

AN EXAMINATION OF SOME EXPERIMENTAL METHODS
OF COMPARING INTENSITIES OF SPECTRUM LINES.

by

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Abstract.

Several methods of comparing the intensities of spectrum lines are described, using photographic plates, photomultipliers and photo-resistive cells as the measuring instruments. The performance of each of these detectors was assessed by using them, in turn, to determine the intensity ratios of the components of a particular mercury triplet. The particular triplet used was selected because of the wide wavelength range between the extreme components, and also because each component originated from a common S level. Theoretical considerations showed that the emitted intensities of such components should bear a constant ratio to one another, whatever the excitation conditions. A variant of the photographic method in which a calibrated step filter was used to compare the intensities of two near spectrum lines was also tried. Doublets in the sodium spectrum were used for this purpose.

The accuracy obtainable with each detector was so determined and the sources of error found. Several factors affecting the emitted intensities of the spectrum lines from the discharge lamps used as sources in the above investigation, are also discussed. It is concluded that for widely dispersed spectrum lines the photomultiplier method gave the greatest accuracy of the methods tried, an

accuracy of about 4% being achieved. An accuracy of 10% was the best that could be obtained using the photographic method, although for two near spectrum lines, and using a calibrated step filter an accuracy of 5% was obtained by this method. The photo-resistive cell was found to be unsuitable for the comparison of intensities.

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1. INTRODUCTION.

For many purposes it is desirable to measure accurately the ratio of the intensities of two or more spectrum lines. The three main methods which are used for these measurements are:-

1.1. Visual Estimates made directly on the Spectrum.

Direct observations of the spectrum lines under consideration are made by an observer, and an estimate of their relative intensities made. A considerable amount of experience on the part of the observer is required before any degree of repeatability can be achieved, especially if the lines to be compared have a large wavelength difference. This is because the human eye has a non-linear response - wavelength characteristic for a constant incident intensity. The accuracy obtainable is in general no better than 40%, although specialists working on one particular application, e.g. steel analysis, claim an accuracy of 20%. The method can only be used in the wavelength range 4000 - 6000 Angstrom units. Much of the earlier work (Meggers, de Bruin, and Humphreys, 1931 and Meggers and Humphreys, 1933) on intensity ratios was carried out by this method, although it is little used these days for accurate work.

1.2. Photographic Method.

This involves the exposure of a photographic plate to the spectrum lines, development of the plate under carefully controlled conditions, and measurement of the density of the image of the lines either visually or by microphotometer. The wavelength range is from below 2000 to 10,000 Angstroms, using special plates.

Visual estimates of the density of the spectrum lines (Johnson, 1924 and Johnson and Tawde, 1932) again depend on great skill on the part of the observer, the usual method being to arrange the visual estimates of density on a scale between 1 and 10, whence the results have approximately a logarithmic relationship to the intensity. The accuracy of the method is greatest when the wavelength range is small, since no account of the wavelength sensitivity of the plate is taken using this method.

For more accurate work a microphotometer is used to measure the density of the spectrum lines on the plates. This instrument consists of a movable table of glass on which is mounted the photographic plate, and beneath which is mounted a photoelectric cell. A beam of light is focussed on to the plate mounted on the movable

glass table, the light beam passing through the plate and the table, and then falling on to the photocell. The output of the photocell is fed to a galvanometer or recording device. The spectrum lines on the photographic plate reduce the amount of light falling on the photocell and hence the galvanometer reading, as the table is traversed across the light beam. The density of a particular line is calculated from:-

$D = \log \frac{\theta_0}{\theta}$, where θ_0 is the clear plate response of the cell, θ_0 and θ is the spectrum line response.

The photocell response must of course be linear with intensity for the correct estimation of densities.

In order to convert densities into intensities of light incident on the plate it is necessary to calibrate the photographic plate. This may be carried out in several ways, nearly all of which require the use of some standard of radiation, which should ideally be a black body.

Practically, this is usually a strip filament tungsten lamp run at a constant current so that its temperature is also constant. The temperature is often measured by means of a disappearing filament type optical pyrometer with a red window, this giving the brightness temperature of the filament. When using an optical pyrometer in this way it is essential to arrange that the angle the lamp subtends

at the pyrometer is always the same (Forsythe, 1920). The energy at a particular wavelength can then be obtained from the black body distribution curve for the same temperature (Benford, 1943).

In practice a tungsten filament acts more nearly as a grey body, but, providing intensity ratios only are required this need not be taken into consideration as long as the emissivity of the tungsten remains constant over the wavelength range considered, i.e. the fact that tungsten does not act as a perfect black body need not be considered provided that its emissivity is constant. In fact, the emissivity of tungsten changes by 5% in the wavelength range 6000 - 4000 Angstroms (Ornstein, 1936) and can be allowed for if required. The current through the lamp may be kept constant by means of the bridge circuit (Lucas, 1955) shown in figure 1.

The standard of radiation may be used in any of the following ways to effect a calibration of the photographic plate:-

1. Inverse Square Law.

A diffusing screen is mounted in front of the spectrograph slit, a number of exposures of the same duration then being made with the calibrating lamp at varying distances, d , from the screen. The continuous spectra so formed are examined by means of the microphotometer

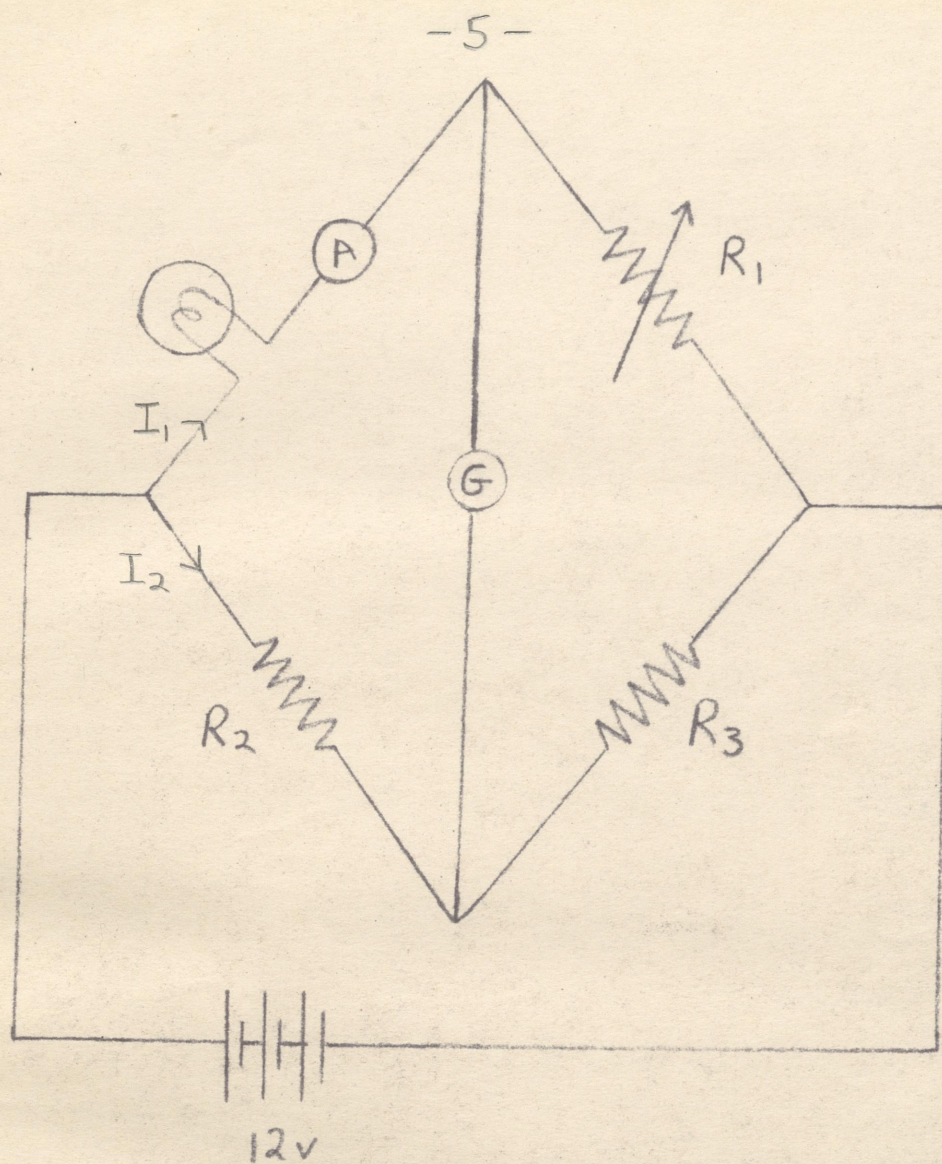


Figure 1

Circuit for maintaining Calibrating Lamp current constant.

along with the spectrum lines required, and at the same wavelength. In this way densities can be converted into intensities.

2. Step Filter.

A neutral filter comprising n steps is mounted over the spectrograph slit, and an exposure made using the radiation standard as a source. If the densities of the steps are accurately known, a calibration of the plate at any particular wavelength can be made as in 1 above.

3. Neutral absorbing wedge of known angle (Johnson and Tawde, 1932).

This method is very similar to method 2 in which a neutral step filter is used. A continuous variation in density of the photographic plate is obtained instead of a step variation.

4. Series of Neutral filters. (Barbier, 1947).

A series of exposures of the same time of the radiation standard are taken with various filters interposed between the slit and source, the filters being arranged at a condensing lens. Otherwise the method is similar to method. 2.

5. Series of Wire Gauzes (Dorgelo, 1923 and 1924).

These are used in the same manner as the filters in method 4.

6. Slit of varying width. (Sambursky, 1928).

If the width of the slit is known at every point in its length, the intensity can be found by taking it to be proportional to the width at the point.

7. Rotation of Nicol Prisms.

Two Nicol prisms are placed on the axis of the spectrograph slit and the radiation standard, a lens being used to pass parallel light through them. The angle between their optic axes is α and is 0° for maximum transmission. The transmission varies as $\cos^2 \alpha$, so that a series of exposures with variable α gives a suitable calibration.

8. Using one known filter, and a series of neutral, unknown filters. (Barbier, 1947).

A series of exposures are taken with and without the known filter using in turn each of the unknown filters to reduce the intensity. A graph is then plotted, at a particular wavelength, of the density obtained with the known filter against the density obtained without it. Knowing the density of this filter, and assuming an arbitrary intensity to produce a known photographic density through the known filter alone, a characteristic curve for the emulsion may be obtained from the first graph. This method is similar to the method of Schwarzschild.

9. Using a Knife edge on the axis of the collimator.

(Barbier, 1944).

By this means the density of the image varies along its length, the variation depending in a way that can be calculated on the shape of the slit, and the geometry of the instrument. This method is due to Hirsch and Schon (Hirsch and Schon, 1930).

Various other methods of calibrating photographic plates have been used, but these make use of the reciprocity law, e.g. Rotating sector. (The reciprocity law is that the product of the incident intensity and time of exposure gives a constant photographic plate blackening, for a given product, for all values of intensity and time of exposure). Reciprocity law failure is known to occur for large values of exposure time (Mees, 1954) so that results obtained by these methods may be uncertain.

A method of calibrating a plate without a standard radiation source can be used where two close spectrum lines are to be compared. This is to take a photograph of the two spectrum lines through a step filter as described in (2) above. A graph of density v. intensity is then plotted for the stronger line, the maximum density of the weaker line then being used to obtain its intensity from this graph. The method is one of the most accurate available, but is only applicable for lines less than 20 Angstroms apart. It is as well to check that no violent changes in emulsion sensitivity occur in the region of the

test lines, as in regions of insensitivity, or cut-off, the sensitivity can change rapidly in the space of 20 Angstroms. The check must be made with a radiation standard.

The relative intensities of the spectrum lines on a photographic plate may be found from the characteristic curve for the emulsion at each wavelength corresponding to each spectrum line, and the energy distribution of the calibrating lamp.

1.3. Electrical Method.

In this method a device which converts light energy into an electrical signal having a fair degree of correspondence to the incident light energy is used in conjunction with a spectrograph, the device either being moved along the spectrum, or else being fixed to the spectrograph mount, the spectrum lines being moved past the entrance slit of the device by rotating the prisms of the spectrograph. Such devices are the Thermopile, Photo-electric cells, Photomultipliers and Photo-resistive materials.

The thermopile is the most fundamental of these measuring devices; it provides the only absolute method of measuring spectrum line intensities. In conjunction with suitable optical gear, the wavelength range over which measurements may be made, is very wide. Conventional

thermopiles are described elsewhere, (Forsythe, 1937) typical couples used being iron-constantan and bismuth-silver. The requirements other than the purely thermoelectric properties for a suitable couple material are that it should have a good electrical conductivity, and a poor thermal conductivity, two properties which according to the Wiedemann-Franz law are unfortunately conflicting one with the other. However, with the advent of semi-conductors, materials having these properties were found, and thermopiles of increased sensitivity with a high speed of response made (Schwarz, 1952). These semi-conductor couples consist essentially of an excess semi-conductor in contact with a deficit semi-conductor, an example being a mixture of silver sulphide and silver selenide in contact with a mixture of silver, copper, tellurium and selenium.

Single-cathode photo-electric cells have not found popularity as a device for intensity measurement, the photomultiplier type of cell being used almost exclusively on account of its greater sensitivity (Rodda, 1953). Both of these devices use the external photo-electric effect (Becker, 1949) in which photons in the incident light beam actually expel electrons from the sensitive cathode of the device. In the case of the photo-cell the electrons are collected by the anode, there being amplification at

the expense of linearity if the cell is gas filled; in the photomultiplier the electrons are collected by the first dynode, an electrode positive with respect to the cathode, More electrons are emitted from the first dynode (because of the field energy imparted to the initial electrons) then by the geometry of the electrode structure, these are made to impinge on the second dynode, and so on, until the final anode is reached. Photomultipliers in current production have 9 or 11 such stages so that there is considerable amplification. The wavelength range of photomultipliers is 2000 - 6000 Angstroms, using quartz envelopes.

Semiconductors used as photo-resistive elements are comparatively new devices. They use the principle of the internal photo-electric effect in which the electrical resistance of the material varies according to the distribution of its extra-nuclear electrons in their permitted energy bands. The incident photons raise electrons from non-conducting bands to the conducting band so decreasing the resistance of the material. Electrons so raised leave behind "positive holes" in the non-conducting bands which behave similarly to electrons in the conducting band so giving an enhanced effect.

Materials exhibiting this effect are numerous, examples of the better known ones are germanium (Shive, 1949 and Burstein, Davisson, Bell, Turner and Lipson 1954),

selenium, tellurium, bismuth telluride (Gibson and Moss 1950) lead telluride, (Young, 1955) lead selenide (Simpson 1947, Moss and Chasmar 1948 and Gibson, Lawson and Moss 1951) (usually kept below 90°K) lead sulphide (Moss 1949), indium antimonide, cadmium sulphide (Brentano and Davis, 1948 and Frerichs and Siegert, 1948) cadmium selenide, and barium oxide. Most of these materials are more suitable for infra-red work, e.g. germanium photo-diodes have a wavelength response of 5000 Angstroms up to 16,000 Angstroms, with a peak response at 15,000 Angstroms. Lead telluride (below 90°K) has a response extending to 7 microns.

The output of any of these electrical devices usually requires some degree of amplification before a suitable output signal is obtained. This signal, is in general used to deflect a robust form of galvanometer. For a line of given intensity the photomultiplier will require least amplification (for a line in its working wavelength range) the thermopile most. The output of all of these devices is obtained in the form of a d.c. signal of changing level. This signal may be amplified, either by a conventional form of d.c. amplifier, provided with a variable bias supply in order to compensate for the dark signal, or by means of a "chopping" device and an a.c. amplifier.

A "chopping" device consists of some form of

interrupter situated in the path of the light beam. Typical examples are a perforated disc driven by a synchronous electric motor, and an electrical vibrator operating as a shutter before the slit. In this way a more or less square waveform, of intensity with respect to time, falls on the electrical measuring device which thus provides an a.c. output.

For photomultipliers an interrupting frequency of 50 - 200 c.p.s. is generally employed, since a.c. amplifiers of this frequency band are simple to construct, the signal to noise ratio being greatest if a selective band amplifier is employed. For thermopiles an interrupting frequency of 5 - 10 c.p.s. has to be used because of the time delay of the device. A.c. amplifiers in this frequency band are more difficult to construct.

Where a small degree of amplification of the output signal from the measuring device is all that is required, a conventional form of d.c. amplifier probably provides the best solution, but does not eliminate noise, even if the dark signal is backed off. Where larger degrees of amplification than can be obtained from one valve stage are required, the interrupter and a.c. amplifier seem to provide the best solution. This is because drift becomes a major problem with high gain d.c. amplifiers, and although high gain, frequency selective, interrupting systems have

their problems, their use is generally more straightforward. When an a.c. amplifier is used, the output can be displayed either on an a.c. type of instrument (e.g. hot-wire ammeter) or rectified and used in conjunction with a d.c. type of measuring instrument.

In order to convert the meter readings obtained on such an electrical system into intensity values, it is necessary to calibrate the system. This is usually performed with the aid of a radiation standard such as the tungsten strip filament lamp, as for the photographic method described earlier. Calibration methods 1, 4, 5, 7 and 8 are suitable for the electrical method, calibration curves for the apparatus being obtained at each desired wavelength value. These curves are equivalent to the characteristic curves obtained in the photographic method. Method 8 is particularly applicable to the electrical method, and in the particular case where the response of the equipment is linear, no known filter is required. The linearity of the equipment may be checked by using one unknown filter in the following manner:- The deflection given by a source whose intensity can be varied (e.g. the strip filament tungsten lamp) is obtained with and without the filter present. The intensity of the source is then diminished so as to make the deflection obtained without the filter in position, approximately

equal to that obtained previously when the filter was present. The filter is now again inserted and the deflection obtained. This process is repeated a number of times, the intensity of the source being diminished each time. A graph of deflection with filter present against deflection without the filter is a straight line for a system whose response is linear. The known distribution of energy in the light from the standard lamp gives the scale of the intensity - deflection graph obtained.

Precisely the same precautions must be taken in using the electrical method as with the photographic method; the calibrating lamp must be run at constant current; the electrical measuring device must have constant power supplies as must the source. It is the purpose of the present investigation to contrast results obtained using some of the photographic and electrical methods, and to indicate the precautions necessary for the greatest accuracy. Other devices e.g. the Golay cell are mentioned in the literature (Clark - Jones, 1949) but these are more suitable for special applications and for infra-red spectroscopy.

2. Sources used in this investigation.

For the main intensity ratio comparison between the electrical and photographic methods it was decided to use a triplet in the mercury vapour discharge spectrum having the following components:-

5460.74	Angstroms	- green.
4358.34	"	- violet.
4046.56	"	- violet.

These three lines are all produced by electron transitions from a 7^3S single upper state to a 6^3P triplet lower level, this transition being illustrated in figure 2. Because of their origin from a single level, the relative intensities of these lines should be independent of the voltage applied to the discharge lamp, and in the case of the photographic method where all three lines are recorded simultaneously, lamp voltage variations should be of no consequence. (The actual intensity of each line will of course vary with lamp voltage). Another reason for choosing this mercury triplet as a basis for comparison of the electrical and photographic methods of intensity ratio measurement was that the wavelength range almost completely filled the photographic range available at one setting of the two spectrographs used in this investigation, giving the most difficult conditions for accurate comparison.

The transition probabilities of these lines

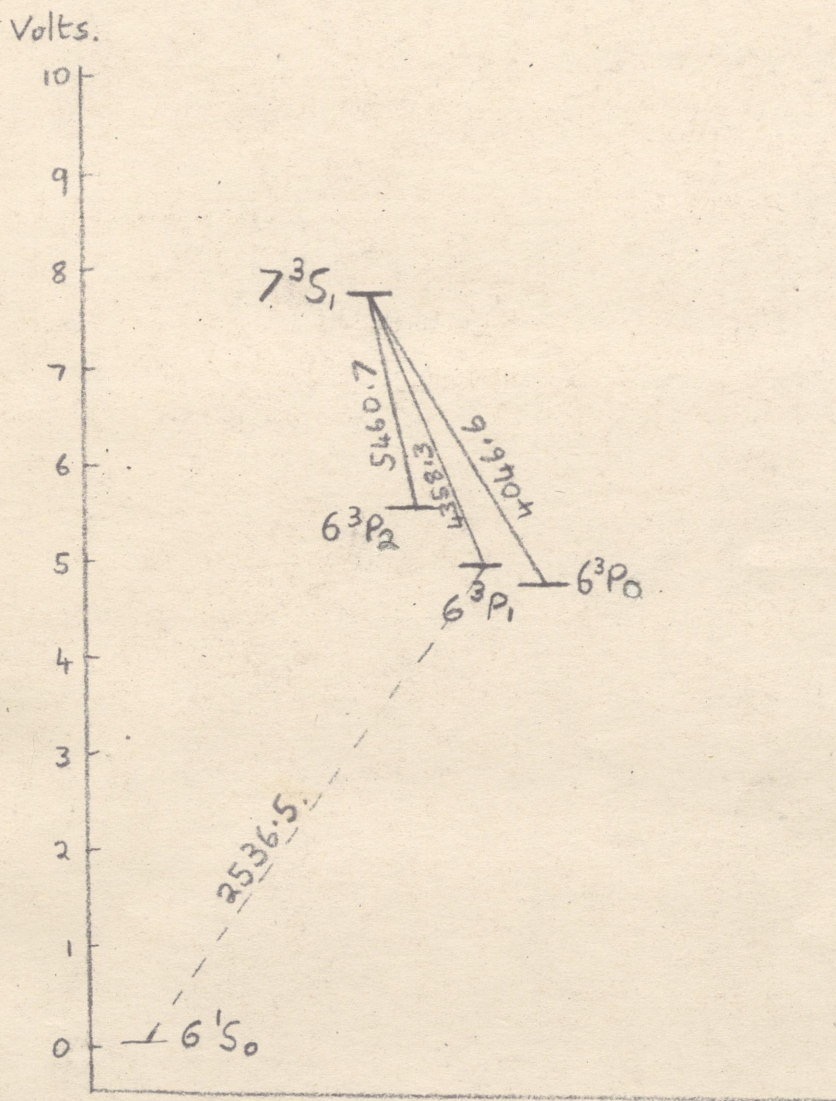


Figure 2.

