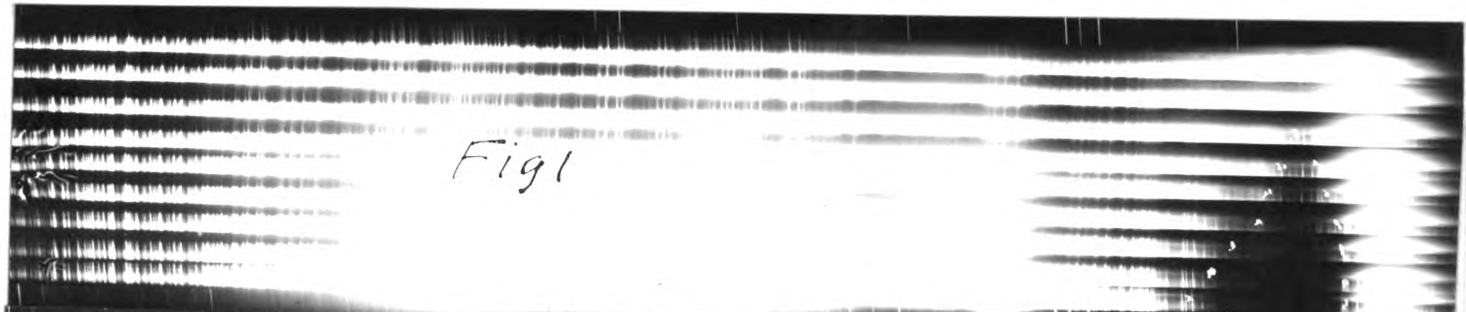


Fig 1

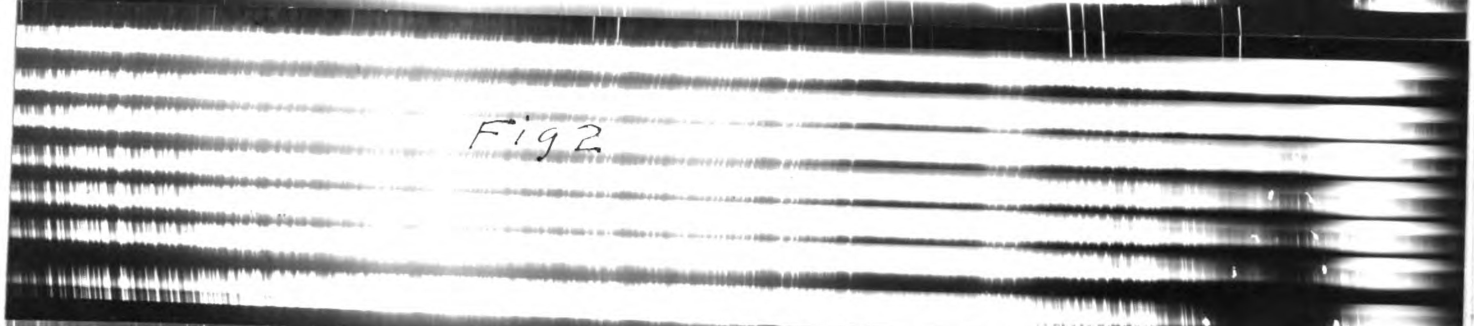


Fig 2

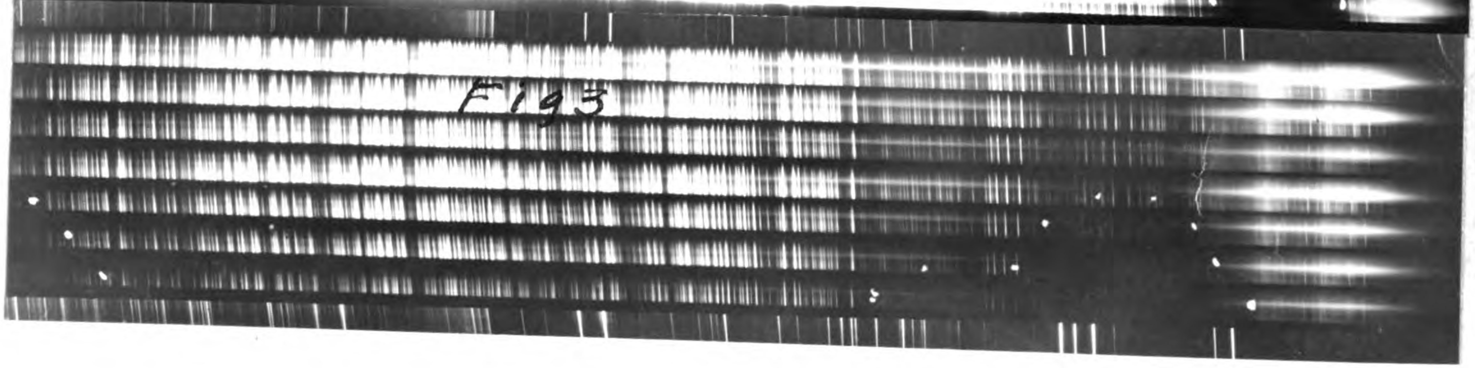


