A CATHODE-RAY SPECTROGRAPH FOR STUDYING EMISSION AND ABSORPTION SPECTRA

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1. INTRODUCTION

EMISSION and absorption spectra in the ultra-violet and the visible regions are generally studied by first photographing the spectrum and then measuring the intensities of the lines and bands or the energy distribution in the spectrum by means of a micro-spectrophotometer. In the infra-red region the photographic method can be employed by using specially sensitized plates, only up to about 13,500 A.U. Beyond this wavelength the spectrum can be studied only by means of thermo-electric methods, viz., thermopile, bolometers and radiometers.

These methods generally take a considerable amount of time before the spectroscopic data are available for analysis. An instrument which will give an instantaneous measure of any of the emission or absorption lines and bands in any region of the spectrum will find great application in spectroscopic research especially in industrial spectro-chemical analysis.

The present paper describes such an instrument which presents instantaneously on a cathode-ray tube screen a graph of energy distribution against wavelength corresponding to any spectrum or region of a spectrum which is focussed on the instrument. The instrument can also be used as a spectrophotometer, and any spectrum plate can immediately be examined or measured on the fluorescent screen of a cathode-ray tube.

Recently, descriptions of two instruments by Daly and Sutherland of Cambridge¹ and King, Temple and Thompson of Oxford² have appeared. They have developed methods by means of which infra-red absorption spectra can be presented on the fluorescent screens of special cathode-ray tubes which have persistence of the order of 15 seconds. The instrument described here is entirely different in the operating principle and makes use of an ordinary short persistence cathode-ray tube oscillograph. A paper describing the earliest model of this instrument was presented by the present writer at a Symposium on "Atmospheric Processes" held at the Royal
Institute of Science, Bombay, in August 1946. Some later results were summarised in a note published in *Nature* and in communications to the Indian Science Congress in 1946, 1947 and 1948.

Here, it is proposed to give a description of the latest model of the instrument which incorporates a number of refinements and new techniques which enable it to be used for quantitative work.

2. WORKING PRINCIPLE OF THE CATHODE-RAY SPECTROGRAPH

The basic principle of the spectrograph developed by the writer is as follows:

An ordinary spectroscope is used for forming a sharp image of a spectrum on a slit which is kept in a steady state of oscillation by mechanical means. This scanning mechanism will be described fully in a later section. This slit executes a simple harmonic motion at a frequency which can be varied by adjusting the speed of the driving motor from about 1 to 25 or 30 cycles per second. The light passing through this slit is received by a photoelectric cell which has a caesiated silver (Cs-CsO-Ag) photocathode. The output of the photocell is fed to a high gain amplifier and then is applied to the vertical deflecting plates of a cathode-ray tube. The vertical displacement of the cathode-ray spot thus becomes dependent on the output of the photo-cell which in turn depends on the intensity of the light passing through the slit to the photocell.

To the horizontal deflecting plates of the cathode-ray tube is applied a voltage which is generated by an electric contact sliding over a potentiometer through which is maintained a steady unidirectional current. As the sliding contact is actuated by the movement of the scanning slit itself, the voltage of the sliding contact undergoes a variation which follows the movement of the slit and has the same frequency as the oscillation of the slit. The output of this potentiometer is amplified by a direct coupled amplifier and then applied to the horizontal deflecting plates of the cathode-ray tube. Thus, the horizontal displacement of the cathode-ray spot is controlled by the movement of the slit.

