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The construction of a new type of spectrograph and its use photographically and photoelectrically as an automatic recording spectrophotometer.

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SUMMARY

A new type of concave mirror plane grating spectrograph has been constructed. The mounting is that of a modified Ebert type and has all the advantages of that mounting whilst being more efficient in its use of the mirror.

The instrument can also be used as an automatic recording spectrophotometer by rotating the grating and scanning the spectrum across a slit behind which is mounted a photomultiplier tube.

The spectrophotometer has been used with D.C. sources such as arcs (using a D.C. amplifier and pen recorder after the photomultiplier); and modulated R.F. sources (using an A.C. amplifier tuned to the modulating frequency and pen recorder after the photomultiplier). The latter method using as it does two filter circuits, (the amplifier and pen recorder) reduces the noise band width of the system to remarkably small proportions and signal to noise ratios of better than fifty to one have been recorded at line intensities corresponding to exposures of half an hour on fast plates.

* This is an account of part of the work submitted for the Degree of Doctor of Philosophy at the University of Durham in September 1954.

1. SURVEY OF GRATING SPECTROGRAPHS

1.1. Introduction

Since Rowland ruled the first concave grating, the plane grating after passing through a period of almost total eclipse has recently come back into favour, largely because of the very good replica gratings now available.

The great advantage of the concave grating was that no ancillary equipment was required in producing a spectrum, as it was, or could be, entirely independent of lenses and mirrors for collimation. Original concave gratings are however difficult and expensive to produce, and in most types of mount are extremely bulky, and usually intricate adjustments are required when changing the region of the spectrum. Thus for instance in the Eagle mounting, quite the most economical from space considerations, and rather less astigmatic than other mounts (except the Wadsworth), it is necessary to turn the grating, change its distance from the plate and rotate the platcholder in changing from one wavelength range to another. The principal disadvantage of the concave grating is that it is very subject to astigmatism, an astigmatism that rapidly increases with the order under investigation. The Wadsworth mounting does produce a stignatic type of spectrum but requires a collimating system. Thus we have the paradoxical situation that we are using techniques of plane grating instruments (techniques which caused Rowland to make his first concave grating for its greater simplification) to produce a spectrum rather inferior to that which can be made with a plane grating and concave mirror. It is possible by using a plane grating and concave mirror, to make mountings with very small and nearly constant astigmatism, which does not increase unduly at higher orders, as well as having a constant focus for all spectrum regions.

Mountings of this type will be considered, and a semiquantitative analysis made of the three principal groups into which

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they can be divided. All of these groups being similar in that they employ a single concave mirror to produce autocollimation and are sketched in Figs. 1, 2 and 3.

2. THE TYPES OF CONCAVE MIRROR PLANE GRATING SPECTROGRAPH

2.1 Type A Mounting

The slit, plate holder, and grating are in the same vertical plane, which coincides with the focal plane of the mirror. Thus the parallel beam resulting from the first reflection at the mirror M of the rays from S_1 proceeds to the plane grating G, whence parallel diffracted beams impinge on the mirror, and after reflection these are reformed as images of S_1 at S_2 or further along the photographic plate P.

Czerny and Turner⁽¹⁾have analysed the wave front distortions produced by the various optical systems, and have shown that reflections of a non-axial spherical wavefront at a spherical mirror, result in an S shaped wavefront. Thus in a system involving several reflections at various surfaces, it is possible to either increase or reduce the distortions produced. A similar analysis of the mounting under consideration shows that it is a non-compensating system, thus the spectra it produces will always be poor.

Apart from considerations of wavefront distortion and its effects on image producing qualities, an astigmatism arises due to the non-axial incidence of light on the concave mirror, which for a single reflection, a point on the slit is imaged as a line of length z, where

 $z = \frac{2V_2}{r} \sin \phi \tan \phi - 1$

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 V_2 being the focal length of the mirror for the vertical image, r the radius of curvature of the mirror and ϕ the angle of incidence of the light on the mirror. Used as a photographic instrument the distortion due both to wavefront curvature, and astignatism,

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increases as we move along the photographic plate. Apart from these defects if an instrument is devised to be used as a monochromator which does not require a high resolving power (i.e. wide slits are to be used) then this method is far superior in efficiency to either type B or type C for the mirror diameter need only be sufficient for the grating surface to be filled with light.