Fig 3

PLATE X

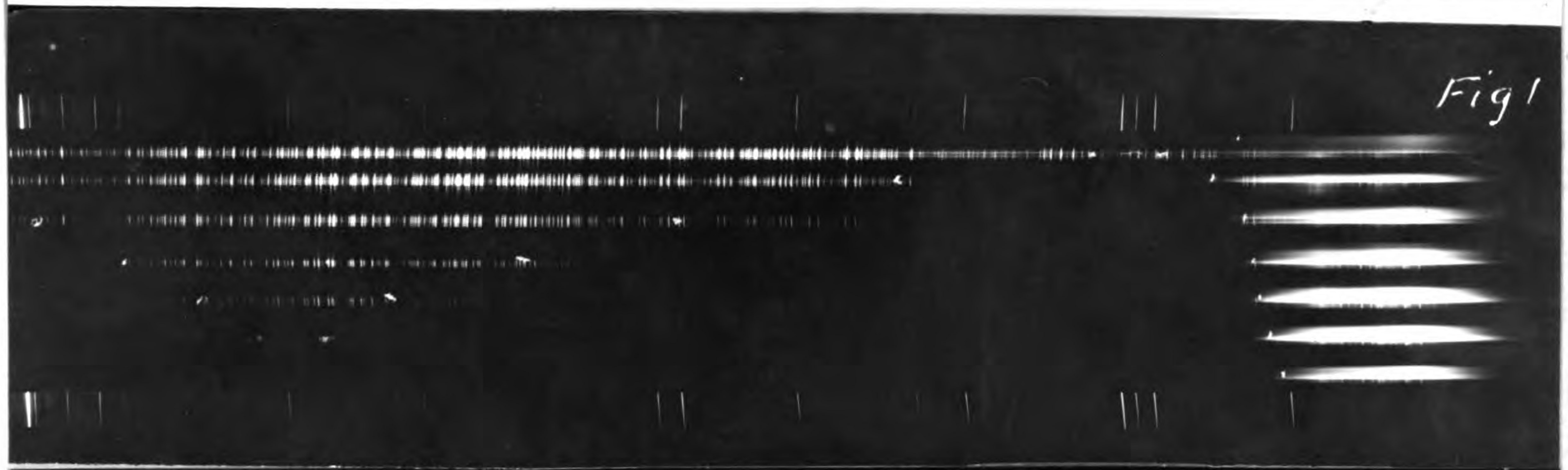


Fig 1

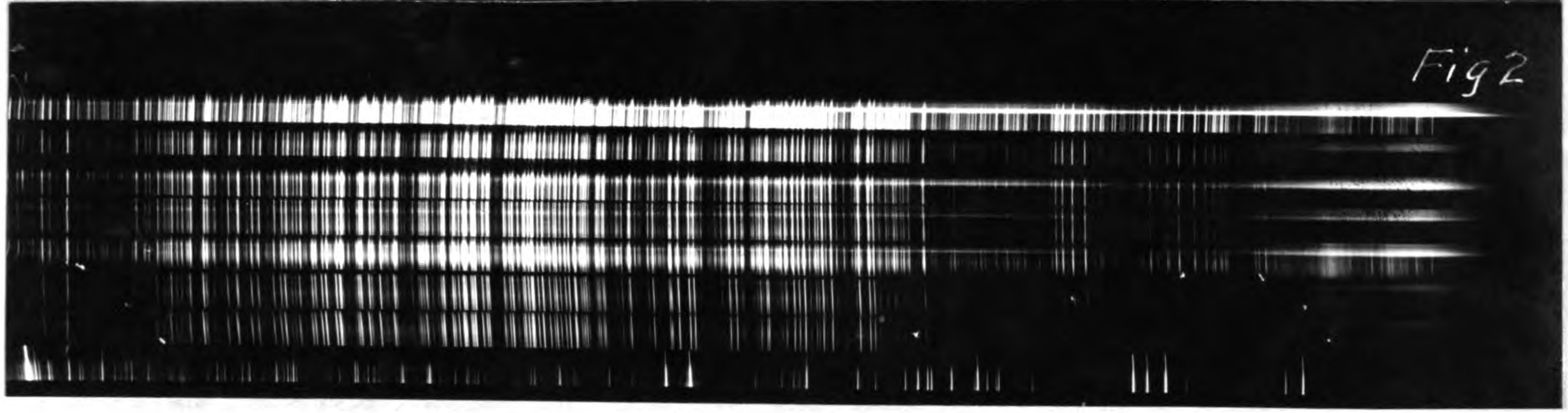