Now, when the instrument is in operation, the slit oscillates in the spectrum at a certain frequency. As the horizontal displacement of the spot is controlled by this movement of the slit, the spot on the screen oscillates horizontally in synchronism with the slit. At the same time, the spot is undergoing also a vertical displacement which is dependent on the intensity of the light passing through the slit at any given instant. As the slit moves along the spectrum, the intensity of the light undergoes a change according
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to the energy distribution in the spectrum being scanned. The cathode-ray spot thus gets a vertical deflection which corresponds to this energy distribution in the spectrum. The presence of any emission or absorption lines or bands in the spectrum produces an increase or decrease in the photoelectric current which is followed faithfully by the cathode-ray spot. The spot thus traces a curve on the screen of the cathode-ray tube, which is a graph of light intensity against wavelength in the region of the spectrum being scanned, the emission or absorption lines appearing as humps or dips respectively on this curve. The height or depths of these humps and dips obviously depend on the intensities of the emission or absorption lines. Fig. 1 gives a schematic circuit diagram of the complete cathode-ray spectro-

Fig. 1. Schematic Circuit Diagram of Cathode-Ray Spectrograph

graph as this apparatus is named. Figs. 7, 8, 9, 10, 12 and 13 show the type of patterns produced on the fluorescent screen by means of the cathode-ray spectrograph.
3. DESCRIPTION OF THE CATHODE-RAY SPECTROGRAPH

The complete apparatus is made up of the following five units:—

(i) The spectroscope,
(ii) The scanning mechanism,
(iii) The photocell and amplifier,
(iv) The synchronising voltage generator and
(v) The cathode-ray oscillograph.

Each group will be described here in outline.

(i) The Spectroscope

The spectroscope used in this apparatus is of the ordinary type with an equilateral prism of flint glass. The base of the prism is 7·8 cm. and its height 4 cm. Sunlight or the light from an artificial source like the mercury arc, pointolite or a sodium arc is focussed on a bilateral slit by means of a 3-inch glass lens with a focal length of 8 inches. An achromatic compound lens collimates the beam of light coming from the slit. Another achromatic lens with an adjustable diaphragm focusses a sharp image of the spectrum at a distance of about 18". With the prism adjusted for the angle of minimum deviation the visible spectrum covers a length of about 2·5 inches.

The glass prism and the system of glass lenses used in this spectroscope have sufficient transmission up to about 1·5 μ, which can be utilised for studying a number of absorption bands due to atmospheric water vapour and oxygen which are present in the near infra-red region.

(ii) The scanning mechanism

During the various stages of development of the instrument the author has used in succession three types of scanning device for the cathode-ray spectrograph, viz., (a) a slit mounted on an oscillating steel reed excited by an electromagnet at 50 cycles per second, (b) a rotating scanning disc with a single slit or a number of identical slits and (c) a reciprocating slit driven by an adjustable speed motor. Out of these the first two have been discarded in favour of the reciprocating type in the final instrument. But for the sake of completeness and as it helps in giving some idea of the design problems encountered during the development of this spectrograph, they will be described here briefly.

(a) The Oscillating reed.—In this scanning mechanism the slit is mounted on a thin steel reed which is fixed at one end. The length of the reed is such that it has a natural frequency of oscillation of 50 cycles per second. The
reed is maintained in a steady state of oscillation by an electromagnet excited from the 50 c.p.s. mains supply. The arrangement gives an amplitude of oscillation of about 1.5 cm. Fig. 2 shows the sketch of the arrangement.

The battery provides a d.c. bias on the 50 cycles per second exciting voltage so that the pull exerted on the reed operates only during half a cycle. If a pure alternating current is used the reed gets an excitation of 100 c/s as the electromagnet pulls during both the positive and negative halves of the cycles.

When the oscillating reed is used the voltage for the horizontal sweep of the cathode-ray spot is also obtained from the 50 cycles per second mains. But, for an exact synchronism between the motion of the scanning slit and the horizontal sweep of the cathode-ray spot which is essential for the satisfactory reproduction of the graph on the screen of the cathode-ray tube, it is necessary that the sweep voltage is in phase with the motion of the slit.