Term diagram for
neutral Mercury atom.

(Allen, 1955) are theoretically 5 : 3 : 1. Wave mechanics shows that the intensity of a spectrum line is proportional to the transition probability function multiplied by the fourth power of the wave number. The theoretical intensities of the mercury triplet components are therefore in the ratios:- 1 : 1.49 : 0.67. However it is thought that when a photographic plate is activated by light photons, the density of the developed image is proportional to the total number of incident photons and not to the total energy of the photons. If this is the case, the intensity of a spectrum line as determined photographically will be proportional to the transition probability function multiplied by the cube of the wave number. That is, the intensities of the mercury triplet components, as determined photographically, will be in the ratios:- 1 : 1.18 : 0.52. The same is true for intensity ratios determined with the photomultiplier and semiconductor detectors. A thermopile should give the intensity values 1 : 1.49 : 0.67.

Certain other lines were used in the experimental work. These were two mercury yellow lines (wavelengths 5791 and 5770 Angstroms) the two sodium D lines (wavelengths 5896 and 5890 Angstroms) and a sodium blue doublet (wavelengths 4983 and 4979 Angstroms). The 5791 Angstrom mercury yellow line is in fact complex, but the resolving

power of the spectroscopes used was not great enough to show this. The observations made on these lines are fully described in later sections.

2.1. Mercury Vapour Discharge Lamp.

The first mercury discharge lamp used as a source for the above mentioned lines was a G.E.C. 100 watt type. The following tests, to investigate the behaviour of the lamp, were carried out:- first, the lamp was fed from a "Variac" variable transformer, the voltage across the lamp and control gear being measured. Using a photomultiplier to receive the 5460.74 Angstroms green line, the discharge lamp was switched on and operated at a constant 200 volts. The photomultiplier anode current was noted every minute for the first 10 minutes after switching on, and then every 5 minutes. This test showed that the output of the lamp varied markedly for the first 20 minutes after switching on, but that after half an hour, the light output was sensibly constant. In use, therefore, it was desirable to allow the lamp a warm-up period of at least half an hour before readings were taken.

Secondly, the voltage applied to the lamp and control gear was varied over the range 150 to 227 volts, the photomultiplier current being noted. The photomultiplier was then arranged to receive the 4358.34 Angstroms violet

line, and the test repeated. The ratio of the readings of green/violet at each voltage were then obtained, these readings being proportional to intensity as the photomultiplier has a linear intensity - current characteristic (see section 6). This ratio was found to be independent of the voltage.

When using any electrical method for intensity ratio comparison it is necessary to maintain the discharge lamp supply voltage constant. This is because the lines are recorded successively instead of simultaneously as in the photographic method. It was for this reason that in all measurements made with the mercury vapour discharge lamp, it was fed from a "Variac" variable transformer, the supply voltage being measured and manually adjusted to be always at 200 volts for both the electrical and photographic methods.

Certain features of the mercury vapour discharge lamp described above were later found to be unsatisfactory (see section 9), and for this reason a mercury isotope discharge lamp which was water-cooled was used as a source, some of the intensity measurements being repeated using this lamp as source.

The isotope lamp contained the mercury isotope of atomic weight 198, and was also of G.E.C. manufacture.

The power supply for the lamp was taken from the 200 volt mains in conjunction with a 700 volt step-up transformer and a current limiting series resistor, the power consumption of the lamp being approximately 5 watts. The cooling water for the lamp was maintained at 20°C (measured at the outlet of the lamp) by adjusting the flow of water. The electrical characteristics of the lamp were otherwise similar to the 100 watt discharge lamp, the supply voltage being adjusted to a constant 200 volts in the same manner.

2.2. Sodium Vapour Discharge Lamp.

The sodium vapour discharge lamp used as a source for the doublets referred to above was a G.E.C. 60 watt type. Tests on this lamp were carried out in the same way as those on the mercury vapour discharge lamp. In all measurements taken with this lamp, a half an hour warm-up period was allowed, the voltage supply to the lamp being maintained constant at 200 volts by means of a "Variac" variable transformer.

3. Calibration Standard.

For both the photographic and electrical methods a tungsten strip filament lamp operating at a brightness temperature of 2800°K was used. This lamp was constructed by the Siemens Electric Company and had a nominal rating of 108 watts at 6 volts. The lamp had a ribbon filament of tungsten with a kink in the centre, enclosed in a quartz envelope. The kink enabled an optical type pyrometer to be focussed on the same point of the filament each time temperature measurements were made, whilst the quartz envelope transmitted radiation in the ultra-violet, and so allowed calibrations to be made in this region.

In order to maintain the temperature of the filament constant during a calibration exposure (some calibrations took 5 minutes) so that repeatability could be achieved, the lamp was supplied from two 6 volt, 57 ampere-hour car type accumulators connected in series, the lamp being connected in a bridge circuit (Lucas, 1955) as shown in figure 1. This circuit enables the current through the tungsten lamp to be kept constant regardless of changes in accumulator e.m.f. contact resistances, etc. The brightness temperature of the tungsten ribbon filament required in order to give a suitable calibration characteristic was found to be 2800°K , this corresponding to a lamp current of 17.5 amperes, R_1 was then 0.24 ohms

at balance, and was in fact a variable resistance. For current $I_2 = 2$ amperes, $R_2 = 3.9$ ohms, and $R_3 = 2.1$ ohms. The galvanometer used to detect unbalance in this bridge circuit was a Pye "Scalamp" type, and with the circuit as used a deflection of 1 cm. of the galvanometer light spot was produced by a change of 0.05 amperes in the lamp current, adjustment of R_1 then restoring the value of the current to the desired value.

When using this circuit for calibrating purposes, the accumulators were fully charged, the lamp then being allowed to run at the operating temperature for about 15 minutes before use. This allowed the filament to reach stable operating conditions, the resistance R_1 to become temperature stable, and at the same time, stabilised the accumulator e.m.f. Adjustments to R_1 were then of a minor nature only during the course of a calibration. Before the lamp was used at all, it was aged for about 20 hours at the operating temperature. With the accumulators fully charged, the lamp could be operated for approximately two hours at a current of 17.5 amps.

The temperature of the filament of the lamp was measured by means of a Cambridge disappearing filament type optical pyrometer. This pyrometer had been initially calibrated by the makers against a standard lamp, and was subsequently checked, in the course of the present work,

by reference to a portable black body radiator. This consisted of a tungsten tube, with a small hole drilled in the side, mounted inside an evacuated glass bulb fitted with a quartz window in one side opposite the hole in the tungsten tube. The glass bulb was filled with an inert gas at low pressure, in order to prevent evaporation of the tungsten at high temperatures. A large electric current could be passed down the tube so raising it to incandescence. The portable black body radiator was calibrated against a N.P.L. standardised lamp by the G.E.C. Research Laboratories, so that its temperature - current relationship was known. The radiator was then used to calibrate the pyrometer. At the operating temperature of the calibrating lamp (2800°K) the pyrometer was found to be accurate.

It is important that the temperature of the lamp be known accurately for as is shown in figure 3. a 50° change in temperature of the calibrating lamp produces a 14% change in the intensity ratio of the emitted intensities at 6000 and 4000 Angstroms. Tests on the use of the disappearing filament pyrometer showed that an accuracy of $\pm 10^{\circ}$ in a temperature of 2800° was the best that could be achieved. The electrical circuit was estimated to keep the temperature steady to within 5 degrees. It was considered that as a result of these variations intensity

Figure 3.

Effect of 50° change in Absolute Temperature on
Energy Distribution of a Black Body Radiator.

E (Microwatts/cm²/100 Angstrom Zone of Spectrum)

$\times 10^5$

2800°K
2750°K

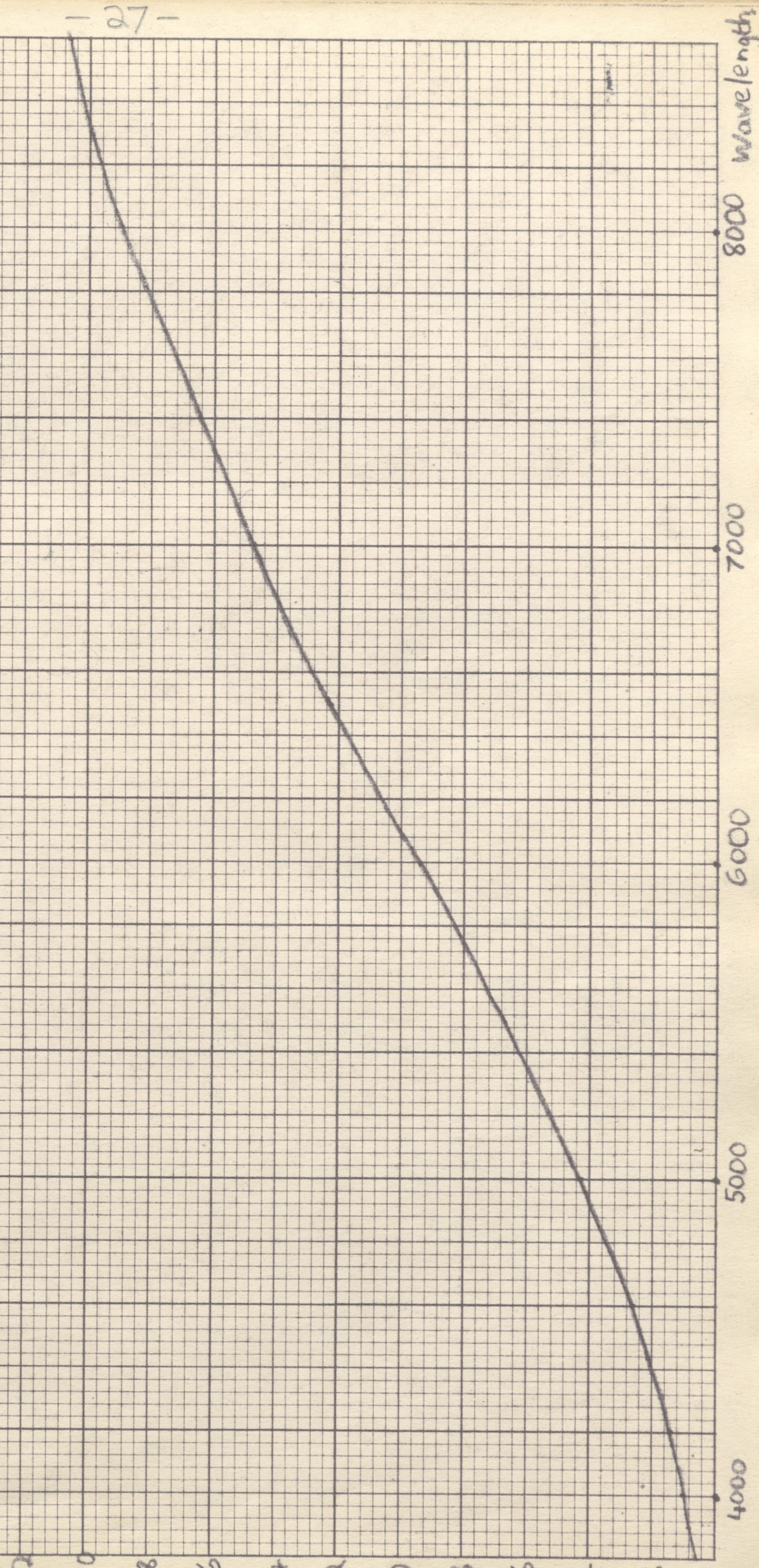
ratios might vary by as much as 5% in the wavelength range 4000 - 6000 Angstrom units.

The intensity emitted at any particular wavelength by the standard lamp may then be obtained from data given in the International Critical tables or from the curve shown in figure 4. These relate to a perfect black body radiator, so that the emissivity of tungsten, and its variation with temperature must also be accounted for. Values taken from the International Critical tables for a black body radiator are given in table 1, whilst table 2 shows the variation of the emissivity of tungsten with wavelength.

Figure 4

Variation of Intensity with Wavelength from
a Blackbody Radiator at 2800°K .

$I_{\lambda} (\times 10^{12} \text{ erg cm}^{-2} \text{ sec}^{-1})$



Wavelength	J_{λ} (erg. cm ⁻³ sec ⁻¹)
10,000 Angstroms.	22.3 x 10 ¹² (max. value)
9,000	21.4 x 10 ¹²
8,000	18.9 x 10 ¹²
7,000	14.7 x 10 ¹²
6,500	12.2 x 10 ¹²
6,000	9.40 x 10 ¹²
5,500	6.69 x 10 ¹²
5,000	4.23 x 10 ¹²
4,200	1.45 x 10 ¹²
4,000	1.00 x 10 ¹²
3,000	0.059 x 10 ¹²

Table 1.

Variation of intensity with wavelength from
a black body radiator at 2,800°K.

Wavelength	Emissivity
3500 Angstroms.	0.463
3750	.469
4000	.463
4250	.453
4500	.449
5000	.441
5500	.439
6000	.434
6500	.428

Table 2.

Variation of emissivity of tungsten
with wavelength. (For a temperature of 2800°K.).

4. Details of Spectrographs used in this work.

The two spectrographs used in the present work were a Constant Deviation type with a glass prism, and a large Littrow type with interchangeable glass and quartz optics both manufactured by Hilger Limited. Both spectrographs as supplied required modification because of a large amount of scattered light to be found in them when their entrance slits were illuminated by any intense source, such as the tungsten ribbon filament calibrating lamp. The effect of this scattered light was to produce blackening on either side of a calibrating spectrum taken using a neutral step filter, and hence also, effectively to increase the blackening produced by the spectrum. This illumination was eliminated from both spectrographs by the means described below.

4.1. Constant Deviation Spectrograph.

Investigation of this spectrograph showed that the scattered light was produced by reflection from the surfaces of the collimating lens. The collimator lens mount was modified by arranging for the mount to be tilted about a horizontal axis, by means of an adjusting screw. It was found that the intensity of the scattered light was much reduced by suitably tilting this lens. Unfortunately resolution was lost in tilting the lens so that it was essential not to tilt it more than was necessary. The

instrument was also lined with black velvet as a further precaution against scattered light.

When used with the photomultiplier the wavelength drum of the instrument was turned to rotate the spectrum past the entrance slit of the multiplier. The mounting constructed for the photomultiplier is shown in figure 5, and consists of a brass tube housing the multiplier and its associated "daisy chain" of resistors. Another brass tube brazed at right angles to this tube and in line with the photo-cathode of the multiplier served to mount the unit onto the exit tube of the spectrograph. Rotation of the wavelength drum was found to alter the dispersion of the instrument and its focus. It was therefore essential to have the instrument as nearly in focus as possible when using the photomultiplier, but it was found that provided the instrument was focussed in the middle of the range traversed (approximately 4000 to 5500 Angstrom units) the slight falling off in focus at the extremes of the range did not affect the readings obtained. The variation of the dispersion due to rotation of the wavelength drum, over this wavelength range, was also found to be small, and providing that the exit slit was wide enough to pass all of the light energy emitted in a single line, its actual value did not affect the relative value of the intensities obtained. For the calibration spectrum the

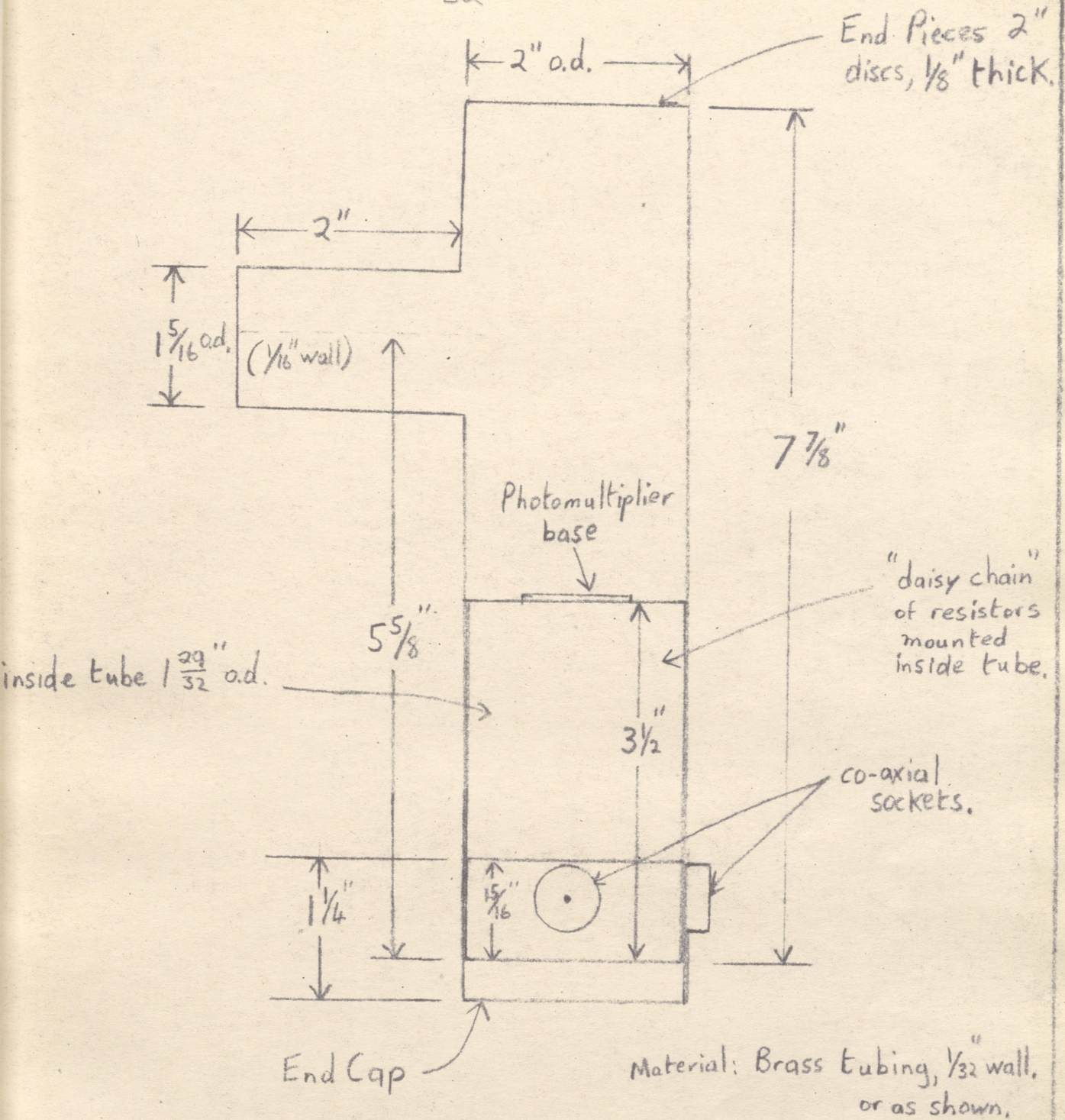


Figure 5.

Photomultiplier Mounting.

value of dispersion obtained photographically, as below, was used.