2.2. Type B Mounting

Mounting type B which is known as the Ebert Monochromator has recently regained much favour and a large one described by Fastie⁽²⁾ has been constructed in the U.S.A. In this instrument the slit, plate holder, and grating are in the same vertical plane, which coincides with the focal plane of the mirror. Rays from S₁ (the entrant slit) on reflection at the mirror M, are sent in a parallel beam on to the grating G, whence parallel diffracted beams proceed once more to the mirror and after reflection there are reformed as images of S₁ along the photographic plate P.

Analysis shows that it is fully compensated for wavefront distortion at S_2 , hence this should be the position of the emergent slit if the instrument is to be used as a monochromator. Thus limitations to the use of the instrument as a monochromator are entirely due to astigmatism which results in a non monochromatic emergent beam produced by a straight entrant slit S_4 .

Using the instrument to photograph spectra the astignatic distortion increases continually as we move along the plate from S_2 . Moreover the diameter of the mirror required to give a spectrum which has any meaning on the photographic plate, increases with the length of the spectrum which it is desired to photograph.

2.3 Type C Mounting

The last type of mounting, type C, is rather similar to

type B the slits S₁ and S₂ being again vertical and hence parallel to the grating rulings but instead of them being mounted so that looking into the spectrograph from the operating end the slits are on the left and right hand side of the grating they are now vertically above and below. Thus a very similar analysis can be made of its advantages and disadvantages.

As with type B it is fully compensated for wave distortion and is equally adaptable as a monochromator and photographic instrument.

Using the instrument as a monochromator means as with type B that it is very wasteful in its use of available mirror aperture, however if it is to be used as a photographic spectrograph as well, it can use as much of the mirror diameter as is available, depending on the photographed length of the spectrum required.

Compared to the type B mounting, it has an advantage in that the physical separation of S_1 and S_2 (using the same components in both systems) is inherently less, because gratings are almost invariably ruled so that the length of the rulings is much less than the width of the grating. Also, the photographed spectrum is displayed symmetrically about S_2 (the stigmatic point) such that for any region to be photographed, the maximum astigmatism introduced by the mirror in type C is half of that introduced by type B.

2.4. Summary of the three types of mounting

It is probably convenient at this point to tabulate the various operational conditions and distortions introduced by using the same components in each of the types of mount. To make it a semiquantative discussion it is considered that a 7 foot focal length mirror and a grating 3 inches by 1.5 inches are used, ruled with 15,000 lines to the inch. These are summarised in Table 1 and it can be seen that Type A despite its more efficient use of the mirror produces wave front distortion and has astignatic distortion rather worse than either type B or type C. Types B and C produce undistorted wave fronts and

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have similar astignatic defects but type C uses its mirror more efficiently. Thus it would appear that for a general purpose instrument, using a plane grating and concave mirror, type C is the most suitable. A spectrograph of this type has been constructed using a spherical concave mirror of focal length 7 feet and a diameter of 12 inches and a replica plane grating 3 inches by 1.5 inches ruled 15,000 lines to the inch.

3. THE MECHANICAL AND OPTICAL DESIGN OF THE SPECTROGRAPH

A drawing is shown in Fig.4 of the complete assembly of the spectrograph.

3.1 The Slit and Platcholder Assembly

The entrant slit Fig.4(J) and emergent slit Fig.4 (D) or the plate holder are mounted in a frame Fig.4(I) so that the slits and the sensitive surface of the photographic plate are in the same vertical plane. Provision is made for rapid conversion from photographic to photoelectric recording and a racking system is available for the photographic plate. The photomultiplier tube together with a bleeder chain of resistances tapped off a various points to supply the dynode voltages, is placed in a cylindrical metal can. (Fig.4(B) A rectangular hole is cut in the can, so that the sensitive surface of the multiplier tube fits symmetrically behind it. A section of rectangular cross section wave guide is then attached to the can by means of a piece of brass, into which the wave guide is soldered. This section of the wave guide terminates in a male coupling, which houses the emergent slit of the spectrophotometer. The female coupling is attached to the spectrograph slit holder, together with the tilting arrangement (Fig.4(C))

This system has many advantages over other types of multiplier mounts. It can be readily uncoupled, if the slit is to be changed for instance, by merely unscrewing the coupling ring and recoupled when the operation is complete by placing the coupling together and screwing up the coupling ring. The section of wave guide is made of such a length, that the light contributing to a line in a spectrum is spread out to fill the whole of the sensitive surface of the multiplier tube, thereby increasing the signal to noise ratio of the detector.