Although this scanning was found to be fairly satisfactory for examining narrow regions of the spectrum at a time, it had several defects. The slit was truly vertical only when it was in its normal position during the course of the oscillation. When it was pulled out by the electromagnet it was not parallel to the lines in the spectrum, but made a slight angle. This was equivalent to an effective increase in the scanning slit width and resulted in loss of resolution towards the edges. Thus, the true intensities of the lines could only be estimated in the centre of the pattern produced on the cathode-ray tube; and any band which had to be measured must first be centred on the screen. The second defect was that a base line corresponding to zero intensity of light could be produced if only one half of the oscillation of the slit was used for scanning and during the other half light was not allowed to pass through the slit. This not only reduced the already small scanning range of the slit but also necessitated the shifting of phase of the sweep.
voltage through a large angle in order to get the base line on the screen in
the correct position. This resulted in a certain amount of distortion in the
horizontal plane, i.e., the wavelength scale was distorted.

Another difficulty experienced was that due to the high speed of
scanning the output of the photo-cell contains very high frequency compo-
nents, especially if the region of the spectrum being scanned contains a
number of sharp absorption bands and lines. In order to deal with such
high frequencies the input circuit of the photo-cell amplifier requires great
care in designing and a certain amount of compromise has to be made in
choosing the load resistance for the photo-cell in relation to input capaci-
tance of the first valve and its grid current. A high load resistor which is
desirable for high sensitivity cannot be used as it results in a low amplification
at the higher frequencies. This effect is very pronounced if an ordinary
radio amplifier is used as the input valve. It can, however, be greatly
reduced by using special tubes of the miniature and electrometer type which
have extremely low input capacitances and low grid currents. As none of
these special tubes are available in India at present, we had to be satisfied
by reducing the load of the valve and making up for this loss of gain by
extra amplification in later stages. This, however, is not the best arrange-
ment, as it greatly increases the noise of the amplifier which appears as a
wavy pattern superimposed on the graph.

Except for these defects the arrangement was satisfactory and gave
steady patterns on the cathode-ray screen which could be examined with
great ease, especially while working with the bright solar spectrum.

(b) Rotating Scanning Disc.—This consists of a metal disc with a
diameter of about 12 inches and with a number of identical slits cut near
the edge of the disc which are about an inch apart. Fig. 3 gives a sketch
of the scanning disc. The disc is mounted in such a way that the spectrum
is focussed on these slits. As the disc is rotated by means of a small electric
motor, the spectrum is scanned by the slits which move across the spectrum
in succession. By placing a rectangular window whose length is exactly
equal to the distance between the slits, the spectrum is scanned by only one
slit at a time. As one slit moves out of the window, the next one appears
at the other edge. This arrangement had certain advantages over the
oscillating reed type of scanning. Firstly, by making the diameter sufficiently
large the error due to the change of angle of the slit due to rotation can be
greatly reduced, which gives better resolution at the edges. In a large disc
of about 15" diameter, it is possible to keep the distance between the slits
as large as 1.5 inches without introducing serious error due to change of
slit angle at the edges. Thus a larger portion of the spectrum can be examined at a time.

The main difference between the rotating disc and the oscillating reed type of scanning, however, is in the type of motion of the slits. While in the oscillating reed type the slit executes a simple harmonic motion, the slits in the rotating disc have a uniform and almost linear motion. The voltage with a sinusoidal waveform used for producing the horizontal sweep in the reed type of scanning is quite unsuitable for this rotating disc type of scanning. The linear motion of the slit in this type of scanning requires a sweep of a wave form of the type known as the "saw tooth" type (Fig. 4)

which is generally used for the time base in cathode-ray oscillography. Most modern cathode-ray oscillographs are provided with a "saw tooth" oscillator of this type which can be used for this purpose.
The frequency of this "saw-tooth" horizontal sweep voltage must be carefully adjusted so as to be exactly equal to the frequency at which the spectrum is scanned by the slit. The motor used for rotating the disc should be of the synchronous type so that once the adjustment of the sweep voltage frequency is made it should remain in synchronism. In addition to this the output of the photo-cell itself can be used for 'locking' the sweep voltage with the signal, thus holding the pattern stationary on the cathode-ray tube screen.