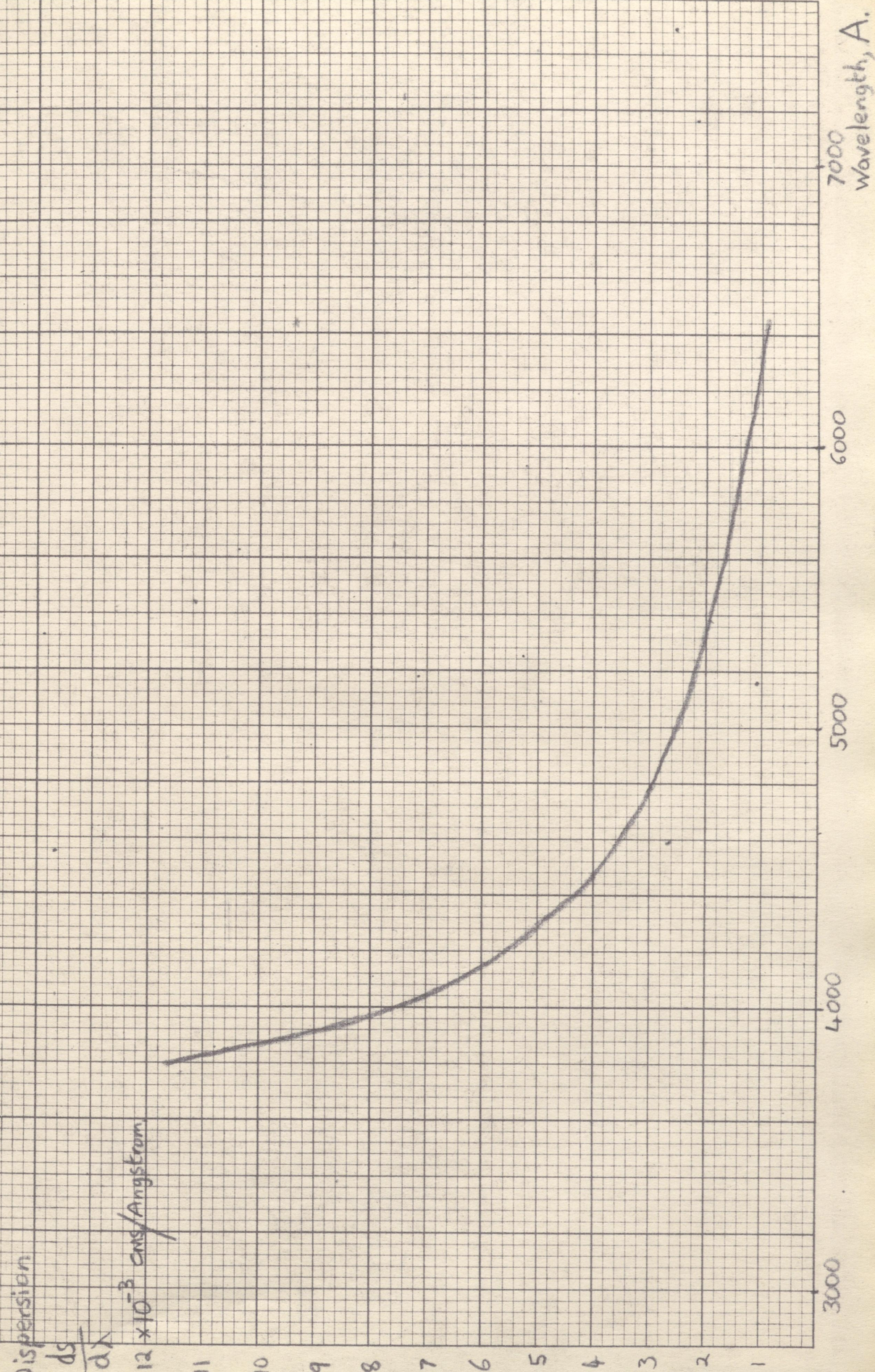
In the early part of the investigation, the manner in which the dispersion of the instrument would enter into all the intensity calculations was not known precisely. A dispersion curve was therefore obtained for the instrument by taking an exposure of an iron arc spectrum and then measuring the distance between known wavelengths with a travelling microscope on the plate obtained. This curve is shown in figure 6. In view of the effect of position of the prism on dispersion, the plate was taken with the wavelength drum in the setting used for the investigation of the mercury triplet.

A Schwarz cell (see section 7) was also used with the Constant Deviation spectrograph, this being obtained in a housing suitable for mounting directly onto the exit slit of the spectrograph. A cooling tank was constructed for the Schwarz cell mounting in order to maintain its temperature uniform. This is shown in figure 7.

The electrical measurements were of greater accuracy than the photographic ones made on the Constant Deviation spectrograph. This was because the short entrance slit of the instrument would only enable 5 steps of the 7 steps calibrating filter (see section 5.3) to be used, consequent extrapolation of the characteristic curves being

Figure 6

Dispersion of Constant Deviation Spectrograph.



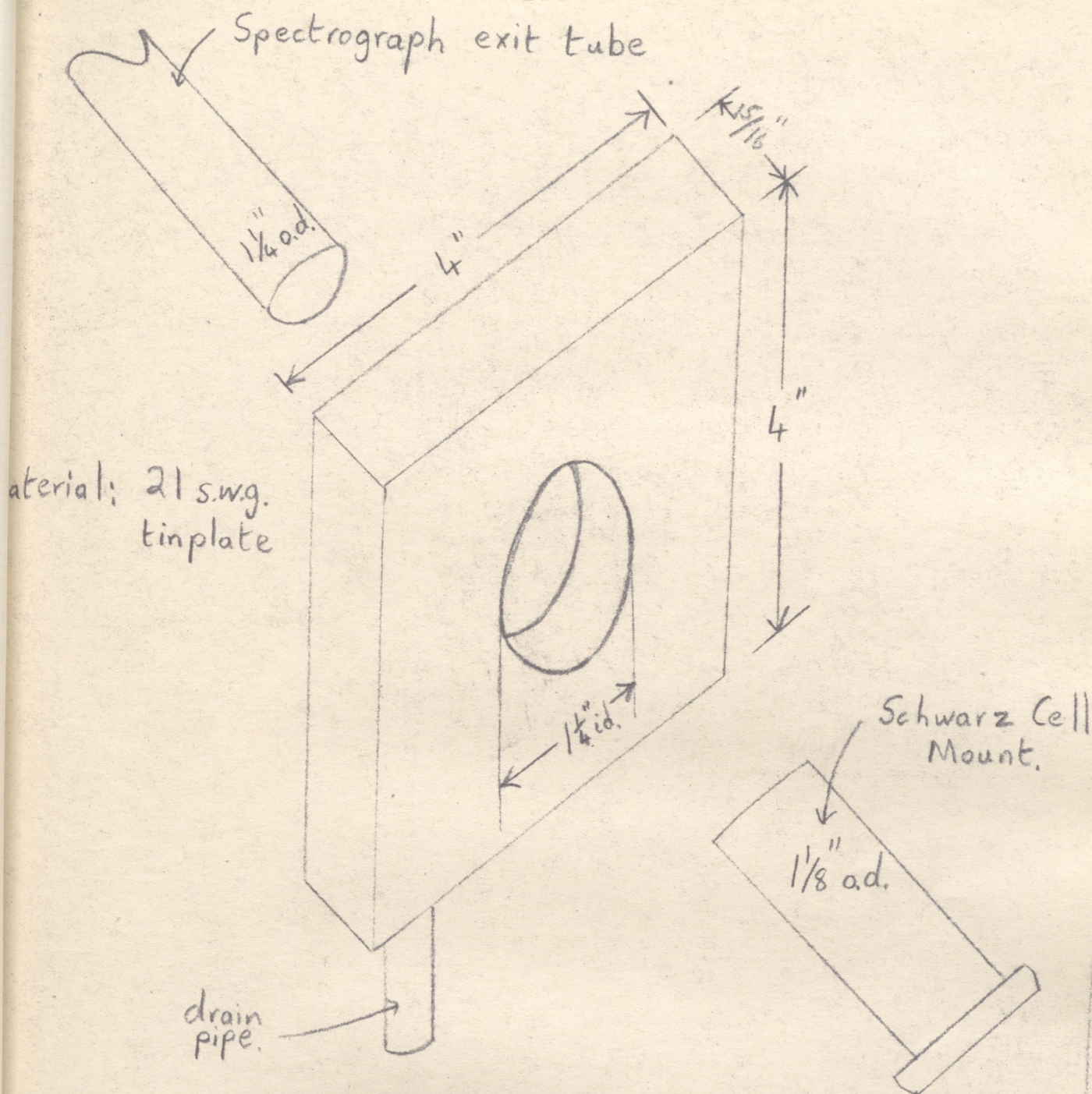


Figure 7

Schwarz Cell Cooling Tank.

necessary.

4.2. Large Littrow Spectrograph.

This instrument has two optical trains, one of glass, the other of quartz. The dispersion of the instrument is greater with the glass setting, but the shortest wavelength transmitted is of the order of 3,800 Angstroms. With the quartz setting the range is extended to approximately 2000 Angstroms. Both of these settings however, showed large amounts of scattered light on plates taken of a continuous source for example the tungsten ribbon filament calibrating lamp.

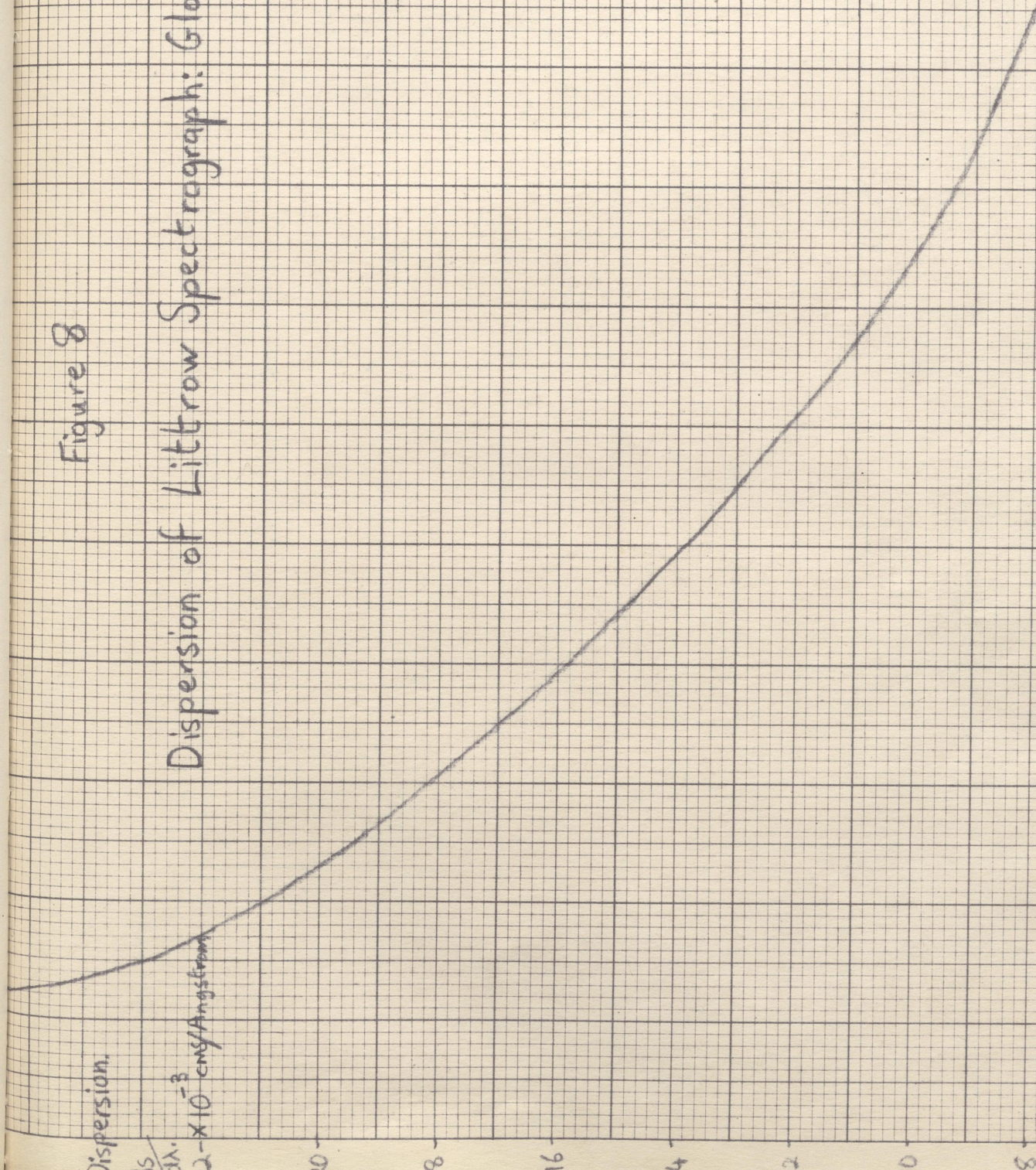
In order to eliminate this scattered light, the collimating lenses of each optical train were canted on shims, plates being taken of the calibrating lamp to note any improvement obtained. Canting the lens in both cases removed the "flare" but at the same time spoiled the focus of the instrument. By canting the collimating lens downwards, in the case of the glass optical train, and adjusting the focus control carefully, a compromise could be obtained where a reasonably good focus was obtained, and practically all of the "flare" removed. In the case of the quartz optical trains the "flare" was more severe, consequent greater canting of the collimating lens being required to eliminate it. Unfortunately compromise was not fully satisfactory in this case, the two adjustments being

incompatible. It was for this reason, and because of the greater dispersion that all intensity measurements were taken on the glass setting of the spectrograph. A dispersion curve for the instrument was obtained in a similar manner to that for the constant deviation instrument and is shown in figure 8.

The large Littrow instrument was also used for both electrical and photographic measurements. To enable the photomultiplier to be used with this instrument, a special mounting plate to fit into the existing plate holder, was made up, and is shown in figure 9. This plate had an elliptical hole cut at its centre, a hollow tube then being brazed on to the plate at such an angle ($28^{\circ} \pm \frac{1}{2}^{\circ}$) that light falling on the elliptical hole would pass directly down the tube. The photomultiplier holder previously described (see figure 5) was a push fit on to the end of this tube. A Ramsden type eyepiece was mounted in the tube in such a position that the image of the spectrograph slit formed at the mounting plate was refocussed on to the entrance slit immediately in front of the photomultiplier cathode. By this means no change of the focus setting of the instrument was required when changing from photographic measurements to electrical. The spectrum lines under investigation were in this case brought on to the photomultiplier cathode in turn, by rotation of the range-changing control. This

Figure 8

Dispersion of Littrow Spectrograph: Glass range.



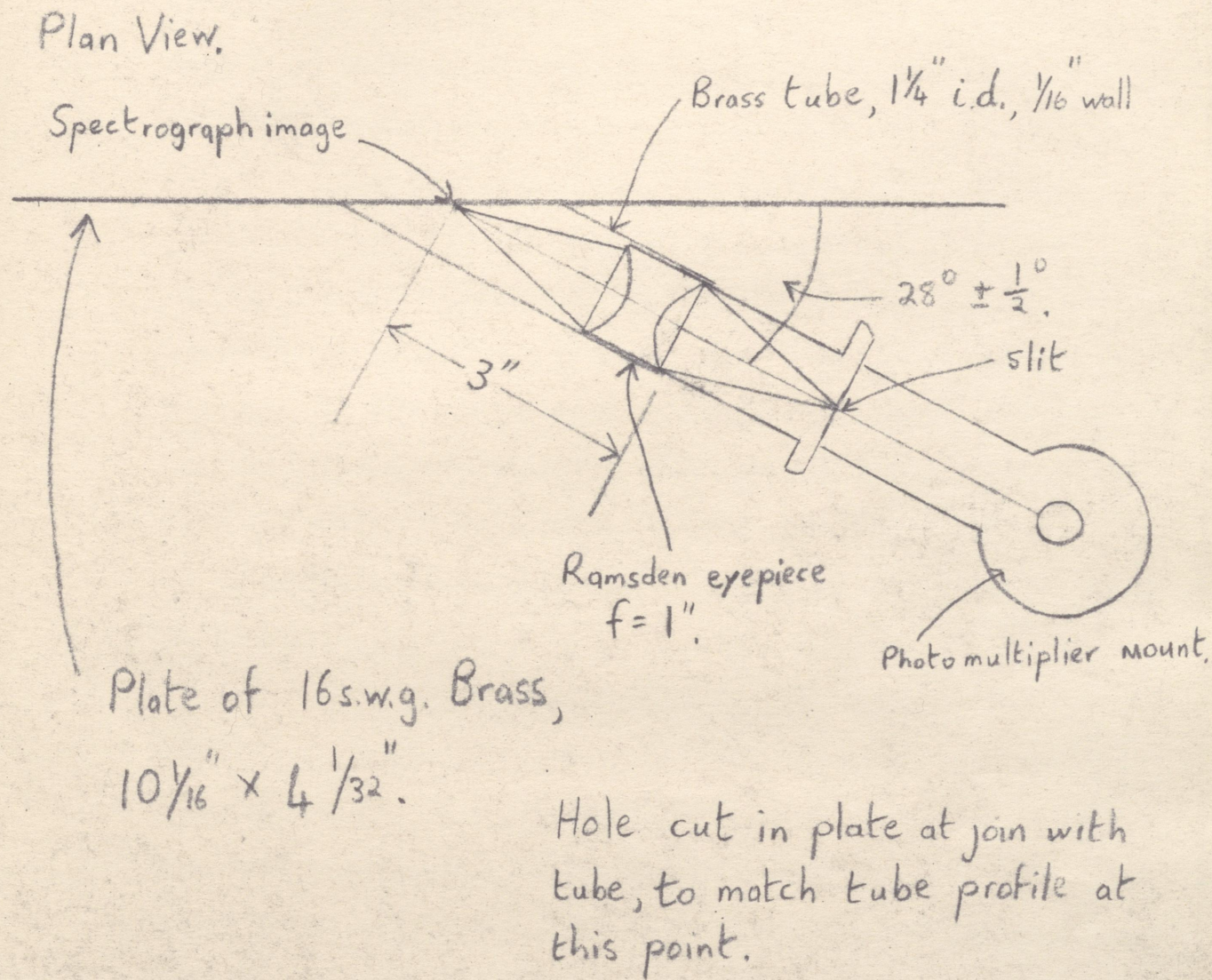


Figure 9.

Photomultiplier Mounting Plate for Littrow Spectrograph.

control has a rather coarse action, such that in the region of 6000 Angstroms, differentiation of lines closer together than 20 Angstroms was impossible.

The uniformity of the entrance slits of both spectrographs over their lengths was investigated by making two exposures on a photographic plate of the standard calibrating lamp through the 7 step filter mounted either way up. If the slits were uniform, equivalent characteristic curves for the emulsion for both orientations of the step filter should be obtained. Within the limits of experimental error, this did prove to be the case for both instruments.

With both spectrographs, the practice was adopted of focussing the light from all sources under investigation, on to the prism of the instruments. This was most desirable when a step calibrating filter was being used, as it was essential to ensure that the same amount of light from the calibrating source fell on to each step of the filter. For consistency the method was adopted for all sources.

5. Photographic Method.

In the photographic method a suitable photographic plate was exposed to the required spectrum, the plate then being developed under carefully controlled conditions. Many factors can affect the density of the photographic image and it is therefore necessary to time carefully the development process and to ensure constancy of temperature of the developer. As a further precaution all plates were brush developed, i.e. the plate brushed with a soft camel hair brush whilst in the developer. The density of the images of the spectrum lines was then measured on a microphotometer. A characteristic curve for the plate was obtained from the calibrating spectrum put onto the plate by means of the standard strip filament lamp. The densities of the lines were then translated into intensities by means of the characteristic curve, the intensity ratios so being found. Experimental work was carried out on the various aspects of this process with the view to eliminating or making as small as possible any errors which could occur, the details are set out below.

5.1. Photographic Plate Characteristics.

Four photographic emulsions were investigated:-

1. Ilford Rapid Process Panchromatic (R.P.P.)
2. Ilford H.P.3.
3. Ilford F.P.4.
4. Ilford Astra.

The last of these emulsions was a long range type having a response extending up to approximately 7000 Angstroms. For spectroscopic intensity work the F.P.4. emulsion was judged to be the most satisfactory for general purposes whereas the H.P.3. emulsion was first preference when high speed was of importance. Both emulsions had otherwise very similar characteristics, with the F.P.4. emulsion having much less background fog. The intensity range over which the density of the R.P.P. emulsion lay on the straight portion of the characteristic curve was smaller than these two emulsions, but this range could be extended for all emulsions by using a smaller development time than that given by the makers for normal use. Therefore the H.P.3. and F.P.4. emulsions were used almost exclusively throughout the present work, using a development time of 2 minutes with standard Ilford I.D.2. developer (1 part I.D.2. to 2 parts water) at a temperature of 20°C.

The Astra emulsion was only of value for lines in the range 6400 to 7000 Angstroms. The speeds of the Astra, R.P.P. and F.P.4. emulsions were approximately equal, and about one half that of the H.P.3. emulsion. Some characteristic curves obtained for H.P.3. emulsion at various wavelengths under these conditions are shown in figure 10.

The uniformity of the emulsion of the photographic

Density.

Figure 10.

5461

4358

1.8 1.4

1.7 1.3

1.6 1.2

1.5 1.1

1.4 1.0

1.3 0.9

1.2 0.8

1.1 0.7

1.0 0.6

0.9 0.5

0.8 0.4

Characteristic Curves;
Ilford H.P.3. Emulsion.