Both the entrant and emergent slits can be tilted independently. The whole assembly can be traversed horizontally by means of a screw over a distance of three inches in order to focus the instrument. (Fig.4 (A).)

If a high resolution is required from the instrument, in studying line structures for instance, it is essential that the emergent slit be a small fraction of the width of the line to be studied. If however, the instrument is to be used as a spectrophotometer, when high resolution is not called for, there is no virtue in using such a narrow slit, in fact it is much better if a wide slit is used, so that flat topped images are always formed. In this latter case, a considerable relative tilt can develop in the slits without affecting the intensity maximum response, and so long as the emergent slit width is in excess of the line width, a wide variation in the line or band widths to be studied can be made without altering the meaning of the response intensities for those lines or bands.

The theoretical resolving power of a grating of three inches, ruled at fifteen thousand lines to the inch, is 45,000 or as the theoretical dispersion in the first order is approximately 8.5A per mm. at 3000A and 8.3A per mm. at 5000A and resolving power is defined as $\frac{\lambda}{d\lambda}$, then $d\lambda$, the smallest resolved wavelength difference at three thousand Angstroms, is a fifteenth of an Angstrom, and at five thousand Angstroms, a ninth of an Angstrom. These represent 1/128 mm. and 1/75 mm. respectively. Van Cittert, ⁽³⁾however, has shown that to achieve

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maximum resolution for optimum brightness at any particular wavelength, the entrant slit width is given by

$$D = \beta f \lambda$$

 β being between 1 and 2 depending on the nature of slit illimination, f being the numerical aperture of the system, and λ the wavelength under investigation.

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For this spectrograph, D varies between 0.0125 and 0.025 mms. at 4500A in the first order, or an average of 0.019 mms. Now, from Table I in the Appendix I, we can see that astigmatic broadening of about 0.005 mms. results. This sets a limit on the resolution obtainable, but fortunately, it is within the average range for optimum slit widths in the first order. Thus an entrant slit of 0.019 mms. can be used, and as far as resolution goes, an emergent slit of0.008 mms. or thereabouts proves adequate.

Indeed the condition for the first diffraction maximum to fill the sensitive surface of the photomultiplier tube requires an emergent slit of 0.008 mms. at 6000 Angstrom. At shorter wavelengths then, with a0.008 mm. slit the first diffraction maximum always lies entirely on the sensitive surface. It is thus not advisable with the length of wave guide used to have a narrower emergent slit. For spectrophotometric work, where a flat topped line is required, one can work on the second maximum of the intensity ourve where β varies between 3 and 6, and use an entrant slit of between 0.038 and 0.076 mms., and hence an emergent slit greater than this, possibly 0.10 mms.

The following slits were constructed, and to the stated tolerances:-

Slit 1 was 0.024 mms. wide ± 0.004 mms. Slit 2 was 0.044 mms. wide ± 0.003 mms. Slit 3 was 0.028 mms. wide ± 0.007 mms.

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3.2. The Grating Turntable

The position of least distortion for the location of the emergent slit is S_2 , at all other positions in the focal plane the image is extended by astigmatism in increasing amounts. Thus, it seems desirable to place the photomultiplier at this position and rotate the grating, whereby the spectrum is scanned across the emergent slit. The alternative to this is to move the emergent slit, together with the multiplier and its associated equipment, slowly across the spectrum. This would introduce errors in intensity measurements, which would increase as the length of the entrant slit decreased.

The turntable was designed so that the rays contributing to the spectrum are in n0 way obstructed by the grating, or any part of the mount. The motor (Fig.4(H)) drives the grating (Fig.4(E))round by a one to one gearing through a clutch so that about 22A per minute of the 1st order spectrum is scanned across the emergent slit. The torque required to turn the grating is about 10 gm. cms. and the torque required to make the clutch slip is about 500 gm. cms. Thus under application of the motor drive through the clutch to the grating support, the clutch will not slip, yet the grating can be set up to any desired position by making the clutch slip.