The base line is easily produced by masking alternate slits on the disc, but keeping the sweep voltage frequency the same. The spot traces the curve during one cycle and the base line during the next, when no light reaches the photo-cell. No shifting of the phase is required in this system.

One great difficulty which was experienced with this system is that to get a perfectly steady graph on the screen it is absolutely essential that all the scanning slits on the disc must be optically identical, and the distances separating them must also be exactly equal. This, however, may not prove to be a problem of great difficulty if such slits are produced by some type of photo-engraving method or are cut with an accurate punching machine. If the slits are not identical each slit traces a curve which has a different amplitude, and on the screen is seen a multitude of graphs instead of a single steady pattern. If photographic record only is required and no visual examination is to be made this difficulty can be overcome by using a single slit on the disc.

(c) The Reciprocating Slit Scanner.—All the problems and difficulties encountered in the oscillating reed and rotating disc type of scanning are solved in the reciprocating slit type of scanning which in conjunction with its automatic sweep voltage synchronising arrangement produces a perfectly steady pattern on the cathode-ray tube screen. Fig. 5 shows a sketch of this type of scanning mechanism.

D is a metal disc which is coupled to a small electrical motor by means of a pulley and string belt. The motor has an adjustable gear ratio mechanism so that the speed of the disc can be varied from 1 to about 30 revolutions per second. P is a smooth and well-polished metal plate which can slide freely in the metal frame F. This plate P is coupled to the rotating disc D by means of a coupling shaft C which has loose joints at A and B. The coupling arrangement is similar to that used in the ordinary reciprocating engine. The rotatory motion of the disc is communicated to the plate which slides back and forth in the frame F, and executes a simple harmonic motion.
On this plate is mounted an adjustable slit $S$ which oscillates when the motor is switched on. The spectrum is focussed on this slit.

It will be noticed from Fig. 3 that a circular slot has been cut in the disc $D$. This arrangement makes it possible to obtain the base line corresponding to the zero light intensity for the graph traced on the cathode-ray screen. This slit allows the light passing through the slit to reach the photocell only when the slit is passing from left to right, while on its return journey the light is cut out by the opaque portion of the disc.

Attached to the plate $P$ is a sliding electrical contact $K$ which moves over the potentiometer $G$ and generates the horizontal sweep voltage. The function of this mechanism will be explained later on. All that this mechanism does is that it keeps the slit oscillating at any desired frequency. It cuts out the light passing through the slit during half the cycle of oscillation and generates a sweep voltage which has the same waveform, phase and frequency as the motion of the slit.

The error due to change of angle is absent in this scanning mechanism as the slit remains vertical throughout the cycle. The sweep voltage is produced by the movement of the slit itself so that the two are automatically in perfect synchronism. Any drift in the speed of the motor, therefore, does not upset the synchronization.

(iii) The Photoelectric cell and Pre-amplifier

The light passing through the scanning slit is received by the photoelectric cell. Any photoelectric cell of the vacuum type, sensitive in the
spectral region to be studied may be used. In the present instrument 3 photo-cells have been tried, viz., 918, GL 929 and 71 A visitron. Out of these 918 and 71 A visitron are gas filled type of cells. GL 929, however, is of the vacuum type. Gas filled cells have a greater sensitivity than vacuum cells, but their characteristics are not stable and undergo unpredictable changes which make them unsuitable for quantitative work. Their noise level also is much higher than vacuum photo-cells. Gas-filled cells may, however, be used where percentage absorption in any particular band is to be measured as such measurements are independent of the characteristics of the photosensitive element. In fact, the present apparatus was originally developed in connection with our investigation of the total precipitable water vapour of the atmosphere as estimated by measuring the percentage absorption in some of the water vapour bands which occur in the near infra-red region of the solar spectrum between $0.75 \mu$ and $1.3 \mu$. (See Figs. 7 and 8.)