$\lambda = 4358$

$\lambda = 5461$

4047

$\lambda = 4047$

2.0

2.2

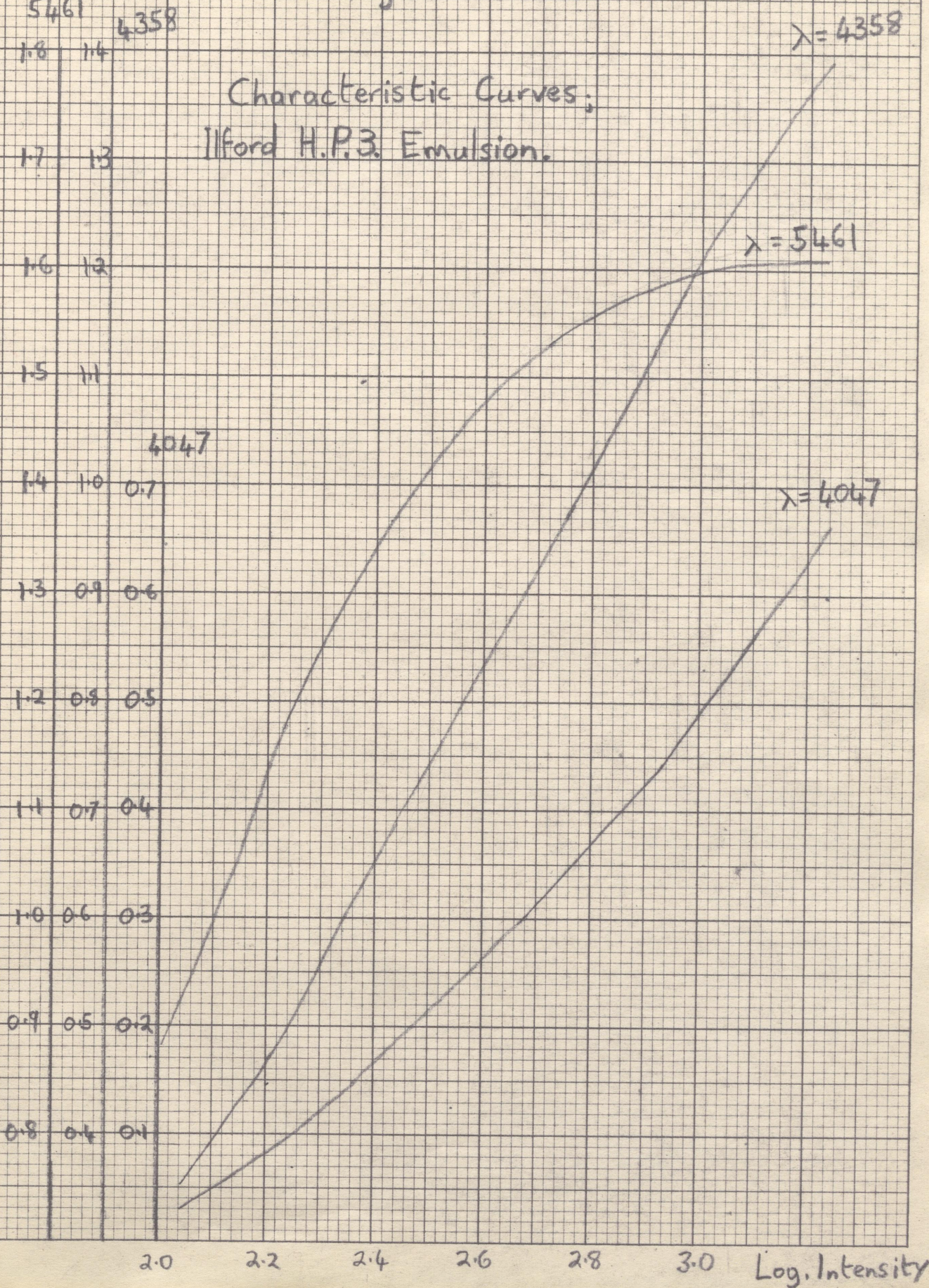
2.4

2.6

2.8

3.0

Log. Intensity



plates was checked by making a series of exposures of the standard strip filament lamp, on one photographic plate. The temperature of the lamp and the times of exposures were carefully controlled. The microphotometer was then run over the continuous spectra so obtained, at various wavelengths, the corresponding densities being evaluated. At one wavelength these should all have the same value. The densities actually obtained varied by 0.75%. The corresponding variation in intensity depended on the portion of the characteristic curve utilised; on the linear portion this was of the order of 2.5%, but the error is considerably greater outside this range.

A further point which must be observed in intensity work is the question of the exposure time of the calibrating spectrum in relation to that of the line spectrum and possible reciprocity law failure. The reciprocity law is that the product of the intensity and time of exposure gives a constant blackening for a given product, for all values of intensity and time. This law can easily be shown to break down, especially when time ratios get bigger than 5:1. Schwarzschild (1899) gave the following relation between intensity, time of exposure, and density:-

$$I t^p = \text{constant density.}$$

where p has a value of approximately 0.8 for most emulsions.

This relationship is generally true, but breaks down for very short, intense exposures. Kron later found:-

$$\log I_t = \text{constant} + \alpha \sqrt{\left[\log \left(\frac{I}{I_0} \right) \right]^2 + 1}$$

where α and I_0 are constants for a particular emulsion,

and Halm gave the equation:-

$$\log I_t = \text{constant} + \log \left[\left(\frac{I}{I_0} \right)^\alpha + \left(\frac{I}{I_0} \right)^{-\alpha} \right]$$

α and I_0 again being constants for a particular emulsion.

At low intensities this equation reduces to Schwarzschild's.

As far as intensity ratios are concerned the exposure time of the calibrating spectrum can be any multiple of the line spectrum exposure providing:-

1. No other calibrating exposure having a different time multiple is to be used.
2. That p in the Schwarzschild equation does not vary with the intensity and / or wavelength.

Proviseo (1) can be satisfied by using a calibrating step filter having a sufficient number of steps to cover adequately the strongest and weakest intensities in the line spectrum.

To investigate proviseo (2) test plates were taken

on which exposures of the calibrating lamp through the step filter at various times were made. An iron arc spectrum was taken on the same plates and used as a wavelength reference. The calibrating spectra were microphotometered and values of p obtained at various densities and wavelengths. Allowing for experimental error, the results obtained suggested that p was independent of the density and virtually independent of the wavelength over the range considered (5,500 - 4000 Angstroms). The characteristic curves obtained from one of these test plates at a wavelength of 4957 Angstrom units is shown in figure 11. The shift in the characteristics produced by the increasing exposure can be seen by reference to this graph; the times of exposure had been so chosen that the points shown circled would have fallen on a line corresponding to constant density if there were no failure of the reciprocity law. Values of p were obtained as follows:-

by Schwarzschild:- $I_1 T_1^p = I_2 T_2^p$ for a constant density.

$$\text{i.e. } \frac{I_2}{I_1} = \left(\frac{T_1}{T_2} \right)^p ,$$

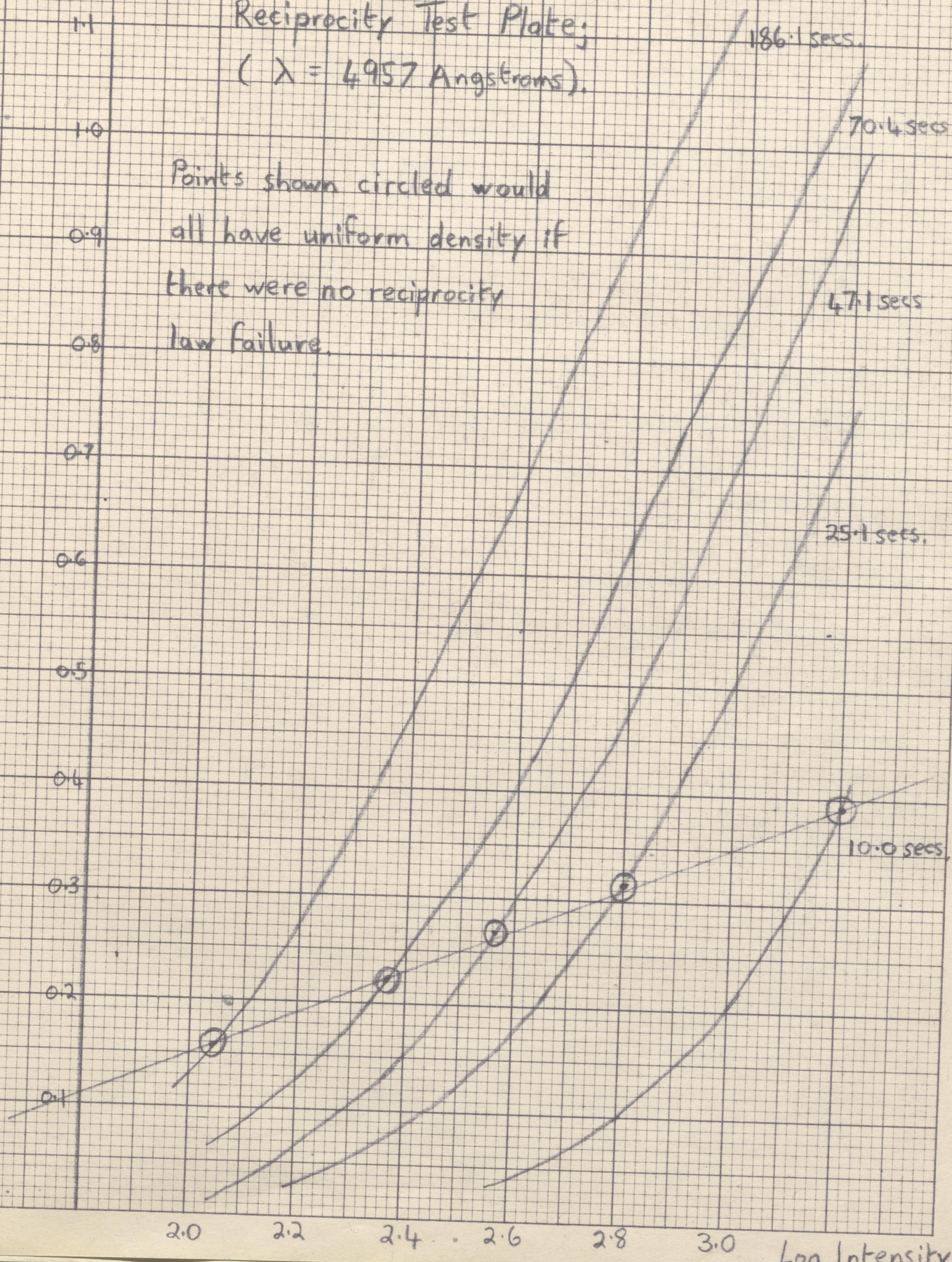
$$\text{i.e. } \log I_2 - \log I_1 = p \log \frac{T_1}{T_2}$$

Density.

Figure 11.

Reciprocity Test Plate;
($\lambda = 4957$ Angstroms).

Points shown circled would
all have uniform density if
there were no reciprocity
law failure.



$$\text{or } p = \frac{\log I_2 - \log I_1}{\log \frac{T_1}{T_2}}$$

For a constant density e.g. .157 (see figure 11) $\log I_2 - \log I_1$ is obtained directly as the abscissa; for the two extreme curves whose time parameters are 186.1 secs., and 10 secs.,

$$\log I_2 - \log I_1 = 0.88., \quad \frac{T_1}{T_2} = 18.61 \text{ secs.}, \text{ hence}$$

$$\log \frac{T_1}{T_2} = 1.27$$

$$\text{i.e. } p = \frac{0.88}{1.27} = 0.693.$$

Having found the conditions in which different exposure times could be given for two sources, it was decided to investigate methods of absorbing or reducing light from one source in order that convenient values of exposure could be arranged. For example, some sources require such short exposures that timing becomes a difficulty; by suitable attenuating the intensity, the exposures could be increased to convenient values for timing purposes.

Two methods suggested themselves:-

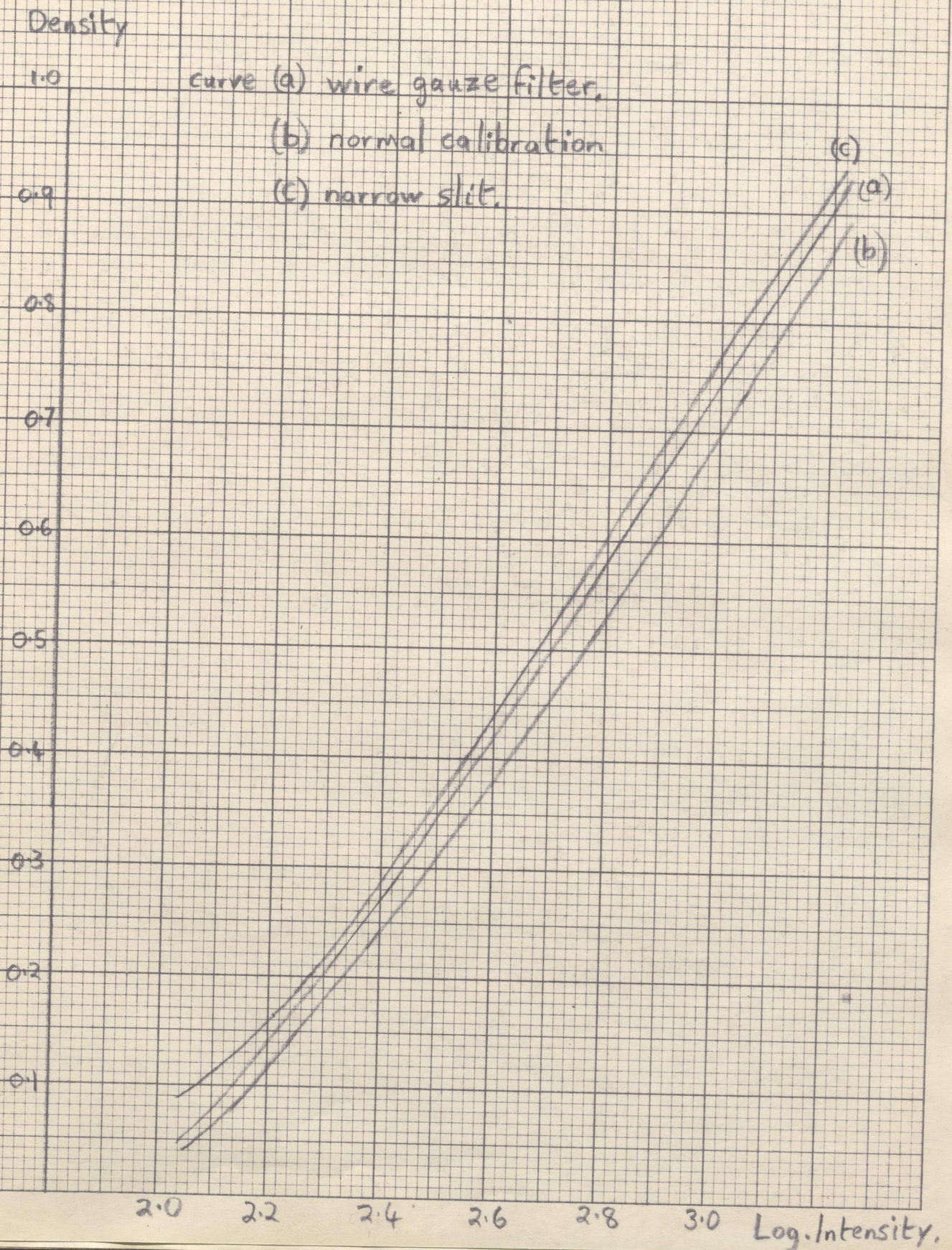
1. Neutral Filter.

2. Narrow Slit.

Neutral filters are difficult to obtain, the simplest possible being a wire gauze. Three thicknesses of a wire gauze were used here, the thicknesses being clamped securely together to prevent movement. Several test plates were taken as follows:- a sodium lamp exposure was made, followed by a calibrating tungsten filament lamp exposure. The calibrating lamp exposure was then increased, but the photographic density was kept approximately constant by (a) narrowing the spectrograph entrance slit, and then (b) by inserting the neutral gauze filter described above, two further calibrating spectra thus being obtained. The extra exposure time required had been predetermined in each case. Characteristic curves were obtained for each of the calibrating exposures (see figure 12) and the intensity ratio of the sodium blue doublet (4983 and 4979 Angstrom units) then found using all three of the characteristic curves. Results obtained from each characteristic curve were within experimental error.

It was concluded that both a wire gauze filter or a narrower slit may be used to reduce the intensity of a source. The wire gauze filter was used extensively in present work owing to the difficulty in resetting exactly

Figure 12.
Attenuation Calibration Test Plate.



a slit width, this being due to backlash in the micrometer screw drive. It was also concluded that reciprocity effects can be ignored providing that the wavelength range is not great, and only one calibrating spectrum is used.

5.2. Microphotometer.

The microphotometer used in the present work was a fully automatic recording type. The table and lamp unit was a modified Hilger type H481, the modifications consisting in the fitting of a two-speed, reversible, synchronous motor to drive the table in either direction, and the replacing of the original photocell with a photomultiplier. A friction type clutch was fitted to the motor in order to prevent damage to the gear train should the table reach its end stop. The photomultiplier was fed from a stabilised power supply having coarse and fine selection of the output voltage for adjustment of sensitivity. The output of the photomultiplier was fed into a d.c. amplifier consisting of a single "long tailed pair" stage. The output of this amplifier was in turn fed into a Honeywell-Brown "Elektronik" recorder. A constant voltage transformer was used to supply the microphotometer lamp, a similar constant voltage transformer being used to supply all the electronic equipment. To reduce effects of mains-borne interference and direct pick-up, screened cable was used for the supply leads, and coaxial cable for the signal leads. Before using the equipment it was allowed a warm-up

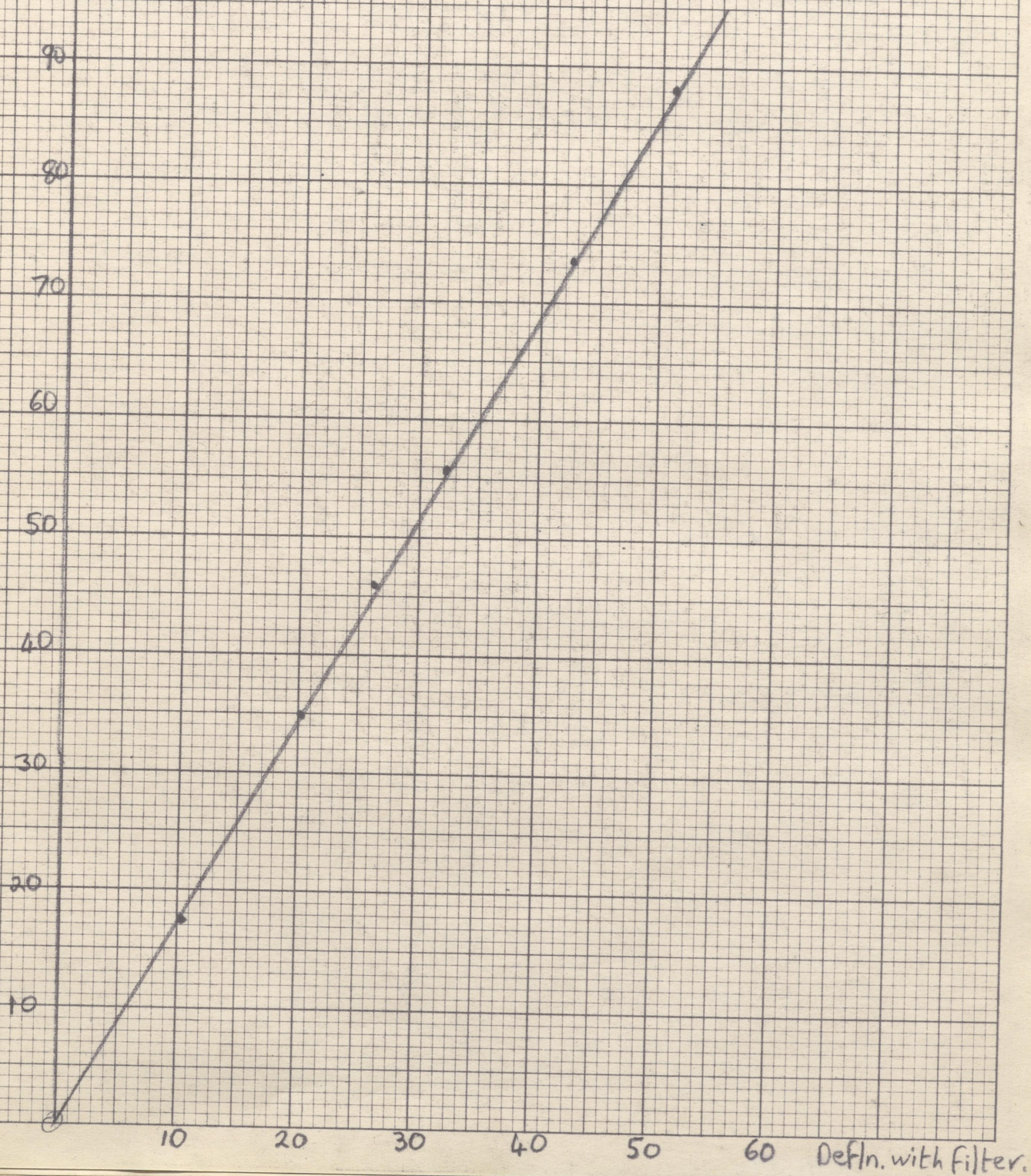
time of half an hour, in order to stabilise itself.