3.3. The Mirror Mount

The mirror rests in a teak frame which is retained in a spring loaded fashion in a metal case with screw adjustments for varying the tilt of the mirror (Fig.4(F))

3.4. The Spectrograph Bed and Assembly

The spectrograph bed consists basically of two iron channel bars joined by bolts and sleeves every eighteen inches and at either end a platform of three sixteenth inch steel is mounted. (Fig.4(G)) On one of these rests the mirror and on the other both

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the grating mount and the slit carriage.

The spectrograph was boxed in by a cover which is made of a wooden frame filled in with soft board.

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It is necessary to construct baffles to prevent photographic fogging, or contributions to a background level in the photoelectric recording. The main source of fogging is due to light from the slit being reflected over the top of the grating and onto the photographic plate. This can be eliminated by reducing the permitted aperture of the entrant and emergent beams.

4. THE PHOTOELECTRIC DETECTOR

The instrument is to be used for the detection and measure -ment of low intensity spectra and on a basis of the analysis which follows a photomultiplier tube is used rather than a simple photocell for the detector.

It can be considered that down to operating conditions of 10^{-14} amp. initial photocurrent and with a megohm resistor in the output, that a nine stage multiplier, working so that the multiplication factor per stage is four, has a Schottky noise voltage developed across the resistance greatly in excess of the Johnson noise. In fact at these operating conditions Schottky noise develops 4.0 x 10^{-6} volt and Johnson noise 1.2×10^{-7} volt, neglecting the latter then introduce an error of three per cent at initial photocurrents of 10^{-14} amp. and at greater initial currents than this the error is very much less.

It has been shown by Lallemand⁽⁴⁾ that due to the Schottky perturbation in a multiplier tube of n stages and multiplication δ per stage, with an initial photocurrent of I_o , that over an infinitely wide bandwidth the final current I_n is given by

$$I_n^2 = 2I_0 e^{\delta n} \left(\frac{1 - \delta (n + 1)}{1 - \delta} \right) \qquad \dots 3$$

Thus neglecting Johnson noise in the resistor R_1 across which the working voltage is developed, the voltage developed due to Schottky noise E_R can be written

$$E_{R_{1}} = I_{n}R_{1}$$

= 2 $I_{0}e\delta^{n}\left(\frac{1-\delta^{(n+1)}}{1-\delta}\right)^{\frac{1}{2}}R_{1}$

In the case of the simple photocell followed by a resistor R_2 the Johnson noise cannot be neglected. Thus the total noise voltage developed across R_2 is given by E_R .

$$E_{R_2} = R_2 \sqrt{2e I_0} + \sqrt{4KTR_2}$$
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K being Boltzmans constant and T the Absolute Temperature

Thus if E_{R_1} exceeds E_{R_2} then the simple photocell is better than the photomultiplier from considerations of noise voltage produced only, so if E_{R_1} is greater than E_{R_2}

$$\begin{array}{c} E_{R_{1}}^{2} > E_{R_{2}}^{2} \\ \text{or } 2I_{0}e\delta^{n}\left\{\frac{1-\delta}{1-\delta} \begin{pmatrix} n+1 \\ 1-\delta \end{pmatrix} \right\} R_{1}^{2} > \left\{ R_{2} \sqrt{2eI_{0}} + \sqrt{4KTR_{2}} \right\}^{2} \\ R_{1}^{2} > \left\{ \frac{R_{2} \sqrt{2eI_{0}} + \sqrt{4KTR_{2}}}{\left| 2I_{0}e\delta^{n}\left\{\frac{1-\delta}{1-\delta} \begin{pmatrix} n+1 \\ 1-\delta \end{pmatrix} \right|^{\frac{1}{2}}} \right\} \end{array}$$
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Equation 6 gives the maximum value of R_1 to be used to produce the same noise voltage as the simple photocell. Assuming the theoretical photomultiplier efficiency for $\delta = 4$ and n = 9 and assuming that R_2 cannot exceed 10⁹ ohms, the maximum value of R_1 can be calculated for values of I_0 of 10⁻⁶ amp. 10⁻¹⁰ amp. and 10⁻¹⁴ amp. These values are shown in Table 1 Appendix 2, and it can be seen that if a photomultiplier tube is working with even a fraction of its calculated efficiency, it is superior in all respects to a simple photocell. In particular at very low light levels, (where I_0 becomes of the order of 10^{-14} amp.), the photomultiplier displays a remarkable improvement over the simple photocell.