The output of the photoelectric cell has to be amplified several thousand times before it will have sufficient strength to produce the required deflection of the cathode-ray spot. This amplification is achieved by means of a high gain amplifier. The amplifier consists of two main sections, viz., (i) the pre-amplifier which forms a part of the photo-cell pick-up assembly and (ii) the main amplifier which may form a part of the cathode-ray tube assembly.

(i) The Pre-amplifier.—The design of the pre-amplifier presents some special requirements which have to be met in order to obtain the desired amount of detail in the record produced on the cathode-ray tube screen. When a spectrum containing a large number of lines and bands with various intensities is scanned the output of the photoelectric cell may contain frequencies which may be as high as 50 kilo-cycles per second. Therefore, the amplifier must be designed to have a gain which is constant from about 50 kc/s down to the frequency of the scanning slit oscillation (i.e., the repetition frequency of the trace) which may be sometimes as low as 2 or 3 cycles per second. The main difficulty in this respect arises if the load resistor of the photo-cell is very high and the input capacity and grid current of the first valve of the pre-amplifier are also high. At the same time as high a load resistor as possible is desirable, for, the sensitivity of the photo-cell circuit increases with the value of the load resistor up to a certain limit. But unfortunately an increase in the load resistor decreases the response of the amplifier at higher frequencies, especially if the input capacity of the first valve is also high. An increase in the load resistor increases the time constant of the input circuit and thus its response to frequencies which have a shorter period than this time constant is poorer. With a load resistor of
about 40 Megohms and a 6J7G as the input tube it was found that a
certain amount of detail in the record did not appear on the cathode-ray
tube screen. But if the speed of scanning is reduced, which is equivalent
to reducing the effective frequencies corresponding to this finer structure of
the curve, the detail again appears in the graph, as it now comes within the
range of the amplifier.

The load resistor had therefore to be reduced to about 4 to 6 Megohms
for a satisfactory performance, although this resulted in a considerable loss
in the sensitivity. An attempt to make up for this loss by adding additional
stages of amplification was not very successful as each additional stage adds
to the general noise level of the amplifier, and the 'mush' appears super­
imposed if the spectrum to be spectrum to be studied is weak, requiring the
use of the full gain of the amplifier. By using a miniature tube (IT4) as
the input valve the load resistor could be increased to a value of about 15
Megohms without appreciable loss in the detail of the graph, i.e., loss of
response at the higher frequencies.

The pre-amplifier which uses IT4 type tubes was mounted on a small
aluminium chasis together with the photoelectric cell, and the whole assembly
was enclosed in a small aluminium box with a rectangular slot equal in size
to the photo-cell cathode cut into its side so that the light passing from the
scanning slit could reach the photocathode. It was necessary to enclose
the whole pre-amplifier assembly in a metallic box as it is very important
to shield the photo-cell circuit from all stray fields and electrical pick-up,
which are present in all electrified areas. If this stray pick-up is not carefully
excluded from the input circuit of the amplifier by shielding as described
above, it appears after amplification with the desired signal and with almost
comparable amplitude, making it difficult to distinguish the signal from
the pick-up. The connections to the high tension and low tension voltage
supplies are made through shielded flexible wires. The output of the ampli­
fier is also transmitted to the main amplifier through a shielded cable. The
metal box and the shields of the connecting cables are earthed properly.

Another precaution which has to be taken is to keep the value of the
coupling condenser between the two IT4 stages of the pre-amplifier
consistent with the frequency response desired. Too low a value of the
coupling condenser produces a peculiar effect which is illustrated in Figs. 6 (a)
and 6 (b). If a voltage pulse with a wave form as in 6 (a) is applied to the
input of amplifier, the output waveform takes the shape shown in 6 (b).
With a value of 0·2 μfd this effect was reduced to a negligible value. The
explanation of this effect is again to be found in the time constant of the
circuit formed of the load resistors, coupling capacity and the grid resistor in the circuit.