The linearity of the response of the microphotometer was checked as follows. One step of the seven step calibrating filter of known density (section 5.3 below) and a number of other filters were used; the actual density of these filters need not be known. The deflection of the microphotometer was first obtained with the clear portion of the seven step filter in the light beam, and then with the sixth step in the light beam. One of the other filters was then inserted into the light beam, and the two previous readings (through the clear, and through the sixth step of the seven step filter) again obtained. This process was repeated for the remaining filters. In this case five other filters were used. A plot of deflection with filter against deflection without filter was then made, as shown in figure 13. If the microphotometer response is linear this plot should be a straight line. The plot illustrated was made with a medium gain setting of the microphotometer, and shows the response to be linear. Two other plots were made using high and low gain settings to ensure that linearity was obtained for all operating conditions. This method of checking the linearity of a measuring system involving optical and electrical elements is a general method and was also employed in checking the linearity of the response of amplifier systems used with the photomultiplier described in

Figure 13.

Linearity of Microphotometer:
Medium Gain Setting.

Defln. without
filter.



section 6.

A typical trace of a spectrum line with an attendant calibration is shown in figure 14. A good feature of the recording microphotometer is that it enables the mean density of the steps of the calibrating spectrum to be obtained, in spite of grain variations.

5.3. Plate Calibration:- Step Filter.

In order to calibrate photographic plates both the inverse square law and the step filter methods were tried. These two methods gave plate characteristic curves in close agreement, but owing to the tediousness of the inverse square method, only the step filter method was subsequently used.

The step filter employed was a seven step pattern manufactured by Messrs. Hilger Limited. The optical densities (defined as $\log \frac{\theta_0}{\theta}$, where θ_0 is incident intensity, θ transmitted intensity) of the seven steps were quoted by the makers. However, the filter was about two years old when used for the present work, so that the densities of the steps were checked on the microphotometer. The neutrality of the filter was also checked by placing red, green and blue filters in turn, in the path of the light beam used in the microphotometer, and again measuring the densities. The filter was in fact found to be truly neutral, although some falling off in density on the densest steps had occurred.

Figure 14.
Microphotometer trace; Plate taken with a narrow slit.

Deflection, θ .

20 -

30 -

40 -

50 -

60 -

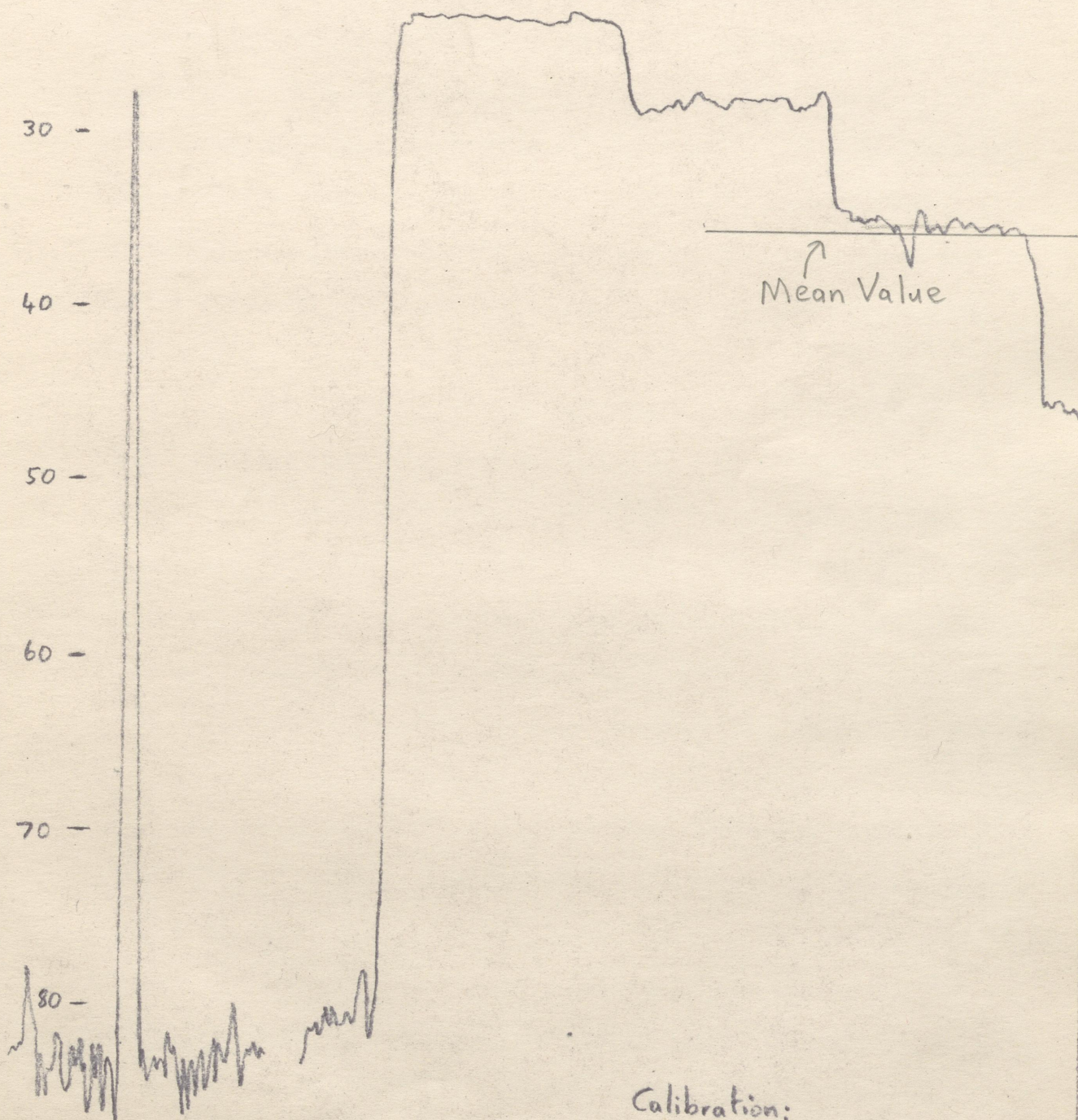
70 -

80 -

Mean Value

Traversed along plate
(Line.)

Calibration:
Traversed accross plate.
(3 steps shown).



This information is summarised in table 3.

5.4. Characteristic Curves and Intensity Ratios.

With a calibration spectrum as obtained in figure 11, the trace is converted into values of $\frac{\theta_0}{\theta}$, where θ_0 is the clear plate reading and θ is the step reading. The logarithm of this ratio is a measure of the photographic density which is plotted against the logarithm of the intensity, this being obtained from the known steps of the filter, assuming an arbitrary incident intensity.

The density of the spectrum line may then be found either from the peak reading of the trace or an integrated value relating to its area. In this investigation both densities were measured, in the case of the integrated intensities the areas under the intensity-wavelength curves were measured by a planimeter. Peak values were found to give the most consistent results especially when a wide slit was used for photographing the spectrum lines. In this case flat topped traces were obtained (see figure 15) which enabled the maximum value of the line to be clearly seen. With a sharp trace as shown in figure 14, the plate variations already referred to may produce a considerable error in intensity values. Integrated values were probably of little value, as in the case of the two spectrographs used here, the instrumental broadening of the lines was certainly

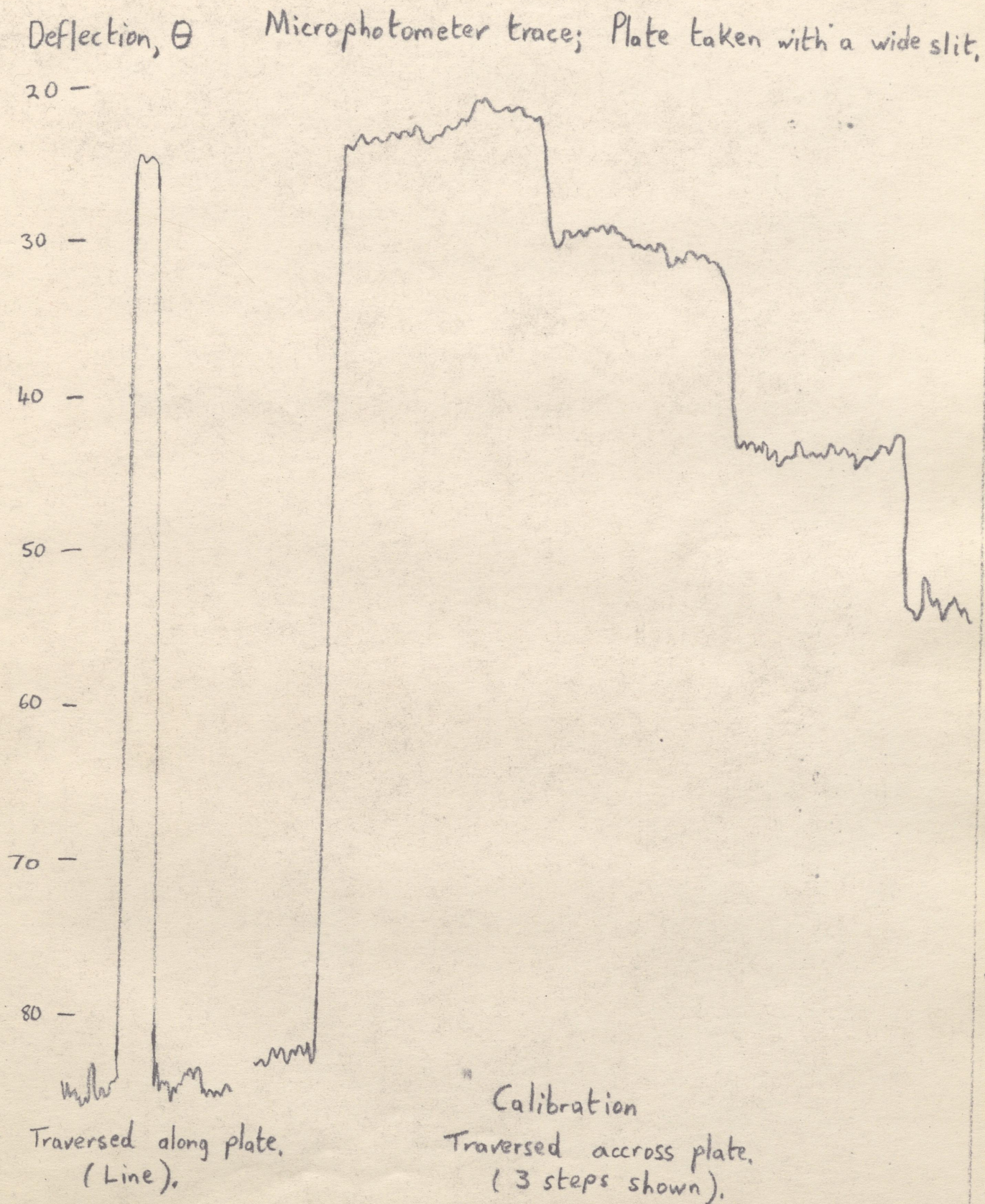
Step.	Av. Red.	Max. Red.	Min. Red.	Av. Green.	Max. Green.	Min. Green.	Makers Figures.
1.	0	0	0	0	0	0	0
2.	.191	.196	.182	.196	.199	.193	.21
3.	.395	.400	.388	.392	.398	.391	.40
4.	.641	.643	.640	.627	.629	.623	.65
5.	.825	.830	.820	.816	.825	.806	.85
6.	1.002	1.010	.997	1.012	1.020	1.004	1.07
7.	1.109	1.119	1.097	1.156	1.170	1.143	1.27

Step.	Av. Blue	Max. Blue	Min. Blue	Av. White	Max. White	Min. White	Makers Figures.
1.	0	0	0	0	0	0	0
2.	.206	.207	.204	.197	.199	.194	.21
3.	.393	.394	.391	.398	.400	.395	.40
4.	.621	.623	.619	.634	.639	.627	.65
5.	.807	.813	.799	.827	.836	.822	.85
6.	1.007	1.020	.999	1.014	1.030	1.000	1.07
7.	1.135	1.170	1.111	1.159	1.190	1.134	1.27

Table 3.

Step densities of neutral, seven step-filter.

Figure 15



greater than the actual width of the lines. This should not by itself prevent a correct result from being obtained.

In conclusion it may be stated that the wide slit technique gave the greatest consistency and should therefore be employed whenever possible. It cannot be used, for example, with two near spectrum lines as coalescing of the images will result. The results obtained photographically from plates taken on the constant deviation and the Littrow spectrographs are given in section 8.

6. Photomultiplier Method.

Two types of photomultiplier were used in the present work. These were an R.C.A. type 931A and a Mazda type 27M1. Large numbers of the American type were available as government surplus items after the last war, but these were found to have very variable characteristics. Several of the photomultipliers were therefore obtained, and the one having the best characteristics selected. Desirable characteristics are high sensitivity and low dark current (of the order of 0.2 microamps with a final voltage of 960 at room temperature). When the Mazda type 27M1 photomultiplier became available later, as a result of improved manufacturing techniques, the characteristics of these were found to be more nearly similar, and at the same time, the overall sensitivity was generally about twice as great as the R.C.A. type (of the order of 6000 microamps per microwatt at 5500 Angstrom units) for the same dark current. The Mazda type 27M1 was essentially a modified version of the R.C.A. type 931A made in Britain under licence. The base connections of the two photomultipliers were the same.

General precautions found to be necessary when using photomultipliers for intensity work were:-

1. New photomultipliers should be aged (i.e. operated at full voltage with a strong incident intensity for at least 20 hours before being placed into regular

service.

2. The temperature should be kept constant. With the present equipment the brass mounting for the photomultiplier (see figure 5) had a sufficiently high thermal capacity to shield the photomultiplier from irregular temperature changes, and provided that the photomultiplier was given half an hour in which to stabilise itself after being switched on, no further precautions were considered necessary. It should be noted however that lowering the operating temperature of the photomultiplier results in a reduced dark current which is an advantage in the case of faint sources, as the signal to noise ratio can be increased in this way. Melting ice or liquid air may be used as coolants, a photomultiplier mounting having a double external wall to contain the liquid being used for this purpose.

3. The power supply should be very stable, otherwise troublesome fluctuations are likely to occur with direct observation or d.c. amplification of the output signal. The requirements are not so stringent if a "chopping" technique is used. It was found that new dry batteries were more stable than commercially available stabilised electronic supplies by a factor of 3:1. Batteries were therefore used in this work.

4. Fatigue effects were likely to occur with intense incident beams. It was therefore found desirable to limit strong sources by using a narrow spectrograph entrance slit.

5. It is desirable to utilise the same portion of the photocathode (Keohane and Metcalf 1955) for comparative purposes as there may be a variation in sensitivity over the cathode.

The constant deviation spectrograph was the most convenient instrument to use with the photomultiplier, and consequently most of the preliminary photomultiplier work was carried out with this spectrograph. As previously stated an adaptor was constructed for the Littrow spectrograph, only direct readings being taken on this instrument.

6.1. Direct measurements with the photomultiplier.

The photomultiplier was mounted on to the constant deviation spectrograph by means of a specially constructed adaptor. The power supply for the photomultiplier (both photomultipliers used were of the 9 stage type) was a number of 120 volt radio-type dry batteries connected in series, the circuit arrangement being shown in figure 16. Eight of these batteries were used to provide a total E.H.T. voltage of 960 volts. This voltage was continuously monitored by means of an electrostatic voltmeter so that any deterioration of the batteries could be immediately observed. The dynode voltage was 96 volts per stage obtained via the potentiometer network of ten 47 kilohms carbon type resistors. These were of $\frac{1}{2}$ watt dissipation to prevent any excessive thermal effects affecting their resistance. The

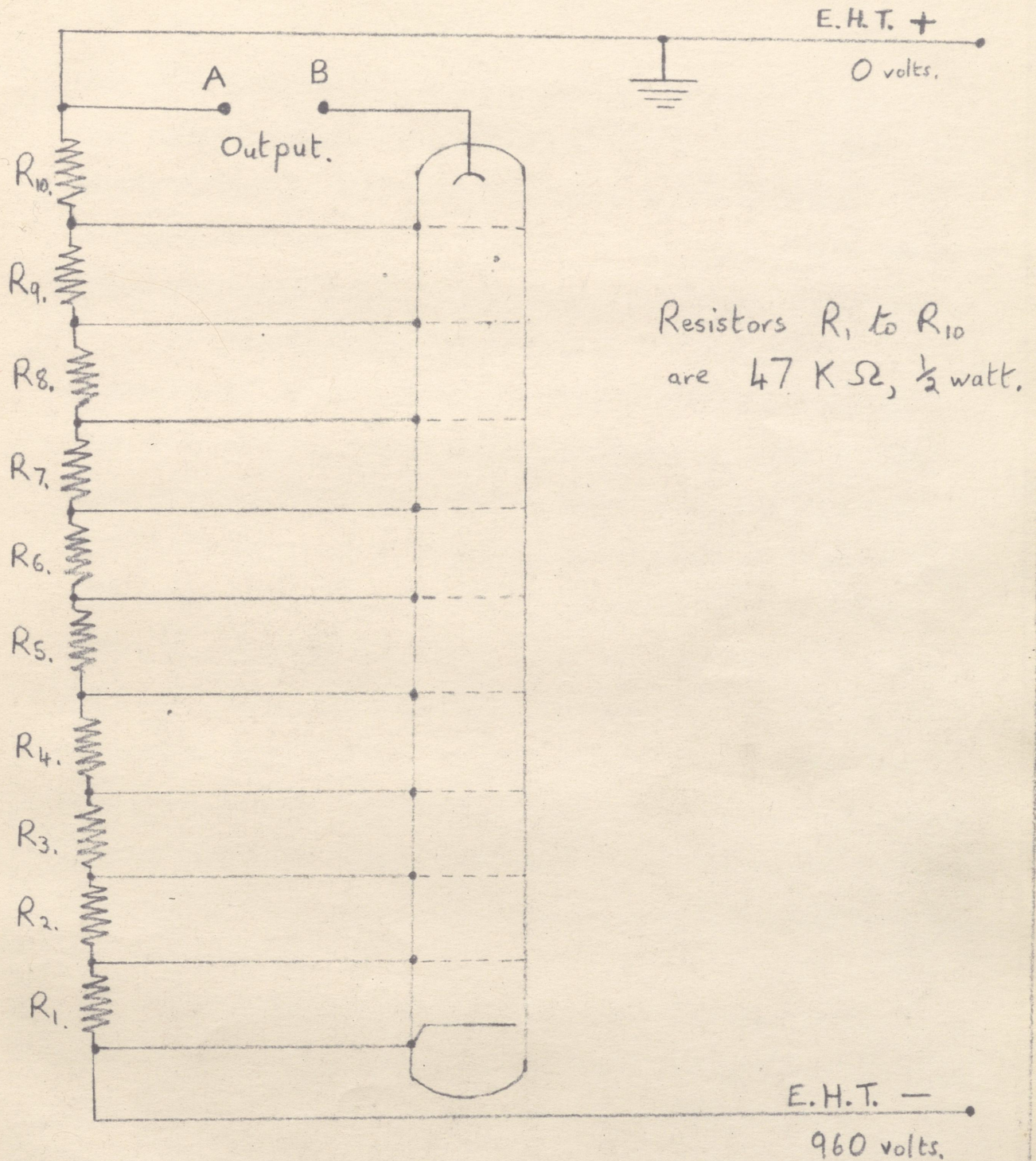


Figure 16.

Photomultiplier power supplies (Type Mazda 27M1)

measuring instrument was connected to terminals A and B, this necessitating the earthing of the positive end of the supply voltage. This instrument was a Pye "Sealamp" type galvanometer when the components of the mercury triplet were being compared, this having a coil resistance of 100 ohms.

Before using the apparatus for intensity measurements it was allowed to have an initial "warm-up" period of half an hour. Readings were then taken on the three components of the mercury triplet by rotating the wavelength drum and so causing each in turn to fall on the photomultiplier entrance slit. This was of sufficient width to allow all the light from one line to fall on the photomultiplier cathode. The procedure was to rotate the wavelength drum until a maximum deflection of the galvanometer occurred; the photomultiplier entrance slit was then widened until no further increase in deflection was obtained, so ensuring that all of the spectrum line was falling on to the photocathode.