5. INITIAL SETTING UP AND FOCUSSING THE INSTRUMENT

5.1 Focussing by the photographic method

Before the focussing of the instrument is started the whole system is aligned. The mirror is placed at approximately the correct distance from the slit plane, which can be done to an accuracy of at least one inch by manual adjustment of the slit carriage or the mirror mount. Light is then introduced into the spectrograph through a very wide entrant slit from an intense source such as an arc. The optical train directing the light into the slit is then adjusted so that the slit image projected onto the mirror is in the correct position. The turntable and grating holder then have to be set so that the spectrum runs true. that is to say, if the grating is rotated through several orders the vertical position of the spectrum does not vary appreciably. Such a vertical shift in the case of a photographic instrument can be tolerated, but it cannot be used in a photoelectric recording system unless one can be sure that the light falls on a surface of the same sensitivity (cr the same surface). As shown by Kesslor and Wolfe (5) photomultipliers do not have the same sensitivity over their sensitive surface. In a recording spectrophotometer it must be arranged so that the lines under investigation fall on equisensitive surfaces. The only really satisfactory way to do this is to make the light energy fall on the same area of sensitive surface. In practice it was found that the spectrum was inclined so that in moving from the third order mercury 5461A line on one side of the grating to the third order mercury 5461A line on the other side a vertical shift of less than a centimetre resulted.

The entrant slit is then narrowed until the first diffraction maximum reflected from the mirror just fills the ruled area of the grating. A systematic photographic focussing is then carried out, the choice between the two or three best positions being made by a microscope analysis of the spectrograms.

5.2 Emergent Slit Alignment

For the best resolution of the spectrograph the entrant slit and grating rulings should be parallel. A series of exposures were made varying the slit tilt by the screw P and the optimum tilt angle selected from the photograph.

In photoelectric recording for maximum resolution the emergent slit should be parallel to the spectrum lines under investigation. To do this a long entrance slit is filled with light from a mercury arc and only the two extremities of the slit are allowed to transmit light. If a spectrum produced by such an entrance slit is scanned across the emergent slit and there is a tilt between them, when the line passes the emergent slit either a "doublet" or a broad line will result, depending whether the tilt is large or small. Beginning with an obvious tilt on one side and scanning the same line repeatedly, the tilt being altered by the micrometer screw each time, until there is an obvious tilt on the other side, a series of traces will result from which the correct angle of tilt can be selected. Fig. 5 shows a series of such traces the difference between the tilt of each being about one degree. In this particular run (e) is the best setting.

The asymmetrical shape of the spectrum line is due to the presence of unresolved Rowland Ghosts present in the grating. The distribution of energy from the grating is shown in Appendix 3 and as can be seen the grating is not blazed in any order and a large percentage of the incident light goes into the zero order. The resolving power of the spectrograph in the first order was

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found to be about two-thirds that of the theoretical resolving power.

6. THE SPECTROPHOTOMETER

6.1. Intense Sources

The instrument can be used as a spectrophotometer for intense sources such as arcs, the output from the photomultiplier tube being fed into a conventional d.c. amplifier followed by a valve voltmeter with a pen recorder as the indiceting device. With a steady arc source the intensity of the lines drawn on the recorder gives an accurate assessment of the relative amounts of the elements present in the arc. The advantage of this method of analysis as opposed to an analysis of a spectrogram is that the photoelectric system is linear whereas the photographic method is very non-linear. An indication of the reproducability of the system can be obtained by comparing the successive traces shown in Fig.6.

6.2. Weak Sources

The signal to noise ratio of the detector can be improved by either cooling the detector down to liquid air temperatures thereby reducing the total noise in the system and/or using a narrow band width detector. To obtain a narrow band width system the source is usually chopped mechanically or electrically and the amplifier following the detector is tuned to the chopping frequency. Band widths of 1.8 c.p.s. have been claimed at low frequencies⁽⁶⁾ however, the response time of such a system is very great and unless the scanning speed is very slow the resolving power of the whole equipment will be determined by the detector rather than the optics.