(ii) The main amplifier.—This is of conventional design and should have a frequency range sufficient to cope with the signal delivered by the pre-amplifier. The built-in amplifier of a DuMont Cathode-Ray Oscillograph Model 208, was found to be quite satisfactory.

(iv) The horizontal sweep voltage generator

In the reed type of scanning slit and in the rotating disc the horizontal sweep voltage was usually obtained from a source which was independent of the motion of the scanning slit. It was necessary, therefore, to provide means for accurately synchronising the motion of the slit with the sweep voltage. It was also necessary to see that the waveform and phase of the sweep voltage exactly corresponded with the motion of the slit.

In the reed type of scanning it was generally found necessary to shift the phase of the sweep voltage in order to obtain synchronisation. This was achieved by passing the sinusoidal sweep voltage through an adjustable phase shifting network. The frequency of the mains supply was also found to undergo small irregular variations which added to the difficulties of obtaining a perfect synchronisation.

In the rotating disc type of scanner where the linear sweep voltage was obtained from a 'saw-tooth' oscillator, the slightest variation in the speed of the motor would upset the synchronisation and an adjustment of the oscillator frequency had to be made, until synchronism was established again. It was therefore felt that some arrangement should be provided by means of which the motion of the slit itself produced the sweep voltage, so that the waveform and the frequency of the sweep voltage will be identical.
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with the motion of the slit and an automatic synchronisation will be obtained. This has been achieved by means of the arrangement described below.

As will be seen in Fig. 5 on the projecting end of the plate P which oscillates in the frame F is mounted a spring contact K which slides over a wire-wound power resistor. A steady unidirectional current is made to flow through this resistor by connecting a battery of about 3 volts to 6 volts as shown in the diagram. One end of the resistor is earthed. Now, as the sliding contact moves over the resistor winding it undergoes a variation in potential. As the movement of the slider is produced by the movement of the slit itself, the waveform, frequency and phase of this variation of potential are exactly identical with those of the slit motion. Any change in the frequency of the slit is faithfully followed by the slider potential. This potential is applied to the input valve of a direct coupled amplifier and then applied to the horizontal deflecting plates of the cathode-ray tube. A slight ripple developed by the slider jumping over the windings of the resistor is easily filtered out by means of a condenser connected across the load resistor of the valve. A value of about $\cdot25 \mu$fd was found to be quite satisfactory for this purpose.

(v) The Cathode-Ray Oscillograph

The pre-amplifier delivers a sufficiently high output with spectra of normal brightness to be used for the direct application to the deflecting plates of a cathode-ray tube, and it does not become necessary to use any additional amplification except in cases where weak spectra produced by laboratory sources are being studied. It is therefore not absolutely essential to use a complete Cathode-Ray Oscillograph with its built in amplifiers and auxiliary equipment. But if an Oscillograph is available, it is advantageous to use it in view of the great ease of adjustment that is possible with the various controls that are provided in a modern oscillograph, and the built in amplifiers provide a reserve of amplification which is very useful for studying weaker spectra.

A DuMont 208 model Cathode-Ray Oscillograph was used in the present investigation and was found to give very satisfactory results. This Oscillograph has a five-inch screen. The Y-axis amplifier has a gain of about 2,000 with almost linear frequency response up to about 30 kc/s. The X-axis amplifier has a gain of about 50 which is quite sufficient as a sweep voltage input of up to 10 volts can easily be obtained by connecting a suitable battery across the potentiometer, in the scanning mechanism. A special circuit used in the oscillograph for the rapid vertical and horizontal positioning of the pattern is very useful. A transparent graph scale which
can be attached to the screen makes it possible to make direct measurement of absorption on the screen.

4. PERFORMANCE OF THE CATHODE-RAY OSCILLOGRAPH

Figs. 7, 8, 9, 10, 12 and 13 give the patterns produced on the screen when various spectra were being scanned.