Fig 2

PLATE XI

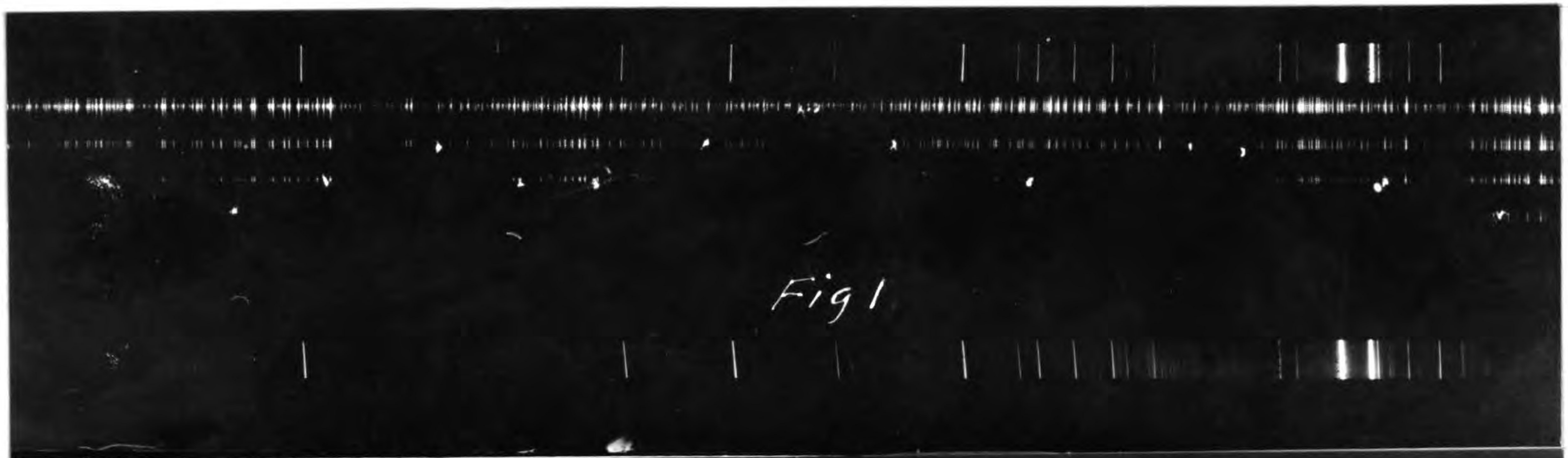


Fig 1

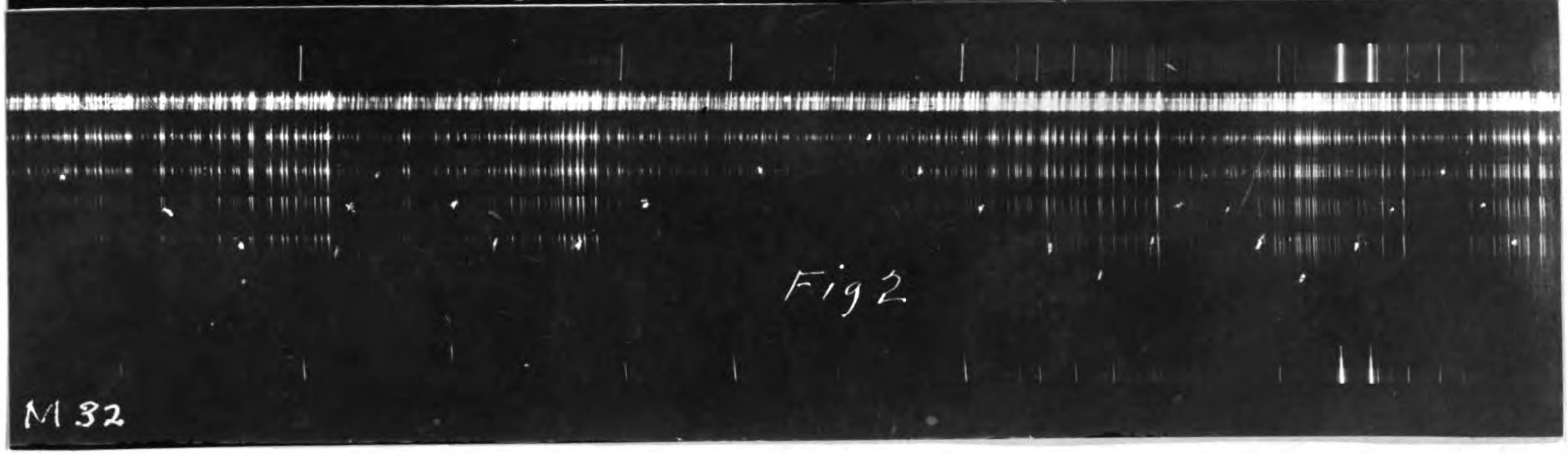


Fig 2