The upper limit of mechanical chopping is rather low and radiation pick up from electrical choppers at low frequencies is very great (particularly in this instrument where the distance between the source and the detector is short).

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An R.F. oscillator modulated at a low level from a multivibrator(Fig.7) at 10Kc/s so that it is completely cut off during the negative half cycle, is used to drive a gas discharge tube the deionization time of the gas being long compared to the frequency of the R.F. The discharge tube is thus modulated at 10 Kc/s.

A receiver is tuned to the chopping frequency and the output after being rectified is applied to a pen recorder which has a response time of a fifth of a second and acts as a high frequency filter. A block diagram of the system is shown in Fig.8. Fig. 9 shows a typical recorder trace of part of the Krypton spectrum. To indicate the great sensitivity of the system it is interesting to note that the line 4301.7A only just makes its appearance on a rapid process panchromatic plate in half an hour's exposure and yet is clearly discernable above the noise level in the photoelectric recording.

Such a system can be used for the estimation of the distribution of isotopes in a gas sample, monitoring an isotope separation plant by continuously scanning a fixed region of the spectrum such as the H α and D α lines in the discharge spectrum of a mixture of hydrogen and denterium in heavy water production.

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APPENDIX I

TABLE I.

The Distortions introduced into the Spectra produced by Spectrographs Type A, B and C because of Astigmatism

SPECTROGRAPH	TYPE A	TYPE B	TYPE C
Minimum slit separation	2 inches	8 inches	5 inches
Minimum mirror diam. required to give (a) 600A on a photo- graphic plate in the first order	7 inches	10.4 inches	9.1 inches
to give (b) 1,600A on a photographic plate in the first order	11.6 inches	18.2 inches	12.3 inches
Astigmatism due to mirror in case (a)	From 0 to 0.002 in.V	From 0.0003 to 0.0019 in.V	0.0002 in.H From 0 to 0.0003 in.V
in case (b)	0.00006 in.H From 0 to 0.011 in.V	From 0.0003 to 0.0080 in.V	0.0004 in.H From 0 to 0.0022 in.V

Explanation of symbols used

0.0006 inches H means that a point on the slit S₁ is imaged as a line in a horizontal direction of length 0.0006 inches. From 0 to 0.011 inches V means that over the spectrum a point on the slit is imaged as a line in a vertical direction varying in length from 0 to 0.011 inches.

TABLE I

The Behaviour of a Photomultiplier and a Simple Photocell under various amounts of Illumination

Initial Photocurrent I in amp.	10-6	10-10	10-14
Maximum value of R (to give the same noise voltage ¹ in both systems) in ohms.	1.4 x 10 ⁴	2.3×10^4	10 ⁶
Cutput volts due to (a) Photomultiplier tube (b) Photocell	3.5×10^3	5.8×10^{-1}	2.5×10^{-3} 10^{-5}
(Signal/Noise) Photomultiplier Signal/Noise) Photocell	3.5	5.8	2.5×10^2

TABLE I

	O	RDER		INTENSITY
1st	, Left	Hand	Side	2
2nd	**	**	**	0.1
3rd	**		**	0.004
1st	Right	11	**	1
2nd	11	11		0.1
3rd	11	11	11	0.04



FIG. I TYPE A MOUNTING



FIG. 2 TYPE B MOUNTING









FIG. 5. EMERGENT SLIT ALIGNEMENT

FIG. 6. SUCCESSIVE TRACES OF PART OF THE MERCURY ARC SPECTRUM

COMPONENT SCHEDULE

R	150Ω	°,	0.002 µF
R	15KΩ	C_2	0.002 µF
R	1 CK Ω	C 3	$1 \mu F$
R	1.8%Ω	C_4	0.01 µF
R	1 OK Ω	C_s	0.01 µF
R	15KΩ	C	$20\mu\mu$ F
R	150Ω	C,	$0.001 \mu F$
R	39KΩ	C	0.001 µF
R	10150		
R	33KO		

FIG. 8. BLOCK DIAGRAM OF DETECTOR

FIG. 7. THE MODULATED OSCILLATOR

FIG. .9 A TYPICAL TRACE OF PART OF THE KRYPTON SPECTRUM