Fig. 7 shows the near infra-red spectrum of sunlight. The absorption bands due to atmospheric water vapour and oxygen can be seen clearly. The bands from left to right are due to water vapour (\(\lambda = 73\mu\)), oxygen (\(\lambda = 76\mu\)), water vapour (\(\lambda = 79\mu\)), water vapour (\(\lambda = 93\mu\)). The percentage absorption in any of these bands can be measured immediately on the cathode-ray tube screen. It may be mentioned that the cathode-ray spectrograph was primarily developed for such measurements in the \(\rho\) and \(\phi\) bands at \(\lambda = 93\mu\) and \(\lambda = 13\mu\) respectively for the estimation of the total water vapour content of the atmosphere. The increase in air mass traversed by the solar rays in the morning or evening produces an appreciable deepening of these absorption bands. The changing amount of water vapour in the atmosphere from day to day is very strikingly reflected in the changes in the depths of these bands. A comparison of Figs. 7 and 8 will bring out this effect clearly. Fig. 8 was photographed on a clear afternoon in January 1947 while Fig. 7 was taken just before the onset of the monsoon in June 1947. The deepening of the band is quite pronounced, while the oxygen band is unaffected.

Fig. 9 shows the oxygen band at \(\lambda = 76\mu\) which has deepened towards evening due to the increase in air mass traversed by sunlight.

Fig. 10 shows the emission spectrum of a low intensity mercury arc. The lines shown in the diagram are from left to right, yellow \(\lambda = 5780\mu\), green \(\lambda = 5461\mu\), blue \(\lambda = 4916\mu\) and violet \(\lambda = 4358\mu\).

The intensities appearing in the graph are not the true intensities of the lines but those modified by the spectral response of the photo-cell and the transmission of the optics of the spectrograph. It is however possible to prepare a simple table of correction to be applied at various wavelengths by making use of the spectral response curve of the photoelectric cell used with the spectrograph. Another simple method of eliminating the error due to photo-cell characteristic is to use a mask of the same shape as the spectral response curve of the photo-cell in front of the photo-cell window. For example, Fig. 11 gives the response curve of a typical photcell with a caesium cathode. Now if a window having the shape of the shaded area in the above curve is cut into a mask and is placed before the photo-cell, it
will be seen that more light will be allowed to reach the photo-cells at wavelength, where it has a poorer response and the amount of light passing to the photo-cell at wavelengths where it has better response will be reduced. Thus the output of the photocell can be made almost linear in the whole of the spectrum.

With such a mask used, the amplitudes of the various lines appearing on the fluorescent screen will correspond to their true intensities.

Fig. 12 shows the absorption at \( \lambda \) 66 to \( \lambda \) 68 due to chlorophyll dissolved in acetone. The characteristic absorption band can easily be recognised by those who are familiar with chlorophyll spectra. As sunlight has been used in this measurement, the chlorophyll band appears superimposed on the solar spectrum. The atmospheric oxygen band at \( \lambda \) 76 can also be seen clearly beside the chlorophyll band.

These experiments demonstrate the utility of the Cathode-Ray Spectrograph for the rapid measurement of absorption in solutions and pigments of this type. Similarly, the transmission characteristic curves of any optical filter can immediately be recorded on this instrument.

Fig. 13 (a) shows the pattern produced when the image of a spectroscopic negative (from an original by R. S. Krishnan) showing the second order Raman spectra in diamond is projected on the scanning mechanism of the Cathode-Ray Spectrograph. The pattern produced may be compared with the microphotometer record of the same negative made with the conventional microspectrophotometer (Fig. 13 b). The Cathode-Ray
Spectrograph can thus be used as a spectrophotometer for the rapid examination or measurement of spectrographic plates. In Fig. 13 (a) the exact intensities have not been reproduced because the negative used was obtained by re-photographing a published photograph from a paper by R. S. Krishnan. Thus the negative used does not exactly correspond to the original negative from which the microphotometer record (Fig. 13 b) has been made, on account of the loss of contrast which usually takes place in the photo-block processing. The shapes of the bands and lines, however, compare satisfactorily with the original microphotometric record.