Calibration of the apparatus then consisted in setting up the standard tungsten strip filament calibrating lamp (at an operating temperature of 2800°K) and then recording deflections of the galvanometer for various wavelength drum settings. In this way a complete response curve of the apparatus to the white light was obtained (see figure 17) which could then be corrected for the black body

Figure 17.
Photomultiplier Response. (Mazda 27M1)

Galvanometer
Deflection.

40

35

30

25

20

15

10

5

Photomultiplier
response to white
light (2800°K)

response to
constant incident
intensity (not
corrected for dispersion)

4500

5000

5500 Wavelength Å.

4000

distribution of the calibrating lamp, as shown, using data obtained from figure 4. Using this curve the intensity ratios of the mercury triplet could be found. These values were corrected for dispersion with corrections for the corresponding wavelengths obtained from figure 6. Strictly speaking, it was only really necessary to take calibrating lamp readings at the desired wavelengths (in this case the wavelengths of the mercury triplet) and this was in fact done when readings were taken on the Littrow spectrograph. Similar readings were taken on the Littrow spectrograph using the photomultiplier mounting plate shown in figure 9. In this case the dispersion corrections were obtained from figure 8.

Before the galvanometer readings taken of the mercury triplet were converted into relative intensities it was necessary to know how the response of the photomultiplier varied with incident intensity. The manufacturers state that a linear response is obtained at all wavelengths. To verify this the seven-step neutral filter was used in conjunction with the standard calibrating lamp, each step being placed over the slit in turn, the corresponding galvanometer readings being taken. This process was carried out at two wavelengths situated at the ends of the wavelength range used, the resulting response - intensity curves obtained being shown in figure 18. These curves show that over the intensity range used, the response was linear. Relative

Figure 18
Photomultiplier Intensity Characteristic (Mazda 27M1)

Galvanometer
Deflection

40

30

20

10

$\lambda = 5400 \text{ \AA.}$

$\lambda = 4000 \text{ \AA.}$

.2

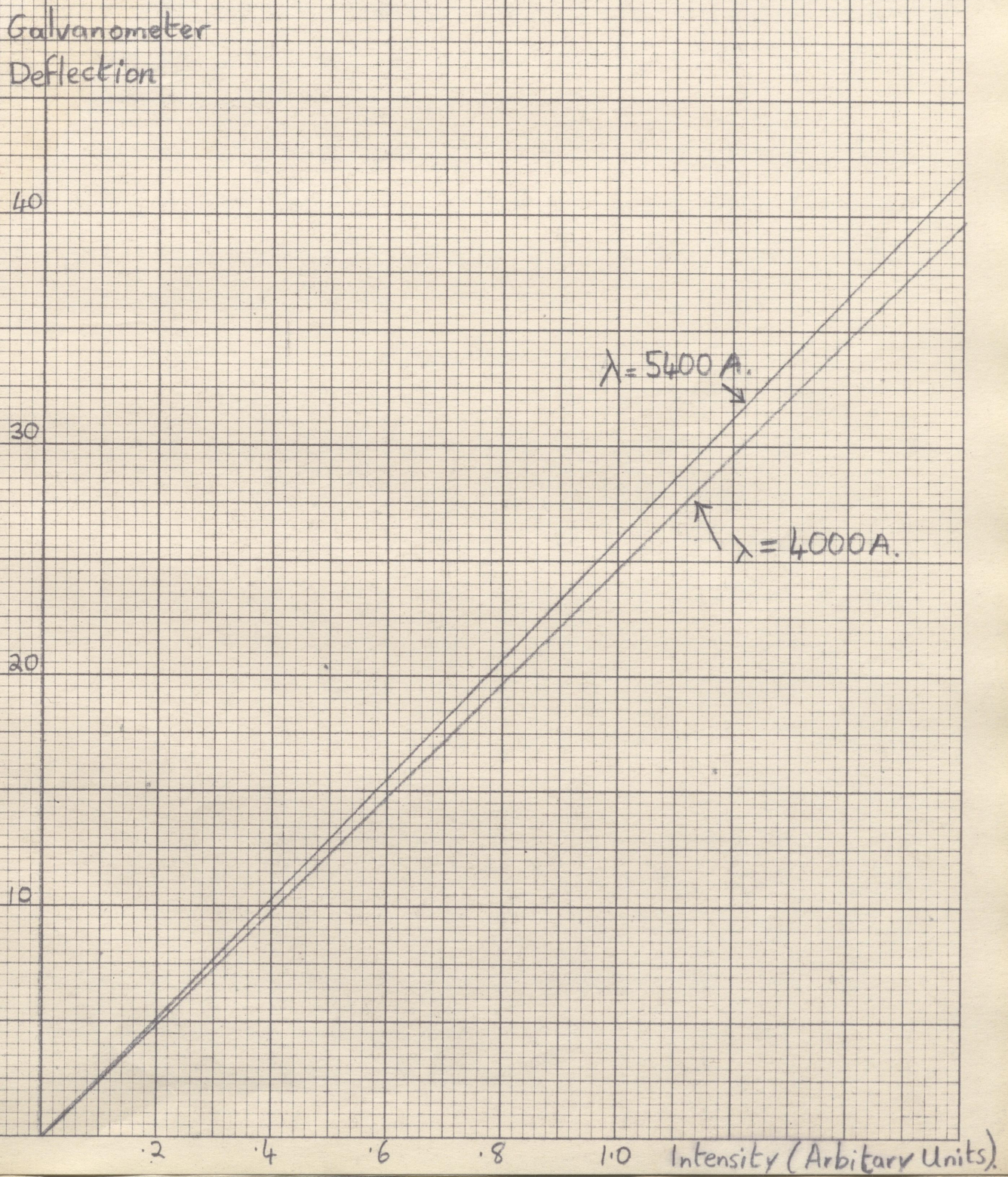
.4

.6

.8

1.0

Intensity (Arbitrary Units)



intensity values for the mercury triplet were then obtained by dividing the galvanometer readings obtained for each line, by the ordinates obtained from the curve corrected for black body distribution in figure 17, at the appropriate wavelengths.

As stated, readings were taken of the components of the mercury triplet on both the constant deviation and Littrow spectrographs. Results obtained are grouped together for comparison purposes in Section 8.

6.2. Electrometer triode amplifier.

When certain weak spectrum lines were being compared it was found that the photomultiplier response was insufficient to give reasonable galvanometer deflections. A specially designed amplifier consisting of a single electrometer triode valve was therefore constructed and used as the measuring instrument, its input terminals being connected to the terminals A and B in the photomultiplier anode circuit (shown in figure 16). The output terminals of the amplifier were connected to a moving coil galvanometer.

The electrometer triode was connected in a stable single stage circuit (Morton, 1932) so as to eliminate variations of accumulator e.m.f. which would otherwise prove extremely troublesome. An electrometer valve has a high input impedance which is ideally suitable for the small currents to be amplified (that is the photomultiplier anode

current). The type used here was an Osram type E.T.1. and this was connected in the circuit shown in figure 19. The E.T.1. requires a filament current of 100 milliamps, its filament resistance being approximately 10 ohms at this current, and it also requires an anode voltage of 6 volts. These are both obtained from a single 18 volt accumulator as shown.

In this electrometer circuit, R_2 is a standard 10 ohm resistance which is used in conjunction with the standard cell for setting the filament current to the correct value. The galvanometer is switched to terminals a and b for so calibrating the filament current, resistance R_3 being adjusted for zero galvanometer deflection. The galvanometer is switched to terminals c and d for measuring the amplifier output. It can be shown that this circuit is independent of accumulator e.m.f. when :-

$$\frac{R_7}{R_5} = \frac{R_F + R_2 + R_6 + \mu R_1}{R_4 + r_a - \mu R_1}$$

where r_a = anode resistance of electrometer valve
= 10,000 ohms.

μ = amplification factor = 1 at the operating conditions of the electrometer valve.

R_4 and R_5 , and R_6 and R_7 are adjusted for this condition to be satisfied. The makers' figures give the bias voltage of the electrometer valve to be -1 volts for minimum grid

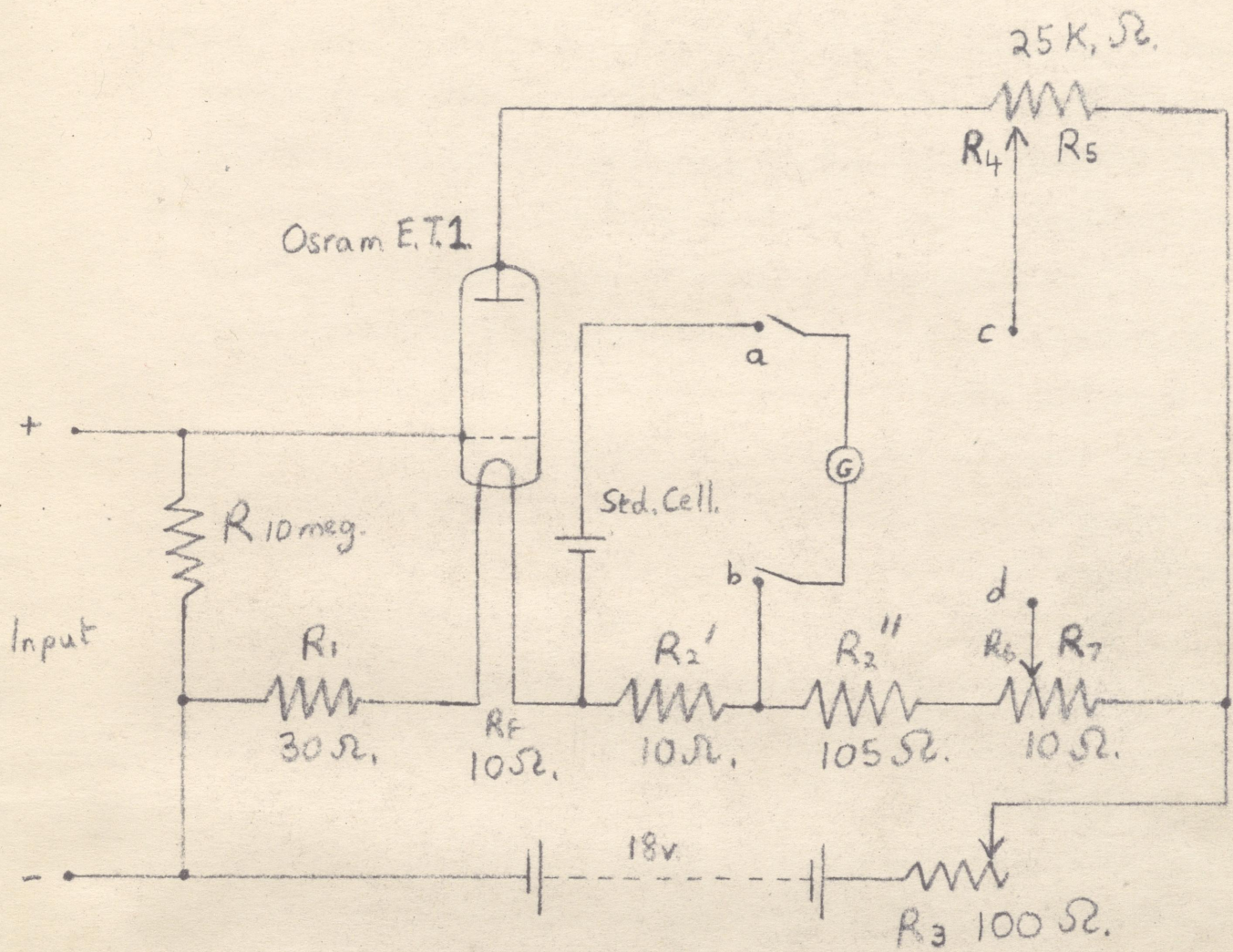


Figure 19.

Electrometer Valve Circuit

current. The bias voltage consists of the voltage developed across R_1 by the filament current minus the voltage developed across R , the input resistance, by the dark current of the photomultiplier. This input resistance was 10 megohms, the voltage developed across it by the dark current of the photomultiplier being approximately 2 volts. Therefore R_1 was made a 30 ohm resistance so that the total grid bias voltage should be -1 volt. The completed amplifier had a current gain of approximately 12 times, with a zero drift of 5×10^{-10} amps per minute. (The currents being measured were of the order of 10^{-7} amps).

The amplifier was used in the measurement of the mercury yellow lines described in section 6.4.

6.3. Interrupted Beam method with photomultiplier.

With this technique an interrupting device was used in the path of the light beam from the source to the spectrograph. Various forms of interrupter have been used in the past, as for example, a rotating sector driven by a synchronous motor (Savitzky and Halford, 1950, and Hornig, Hyde and Adcock, 1950) a rotating mirror (White and Liston, 1950, and Tetlow, McAuslan, Brinley and Price, 1951) and an electromagnetically maintained vibrating leaf-spring (Richards, 1955). Another method which avoids mechanical components is pulsing of the photomultiplier supply voltage, (Hendee and Brown, 1956). The advantage of this "chopping" technique is that drift and

dark current are of little significance, and this is particularly important for weak signals where a large degree of amplification may be required (Kandiah and Brown, 1952).

Utilising this technique on the constant deviation spectrograph, the photomultiplier was mounted in precisely the same way as for the direct method, the E.H.T. voltage again being 960 volts. The output from the photomultiplier was however an alternating current whose frequency depended on the speed of interruption and whose waveform was virtually square. An a.c. amplifier was therefore used to amplify the photomultiplier output, the output of the a.c. amplifier being rectified and then used to deflect a moving coil galvanometer in the usual manner.

At first in this work, a rotating sector driven by a synchronous motor was used as an interrupter. The output of the photomultiplier was fed into a Muirhead type D-669-A selective amplifier, the output of the amplifier being rectified by a bridge of G.E.C. type G.E.X.55 germanium diodes mounted in a light-tight tube, and being smoothed by a 32 microfarad electrolytic capacitor before being fed into a Pye "Scalamp" type galvanometer having a coil resistance of 100 ohms. The selective amplifier was used to prevent or reduce pick-up. Unfortunately, with a synchronous motor operated from the 50 c.p.s. mains supply, the interrupted frequency was always a multiple of 50 c.p.s. With the particular sector

used it was 150 c.p.s. (motor speed 750 r.p.m., sector 12 slots) and it was also found that pick-up was extremely troublesome at this frequency, causing violent wandering of the galvanometer.

A vibrating reed device was therefore constructed, the reed being fitted with a paddle of sufficient area to interrupt the light beam when placed adjacent to the spectrograph slit. The reed length was adjustable (see figure 20) so that its frequency of oscillation (when the coil was fed with an alternating voltage of suitable frequency) could be varied. The coil of the device was fed from a beat frequency oscillator via a suitable transformer. (A later model was wound to operate directly from the B.F.O.). The vibrator could then be operated at various frequencies up to 200 c.p.s. which was the upper limit of its frequency. A check was kept on the galvanometer to observe when the pick-up (in this frequency range) was a minimum. It was found that a frequency of 75 c.p.s. was the optimum. A block schematic diagram of the equipment is shown in figure 21.

Galvanometer readings were then taken whilst each component of the mercury triplet was allowed to fall in turn onto the photomultiplier, by adjustment of the wavelength drum. The intensity-response characteristic of the apparatus was determined for each wavelength by inserting a series of

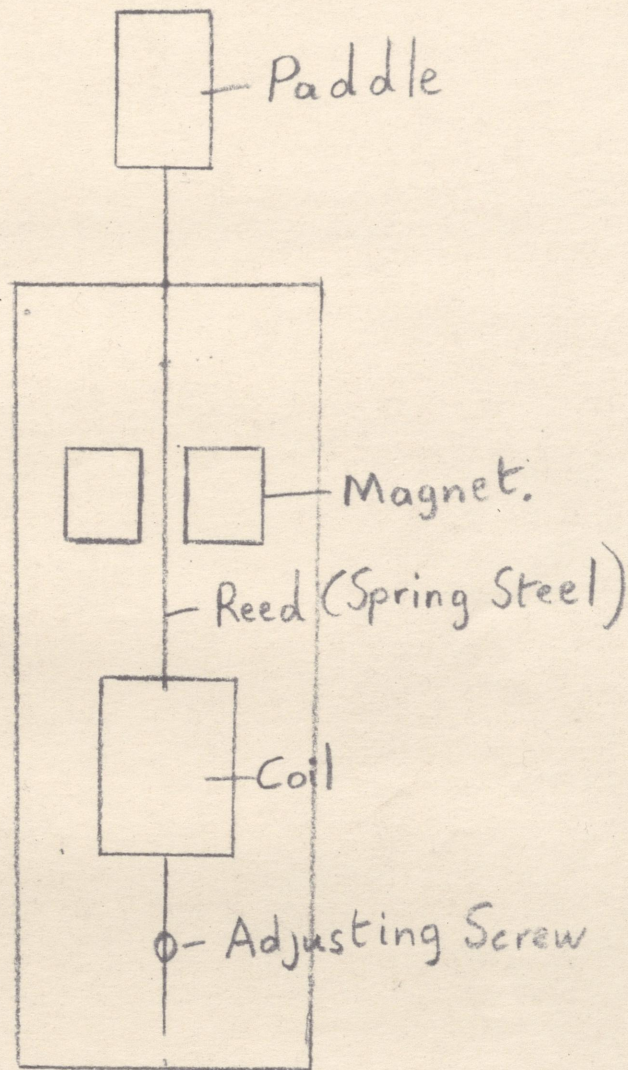


Figure 20.

Vibrating Reed "Chopper"

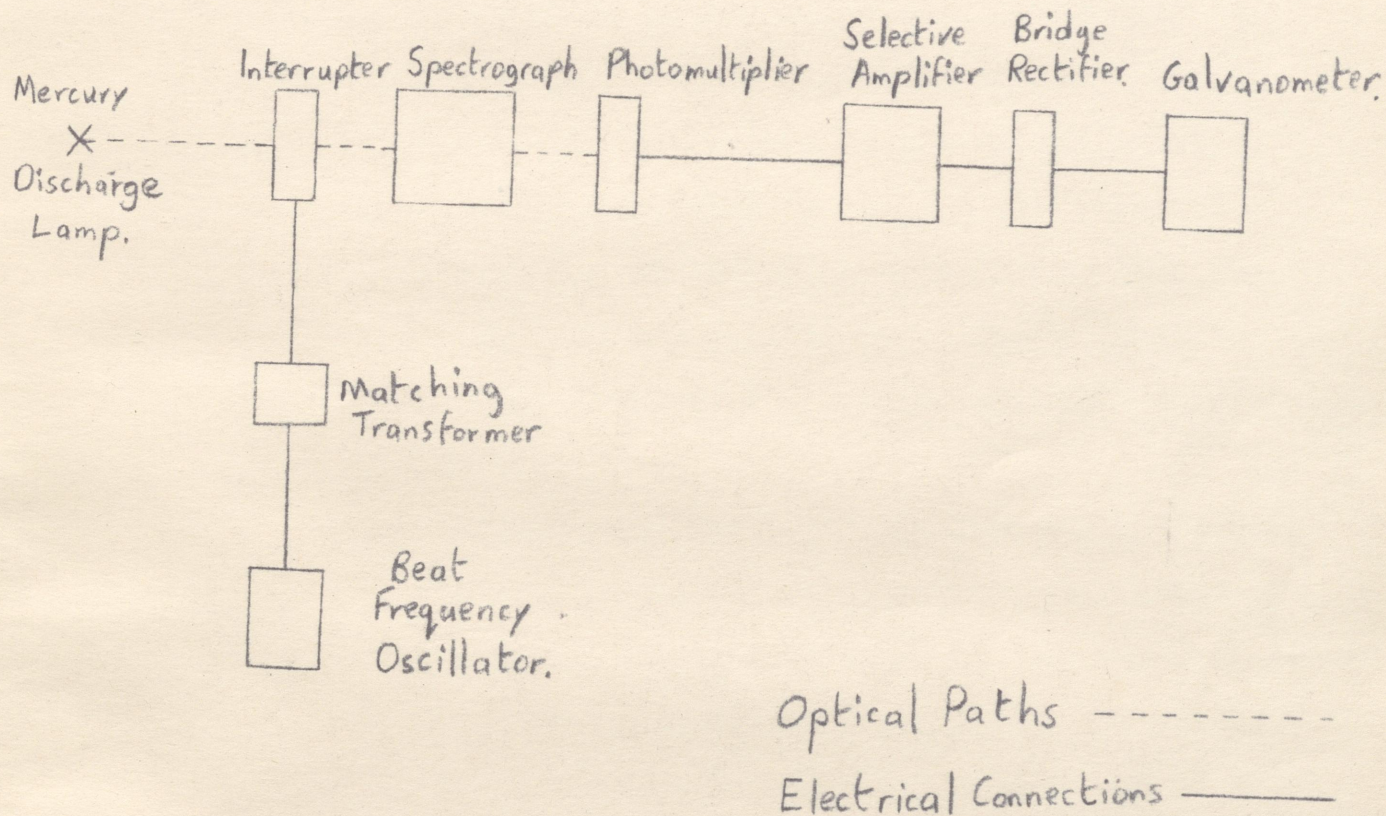


Figure 21.