5. POSSIBLE FURTHER DEVELOPMENT OF THE CATHODE-RAY SPECTROGRAPH

The Cathode-Ray Spectrograph in its present form can be used for exploring the spectral region between about 0.34 μ in the near ultra-violet and about 1.7 μ in the near infra-red. It is thus possible to make measurements of the emission and absorption spectra with sunlight and laboratory sources like the sodium and mercury arcs, pointolites, etc. The spectral absorption of glass filters, dyes and some organic solution like chlorophyll from plants, etc., can also be studied with this instrument. The Cathode-Ray Spectrograph can also be used for the rapid examination and measurement of spectroscopic negatives.

The main limitations of the present model of the Cathode-Ray Spectrograph are its rather restricted spectral range and its low dispersion. In the ultra-violet the limit is set by the glass optics of the spectroscope used which transmit little below about 0.34 μ. In the infra-red the photoelectric cell is the limiting factor. Most commercially available photo-cells with Cs-CsO-Ag cathodes have their long wave thresholds at about 1.2 to 1.5 μ. Some special tubes with quartz envelopes can be used up to about 1.7 μ.

Recent developments in the making of photoconductive cells have, however, extended the longwave threshold up to about 6 μ, thus bringing this infra-red region also within the reach of photo-cells. It is hoped that it will soon be possible to make these new types of photo-cells which make use of extremely thin semi-conducting layers of lead selenide and telluride. By using these cells the region between 1 to 6 μ which contains the vibration-rotation bands of the hydro-carbon group and the hydrogen halides will come within the range of the Cathode-Ray Spectrograph. This will make the instrument a very powerful laboratory tool in the hands of the chemist and the industrial physicist who has to deal with chemical process controls in the laboratory, factory or refineries. The special application of this instrument in the petroleum industry is obvious.
As regards the dispersion of the spectroscope used in the present model it is adequate for the near infra-red region where it is being used for the estimation of the water vapour content of the atmosphere by measuring the percentage absorption in the ρ band (0.93 μ) and φ band (1.13 μ). A further increase in the dispersion of the spectroscope requires a corresponding increase in the sensitivity of the photo-sensitive element. The ultimate limit of the sensitivity of the photo-cell is, however, set by the noise level in the photo-cell circuit due to thermal agitations and ' shot ' effect, etc. This limit has almost been reached in the amplifier where the highest usable gain has been obtained.

A further increase in dispersion in the visible and ultra-violet region is, however, possible if photomultiplier type of cells are used. In these cells the primary emission from a photocathode is multiplied as much as a hundred thousand times by secondary emission from a series of anodes maintained at increasingly high positive potentials. The inherent gain of such tubes using about 9 secondary emission stages can be as high as 150,000 with a comparatively much smaller increase in the noise level. Thus the limitation imposed by the noise level in the ordinary photo-cells will be removed and it will be possible to study extremely weak spectra at high dispersion. In fact, cells of this type have been used for detecting Raman lines which by ordinary methods require hours of exposure with sensitive plates. Work along these lines is in progress.

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Fig. 7. Absorption bands due to atmospheric oxygen and water vapour in the near infra-red solar spectrum. (June 1947)

Fig. 8. Absorption bands due to atmospheric oxygen and water vapour in the near infra-red solar spectrum. (January 1947)
Fig. 9. Absorption due to atmospheric oxygen at 0.76 \mu m in the solar spectrum.
FIG. 10. Emission lines of a low intensity mercury arc.
(From left to right: 0.5780 \( \mu \), 0.5461 \( \mu \), 0.4916 \( \mu \), and 0.4358 \( \mu \).)

FIG. 12. Absorption in chlorophyll at 0.66 to 0.68 \( \mu \).
Fig. 13. Use of the Cathode-Ray Spectrograph as a Micro-Photometer.