Block schematic diagram of interrupted beam method.

neutral filters of known absorption into the light beam, and recording the corresponding galvanometer readings. The results so obtained are shown in figure 22, in which the response is seen to depart slightly from linearity for the higher values of intensity, until, eventually saturation was reached. It was desirable to avoid taking readings on this saturated portion of the characteristic.

Calibration consisted in setting the standard strip filament lamp up, as before, and arranging that the deflections obtained at the desired wavelengths (that is those of the mercury triplet) lay on the intensity - response curves of figure 22.

The galvanometer readings obtained for the mercury triplet could then be converted into comparative intensity values by dividing the intensities obtained for the deflections from figure 22 by the intensities obtained for the calibrating lamp deflections at the respective wavelengths, and at the same time multiplying them by factors proportional to the black body emitted intensities at the equivalent wavelengths. These factors may be obtained from Table 1 or figure 4. Results obtained by this method are given in section 8.

6.4. Photomultiplier entrance slit width.

A test made on the constant deviation spectrograph was to investigate the effect of photomultiplier entrance slit width on the ratio of intensities of two near spectrum lines.

Figure 22.

Photomultiplier Response:- Interrupted Beam.

Galvanometer
Deflection.

10

9

8

7

6

5

4

3

2

1

$\lambda = 4358 \text{ \AA.}$

$\lambda = 5461 \text{ \AA.}$

$\lambda = 4047 \text{ \AA.}$



2

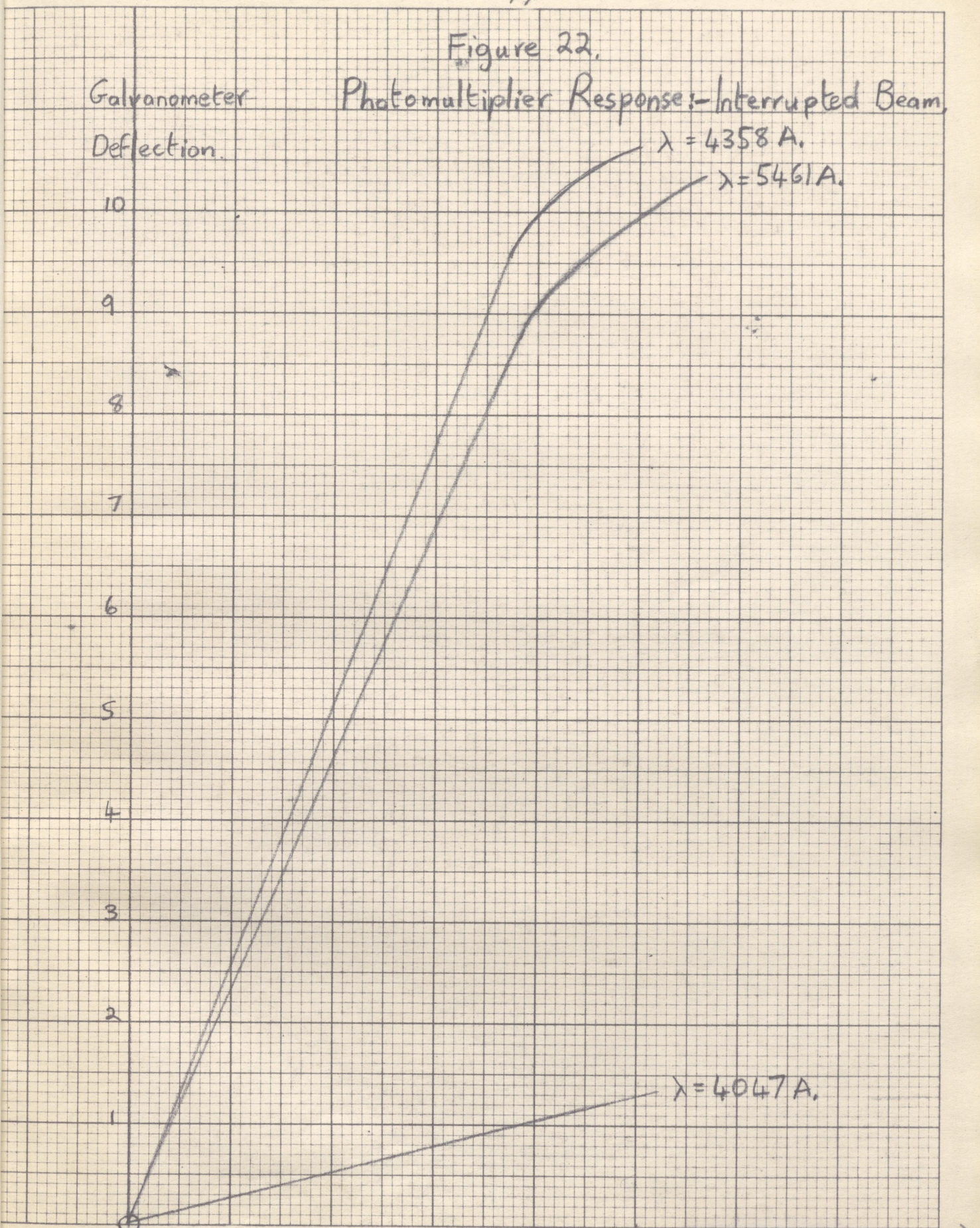
4

6

8

10

Intensity (Arbitrary Units)



The tests were performed using the sodium D lines (6 Angstroms separation) and the mercury yellow lines (20 Angstroms separation). It was found that providing the lines were resolved by the spectrograph, the slit width had no effect on the intensity ratio; but as the entrance slit of the spectrograph was widened, and resolution of the two lines became less perfect, the ratio would become smaller. This was clearly indicated in the case of the mercury yellow lines, although in the case of the sodium D lines the instrument itself was unable to resolve them completely, the maximum ratio of intensities obtained for the sodium D lines was 1.2. (Theoretically the ratio is 2, but the main reason for the low value obtained here was subsequently found to be due to the sodium lamp used as the source; this is explained in section 9.) The intensity ratio obtained for the mercury yellow lines was 1.06, these being measured in conjunction with the electrometer triode amplifier described in section 6.2. above, as their intensity was small compared with that of the sodium D lines.

When calibrating the photomultiplier with the tungsten strip filament lamp, it was found desirable to have the photomultiplier entrance slit width as small as convenient; otherwise too wide a range of wavelengths was passed at any particular drum setting, this giving rise to an inaccurate calibration especially at the extreme wavelengths covered by the instrument.

7. Schwarz Photo-resistive Cell.

The Schwarz cell was a type F.T. 400 manufactured by Hilger Limited, and consisted of a semiconducting element mounted in an adaptor suitable for attachment to the constant deviation spectrograph. The semiconducting element was made of cadmium selenide (Schwarz, 1948, 1949 and 1951) which utilises the photo-resistive effect previously described. The dark current of the cell was 0.36 microamps with an applied voltage of 10 volts, and 0.58 microamps with an applied voltage of 18 volts, a series limiting resistor of 10 megohms being used in each case. These dark currents were increased by about 50% by an incident strong line whose wavelength was in the working range of the cell. The electrical circuit used with the cell is shown in figure 23. The cell was used both directly as shown in this figure, and in conjunction with the electrometer triode amplifier designed for use with the photomultiplier (see section 6.1). In this instance the 10 megohm grid leak resistor of the electrometer valve was joined in series with the Schwarz cell. The makers say that the cell is suitable for the "chopping" technique at 800 c.p.s. but this method was not tried with the cell, because of its subsequent considered unsuitability for intensity measurements.

Measurements with the cell were taken using the mercury yellow lines and triplet, the readings on the mercury yellow lines being taken in conjunction with the electrometer triode amplifier. The readings consisted in

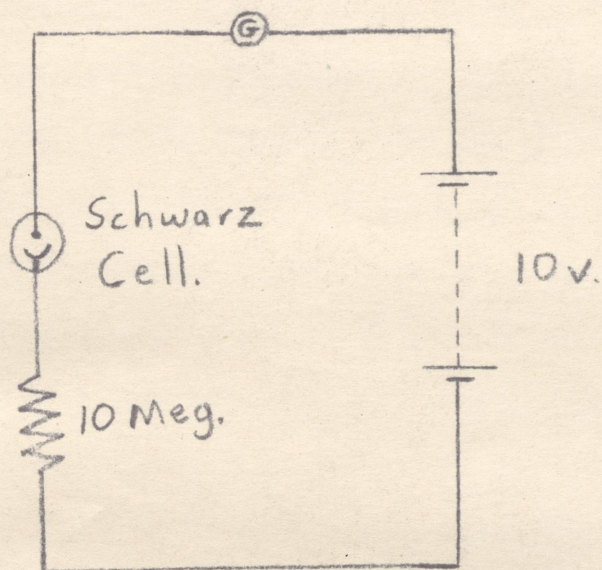


Figure 23.

Schwarz Cell Circuit.

observing galvanometer deflections as each spectrum line was thrown on to the cell by means of the wavelength drum. At first, the readings obtained were extremely variable, and it was subsequently found that the cell element had a large temperature coefficient of resistance. Draughts would produce a large change in the zero reading these being eliminated by surrounding the cell with a box packed with cotton wool. However, it was then found that the radiation itself was heating the element, and was so producing a drift in the deflections. The temperature coefficient of resistance of the cell was investigated by heating the cell to various temperatures and measuring the dark current at each. These results are illustrated in Table 4, and show that a 35°C increase in ambient temperature results in a 65% increase in dark current.

To eliminate these temperature effects a tank was constructed which mounted on the spectrograph exit tube adjacent to the point where the Schwarz cell was mounted, (see figure 7). This tank could be filled with melting ice, or liquid air. Using melting ice much more stable results were obtained, although a period of about 5 minutes was required after a line was received by the cell for the deflection to reach its steady value. Using liquid air as coolant, it was found that although the dark current diminished to negligible proportions and that the sensitivity of the cell was approximately double that at the melting ice temperature,

Temperature.	Galvo. Deflection.	Dark Current.
23.5°C.	71.5 cms.	0.58 μ A.
29.0	80.2.	0.65.
34.0	87.5.	0.71.
39.0	96.0.	0.78.
44.0	103.6.	0.84.
49.0	111.9.	0.91.
53.0	117.9.	0.96.

Table 4.

Variation of dark current with temperature
for Schwarz cell type F.T.400.

(Applied voltage 18 volts)

deflections took even longer to reach their steady values, (10 to 15 minutes being required). No readings were obtained at liquid air temperature because frost formed across the cell connections, effectively shorting it out.

Readings were taken of each component of the mercury triplet with the cooling tank filled with melting ice, each line being received in turn, by the Schwarz cell, on suitable rotation of the wavelength drum. An applied voltage of 10 volts was used for the measurements, and the cell slit width was adjusted in accordance with the comments given previously in section 6.2. A Pye "Scalamp" type galvanometer was used having a coil resistance of 100 ohm. This type of galvanometer is very suitable for use with the Schwarz cell as the extremely convenient zero adjustment enables the dark current of the cell to be effectively biassed off.

Calibration of the cell consisted in observing the deflections obtained with the standard tungsten strip filament lamp at each of the three relevant wavelengths, and then inserting a series of known, neutral filters between the calibrating lamp and the entrance slit of the spectrograph, corresponding galvanometer readings being observed. By this means an Intensity - Deflection graph was obtained for the cell, at each wavelength, these being shown in figure 24. The deflections obtained from each

Figure 24

Schwarz Cell Intensity Response
(Calibrating Lamp Temperature 2800°K.)

Galvanometer
Deflection.

6

5

4

3

2

1

0

 $\lambda = 5461 \text{ \AA.}$ $\lambda = 4358 \text{ \AA.}$ $\lambda = 4047 \text{ \AA.}$

Intensity
Arb. Units.

7

6

5

4

3

2

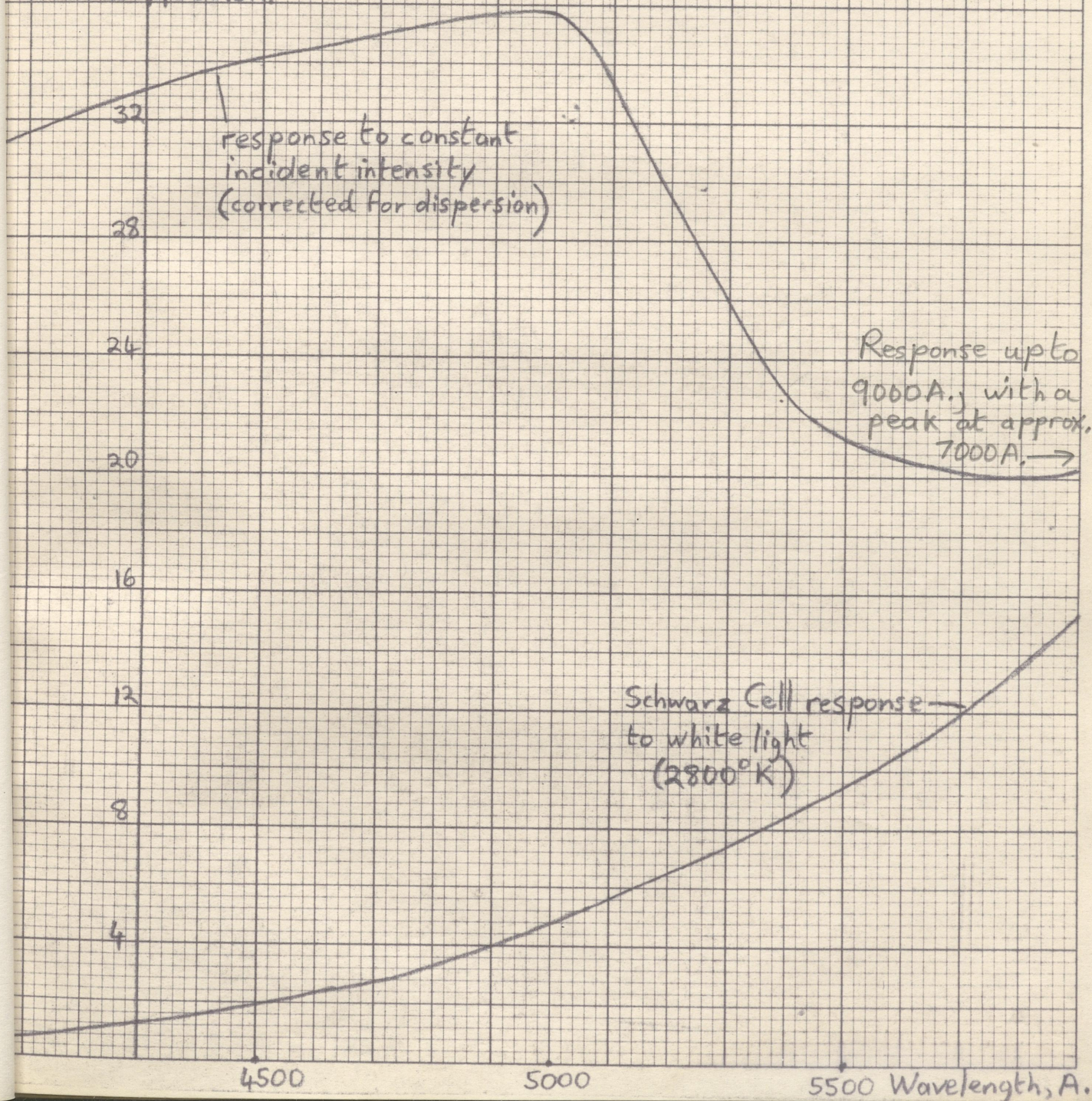
1

spectrum line were then converted into intensities by means of these graphs, and then into relative intensities by correcting for the black body distribution of the lamp, as previously. Further corrections for dispersion and emissivity were also applied in the manner previously described. A response - wavelength characteristic for the Schwarz cell was obtained by using the standard lamp as source and observing the galvanometer deflections for various wavelength drum settings. The curve obtained is shown in figure 25 together with the corrected curve for black body distribution and dispersion of the spectrograph.

Results obtained with the Schwarz cell are given in section 8 below; it is thought that the heating effect of the radiation received by the cell requires that adequate cooling be applied, otherwise anomalous results will be obtained; the cell is slow to use (because of the slow drifts) and it would therefore seem that its use is as a detector of spectrum lines rather than as a measuring device for intensities.

Figure 25
Schwarz Cell Wavelength Response.

Galvanometer
Deflection.



8. Results.

The results of various measurements taken on the sodium and mercury spectra are given in this section. A discussion on the implications of these results follows in the next section.

8.1. Measurements on the Sodium D lines and Blue doublet.

The object of these measurements, which were made on the Littrow spectrograph, was to check the accuracy of the method of determining the intensity ratio of two near spectrum lines by photographing both simultaneously through a neutral step filter. Three plates were initially taken of the blue sodium doublet (4983 and 4979 Angstroms) using the sodium lamp as source. Results obtained were:-

$$4983 : 4979 = 2.09 : 1, \quad 1.98 : 1, \quad 2.04 : 1.$$

these giving an average value of $2.04 : 1$ for the intensity ratio. This value was considered to be in good agreement with the theoretical value of $2.00 : 1$. A total of eight plates were taken of the sodium D lines, using the sodium lamp as source, and using H.P.3, F.P.4, R.P.P, and Astra emulsions. The intensity ratio obtained in this case was

$$5896 : 5890 = 1 : 1, \text{ approximately in all cases.}$$

The theoretical value of the intensity ratio is $1.00 : 2.00$.

In order to investigate this discrepancy between the theoretical and experimental values, further plates were taken of the sodium D lines, but using a bunsen flame in

which sodium chloride was being vaporized as the source. It was found that the intensity ratio of 5896 : 5890 varied from 1 : 1.2 up to 1 : 1.7 according to the amount of sodium chloride being vaporized. A further check was made by taking a plate of the sodium D lines in absorption, light from a tungsten filament lamp being passed through the bunsen flame in which sodium chloride was being vaporized. The intensity ratio obtained by this method was 1 : 1.45.

8.2. Photographic measurement of mercury triplet on Littrow spectrograph.

Several photographic plates were taken of the mercury triplet using the 100 watt mercury lamp as source. The calibration was in this case obtained from the tungsten strip filament standard lamp and the seven step-filter. The intensity ratios found are given in Table 5, the ratios shown being corrected only for the black body distribution of the calibrating lamp. Other correction factors were applied later to the mean values of these ratios. The mean values are shown in the table, together with the deviations from these values. Finally the intensity ratios were corrected for the variation in emissivity of the tungsten calibrating lamp, and for the dispersion of the instrument.

The emissivity correction factors were obtained from Table 2 by interpolation, the main effect of the correction being to increase the intensity of the green line

Readings.	5461	:	4358	:	4047.
1	1		1.29		0.76
2	1		1.09		0.54
3	1		1.09		0.78
Mean	1		1.16		0.69
Error	-		$\pm 8.6\%$		$\pm 17.4\%$ *
Conn. Tungsten Emis.	1		1.13		0.66
Conn. Dispersion	1		0.56		0.27

* See note in Section 9.

Table 5.

Photographic measurements on Littrow spectrograph:-

100 watt mercury lamp.

at the expense of the blue lines. Taking the intensity of the green line to be arbitrarily as unity, the correcting factors applied to the other lines were:-

4358; $\times 0.974$, 4047; $\times 0.953$.

These factors will apply to all measurements taken with the standard tungsten strip filament lamp when operating at a temperature of 2800°K .

The dispersion correcting factors were obtained from figure 8. The theory underlying the choice of these factors is that the spectrum lines require no correction for the dispersion of the instrument since the energy is emitted into such a narrow band of wavelengths as to be unaffected by the dispersion. The calibrating spectrum does however, require correction since the spectrograph slit allows a considerable range in wavelength, especially at the red end of the spectrum where the dispersion is least. The effect of all this is that the lines of longer wavelength must have their apparent intensity diminished due to the enhancement of the calibrating spectrum in this region. The correcting factors therefore increase the intensity of the green line in relation to the blue, as does the emissivity of the tungsten correcting factor previously discussed, but to a larger degree. The dispersion correcting factors obtained for the Littrow instrument, and as applied to the intensities of the violet lines, relative to the green as

unity, are:-

4358; $\times 0.498$. 4047; $\times 0.407$.

These factors will apply only to results taken on the Littrow spectrograph.

It was found that over a period of 9 months, the relative intensities of the mercury triplet as obtained from the 100 watt mercury lamp had changed quite markedly. Further plates were therefore taken using the mercury isotope lamp as source, the intensity ratios obtained being shown in Table 6.

8.3. Photographic measurement of mercury triplet on constant deviation spectrograph.

Photographic plates were also taken on this instrument of the mercury triplet, using the 100 watt mercury lamp as source. The calibration was obtained from the tungsten strip filament lamp and the seven step-filter, although on this instrument only five of the steps could be utilised due to the restriction in slit length. The intensity ratios obtained are given in Table 7, the given ratios being corrected only for the black body distribution of the calibrating lamp. The mean values of the ratios are then given together with deviations. Finally values corrected for tungsten emissivity variation are given (calculated as previously) and for the dispersion of the instrument.

The dispersion correcting factors were obtained

Readings.	5461	:	4358	:	4047
1	1		1.05		0.41
2	1		1.18		0.40
3	1		1.13		0.44
Mean	1		1.12		0.42
Error	-		$\pm 5.8\%$		$\pm 4.8\%$
Corrn. Tungsten Emis.	1		1.09		0.40
Corrn. Dispersion	1		0.54		0.16

Table 6.

Photographic measurements on Littrow spectrograph:-
mercury isotone lamp.

Readings.	5461	:	4358	:	4047
1	1		1.10		0.61
2	1		1.11		0.54
3	1		1.10		0.77
Mean	1		1.10		0.64
Error	-		$\pm 0.5\%$		$\pm 18.0\%$ *
Corrn. Tungsten Emis.	1		1.08		0.61
Corrn. Dispersion	1		0.43		0.16

* See note in Section 9.

Table 7.

Photographic measurements on constant deviation spectrograph:-
100 watt mercury lamp.

from figure 6 in a similar manner to those obtained for the Littrow spectrograph (see section 8.2). These factors as applied to the violet lines, relative to the green line as unity intensity were:-

4358; $\times 0.397$, 4047; $\times 0.268$.

These factors will apply only to results taken on the constant deviation spectrograph, but should apply to the photomultiplier readings as well as to the photographic measurements.

8.4. Photomultiplier measurements on Littrow spectrograph.

Readings were taken of each component of the mercury triplet using the direct method with both the 100 watt and the isotope mercury lamps as sources. The values obtained using the 100 watt mercury lamp as source are given in Table 8, and those obtained with the mercury isotope lamp as source are given in Table 9. Values corrected for black body distribution are given in these tables and the mean values (with deviations) given. These mean values were then corrected for tungsten emissivity variation and for spectrograph dispersion as previously, using the correcting factors given in section 8.2. Each of the values given under "Readings" in Table 8 consisted of the mean of three readings taken on one day. One calibration was used to convert this mean value to the intensity ratio shown in the table. The variation of the three readings comprising the mean value was in the order of 2 to 3%.

Readings.	5461	:	4358	:	4047
1	1		1.00		0.43
2	1		0.99		0.46
3	1		1.02		0.44
Mean	1		1.00		0.44
Error	-		$\pm 1.5\%$		$\pm 3.4\%$
Corrn. Tungsten Emis.	1		0.97		0.42
Corrn. Dispersion.	1		0.48		0.17

Table 8.

Photomultiplier measurements on Littrow spectrograph:-

100 watt mercury lamp.

Readings.	5461	:	4358	:	4047
1	1		1.14		0.41
2	1		1.14		0.41
3	1		1.10		0.41
4	1		1.10		0.41
Mean	1		1.12		0.41
Error	-		$\pm 1.8\%$		-
Corrn. Tungsten Emis.	1		1.09		0.39
Corrn. Dispersion	1		0.54		0.16

Table 9.

Photomultiplier measurements on Littrow spectrograph:-
mercury isotone lamp.

8.5. Photomultiplier measurements on the constant deviation spectrograph.

The photomultiplier mounted on the constant deviation spectrograph was used in two ways namely directly as with the Littrow instrument above, and with a beam "chopping" method. Both the 100 watt and isotope mercury lamps were used as sources for the direct method, the results obtained being shown in Tables 10 and 11. The 100 watt lamp was used as a source for the beam "chopping" method, the results obtained being shown in Table 12. As previously, the values given in the body of these tables have been corrected for black body distribution only. Mean values and deviations are then obtained, the mean values then being corrected for tungsten emissivity variation and for spectrograph dispersion. For these tables, the tungsten emissivity correcting factors used were those given in section 8.2, whilst the dispersion correcting factors used were those pertaining to the constant deviation spectrograph and given in section 8.3.

8.6. Schwarz cell measurements on the constant deviation spectrograph.

The Schwarz cell was mounted on the constant deviation spectrograph and was cooled by melting ice as previously described. Measurements were taken, directly, of the components of the mercury triplet, using the

Readings.	5461	: 4358	: 4047
1	1	1.13	0.81
2	1	1.07	0.76
3	1	0.97	0.55
4	1	0.97	0.58
5	1	0.98	0.55
6	1	0.98	0.52
7	1	1.13	0.66
8	1	1.13	0.66
Mean	1	1.05	0.64
Error	-	$\pm 7.6\%$	$\pm 22.7\%$ *
Corrn. Tungsten Emis.	1	1.02	0.61
Corrn. Dispersion	1	0.41	0.16

* See note in Section 9.

Table 10.

Direct photomultiplier measurements on constant deviation
spectrograph:-
100 watt mercury lamp.

Readings.	5461	:	4358	:	4047
1	1		1.16		0.42
2	1		1.15		0.47
3	1		1.18		0.48
Mean	1		1.16		0.46
Error	-		$\pm 1.3\%$		$\pm 6.5\%$
Corrn. Tungsten Emis.	1		1.13		0.44
Corrn. Dispersion	1		0.45		0.12

Table 11.

Direct photomultiplier measurements on constant deviation

spectrograph:-

mercury isotope lamp.

Readings.	5461	:	4358	:	4047
1	1		0.93		0.52
2	1		1.14		0.64
3	1		1.04		0.81
4	1		1.01		0.74
Mean	1		1.03		0.68
Error	-		$\pm 10.2\%$		$\pm 21.3\%$ *
Corrn. Tungsten Emis.	1		1.00		0.65
Corrn. Dispersion	1		0.40		0.17

* See note in Section 9.

Table 12.

"Chopped" beam photomultiplier measurements on constant deviation spectrograph:- 100 watt mercury lamp.

100 watt mercury lamp as source. The values obtained are shown in Table 13. These values were corrected for the black body distribution of energy in the calibrating lamp spectra, and mean values for the intensity ratios obtained. Maximum deviations from the mean were expressed as a percentage. The mean values were then corrected for tungsten emissivity variations using the correcting factors given in section 8.2., and were finally corrected for the dispersion of the constant deviation spectrograph using the correcting factors given in section 8.3.

A discussion of the results obtained by the various methods used here for the measurement of intensity ratios follows in section 9.

Readings.	5461	:	4358	:	4047
1	1		1.16		0.47
2	1		1.29		0.93
3	1		1.12		0.74
Mean	1		1.19		0.71
Error	-		$\pm 7.2\%$		$\pm 32.4\%$ *
Corrn. Tungsten Emis.	1		1.16		0.67
Corrn. Dispersion	1		0.46		0.18

* See note in Section 9

Table 13.

Schwarz cell measurements on constant deviation spectrograph:-
100 watt mercury lamp.

9. Discussion.

The value of the intensity ratio of the sodium blue doublet (4983 and 4979 Angstroms) obtained when using the sodium lamp as source was in good agreement with theory. An energy level diagram for sodium is shown in figure 26, and it can be seen from this that the blue doublet is the result of transitions between a doublet D level to a doublet P level ($5^2D_{5/2}$, $5^2D_{3/2}$, - $3^2P_{3/2}$, $3^2P_{1/2}$). This actually results in three components, as shown, the fourth one between $5^2D_{5/2}$ and $3^2P_{1/2}$ being a forbidden transition because $\Delta J \neq \pm 1$ or 0. However, two of the components have virtually the same wavelength because the D levels are so close together, that only a doublet could be resolved by the spectrograph. The intensities of these two components can be shown to be in the ratio 2 : 1 for 4983 : 4979. (Herzberg, 1944). The experimental results gave a value of 2 ± 0.05 : 1 for this ratio.

This result was obtained by photographing the sodium blue doublet through the seven step-filter, and shows that very good results can be obtained using the photographic method when there are no other complicating factors (such as calibration and self-absorption) to be taken into consideration. The limit to the accuracy obtainable is the variation in sensitivity of the photographic emulsion itself, which is generally about 2.5%.

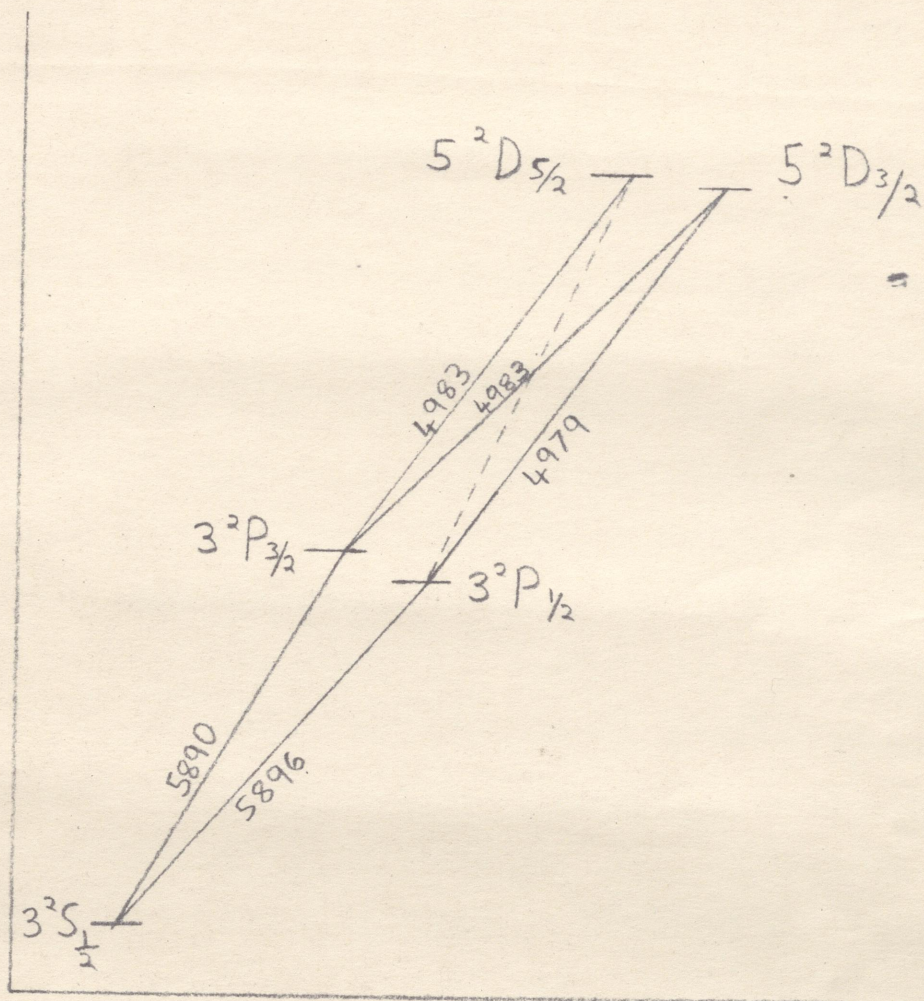


Figure 26

Term diagram for Sodium.

For the sodium D lines, which are the result of $3^2P_{3/2}$, $3^2P_{1/2} - 3^2S_{1/2}$ transitions (see figure 26) the intensity ratio of the two components can be shown to be 1 : 2 for 5896 : 5890. However, values obtained using the sodium lamp as source gave a ratio of 1 : 1 with a variation of less than 5% over a large number of observations. The low value of the ratio obtained by this means is probably due to the fact that the sodium lamp used as source contained neon as the carrier gas. It has been shown earlier by R. Wood that neon and other monatomic inert gases can produce a change in the emitted intensity ratio of the sodium D lines. This is because atoms of the inert gas are involved in collisions of the second kind with sodium atoms in the $3^2P_{3/2}$ level, and as a result of these collisions the sodium atoms are transferred to the $3^2P_{1/2}$ level, the inert gas atoms gaining kinetic energy. This increase in population of the $3^2P_{1/2}$ level at the expense of the $3^2P_{3/2}$ level results in increased emission of the 5896 Angstroms line with a corresponding decrease in emission of the 5890 Angstroms line. As the experimental results show a high degree of consistency amongst themselves, it would seem to indicate again that the step-filter method of comparing the intensities of two near spectrum lines is capable of giving good results.

The values obtained using the bunsen flame as

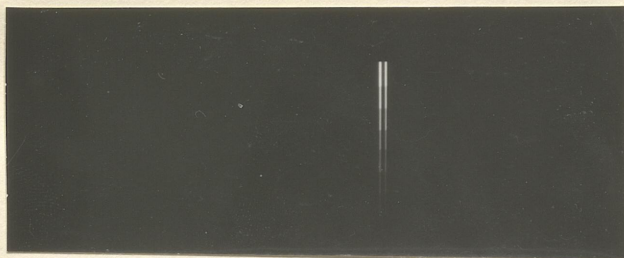
source were shown to depend on the number of sodium atoms present in the flame. A photograph of the sodium D lines through the seven step-filter, obtained using the bunsen flame as source is shown in figure 27. Figure 27 (a) was taken with a small amount of sodium chloride in the flame, whilst figure 27 (b) was taken with a much larger amount in the flame. The more nearly equal intensities of the two lines is easily seen in the latter case. For these large concentrations self-absorption must occur and this will tend to reduce the intensity ratio. This finding has been confirmed by other workers (Snelleman and Smit, 1955).

A further photograph of the sodium D lines was obtained in absorption, this being shown in figure 27 (c). However, the intensity ratio obtained by this method was still below the theoretical value and this may be due to the fact that the absorption lines are narrower than the emission lines, thus allowing some directly emitted light to alter the ratio measured. This is illustrated in figure 28.

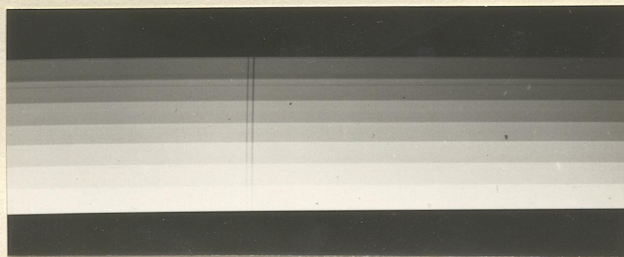
The results of experimental work carried out on the measurement of the intensity ratios of the components of the mercury triplet have been tabulated in Tables 5 - 13 and summarised in Table 14. It will be seen from these tables that the value for the 4358 Angstroms component compared with that for the 5461 Angstroms component gives a fairly consistent ratio, the results for the 4047 Angstroms



(a) Sodium D lines in emission:-
Small concentration of sodium.



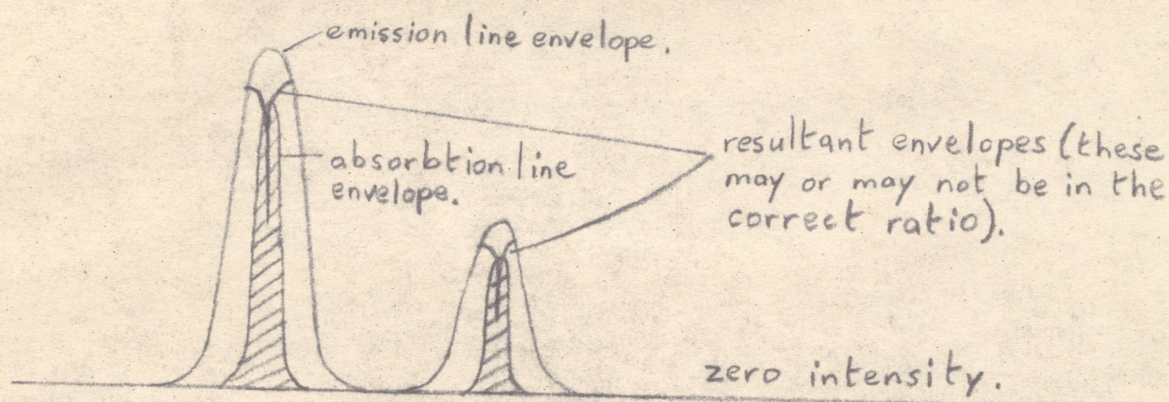
(b) Sodium D lines in emission:-
Large concentration of sodium.



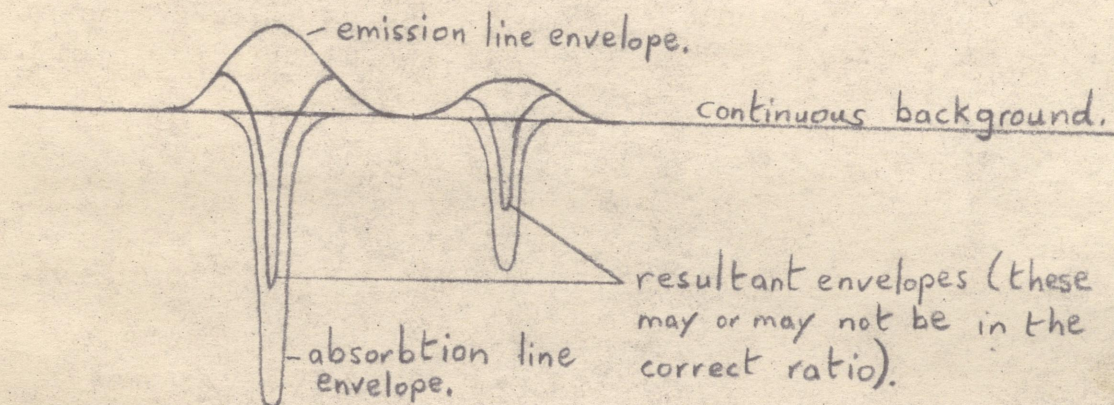
(c) Sodium D lines in absorption.



Figure 27.



(a) Effect of absorption on the measurement of emission line intensity ratio.



(b). Effect of emission on the measurement of absorption line intensity ratio.

Figure 28.

Method	Source	5461	: 4358	: 4047
Littrow, Photographic.	Isotope lamp	1	0.54	0.16
" Photomultiplier	" "	1	0.54	0.16
Littrow, Photographic	100 watt lamp	1	0.56	0.27
" Photomultiplier	" " "	1	0.48	0.17
Const.Devn.Photomultiplier	Isotope lamp	1	0.45	0.12
Const.Devn.Photographic.	100 watt lamp	1	0.43	0.16
" " Photomultiplier	" " "	1	0.41	0.16
Const.Devn.Photomultiplier	" " "	1	0.40	0.17
" " Interrupted.	" " "	1	0.40	0.17
" " Schwarz Cell.	" " "	1	0.46	0.18

Table 14.

Summary of results for intensity ratios of mercury triplet.

line being less satisfactory. This is because the violet 4047 Angstroms line besides being less intense than the other two components of the triplet, is also in the region of detector insensitivity, of low calibration intensity from the standard lamp, and in the case of the constant deviation spectrograph, of instrumental cut-off.

These factors taken together mean that measurements on the 4047 Angstroms line are subject to considerable error, and therefore the value obtained for this line is subject to the biggest deviation. This is especially true for values taken on the constant deviation spectrograph using the 100 watt mercury lamp as source, and such values have been marked in the tables by means of an asterisk. The Schwarz cell in particular has a low sensitivity to this violet line, and hence the deviations obtained with this detector are biggest of all. Nevertheless, the mean ratios obtained with this detector are in good agreement with those obtained with the other detectors. Hence the intensity ratios of the 5461 Angstroms line to the 4358 Angstroms line furnishes the more satisfactory test for accuracy and consistency of the measurements.

Comparing the results obtained with the different lamps for the intensity ratios of these lines it will be seen that those taken with the mercury isotope lamp are much more consistent amongst themselves than those taken

with the 100 watt mercury lamp. It is thought that this is partly due to the fact that the temperature of the 100 watt lamp probably varies, the variation of the temperature affecting the output from the lamp in one or more of the following ways:-

1. The absorption characteristics of the glass envelope of the lamp may change with temperature, this being most likely in the region of 4000 Angstroms.
2. The pressure of the mercury vapour will change as a result of temperature changes. It is possible that resultant pressure broadening of the emitted lines may alter the apparent intensity ratios.
3. The efficiency of the nitrogen present in the 100 watt mercury lamp (see below) in effecting transfers from one excited level to another is probably temperature dependent. This is because the collision cross-section of the nitrogen molecules with the excited mercury atoms increases with temperature (Matland, 1953).

In the case of the mercury isotope lamp there is little temperature variation (because of the water cooling) and hence the above mentioned effects are of little consequence.

Another difference between the 100 watt mercury lamp and the mercury isotope lamp is that self-absorption effects are much greater in the 100 watt lamp, and these, as discussed below, may vary both with temperature and with

time. Self-absorption affects the 5461 Angstroms green line more than the other two components of the mercury triplet. This is because of the fact that the relative number of atoms in the 6^3P_2 state (see figure 2, page 17) is greater than those in the 6^3P_1 and 6^3P_0 , states (Kenty, 1950). The effects of self-absorption have been greatly minimised in the case of the mercury isotope lamp by having a positive column only 5 millimetres in diameter.

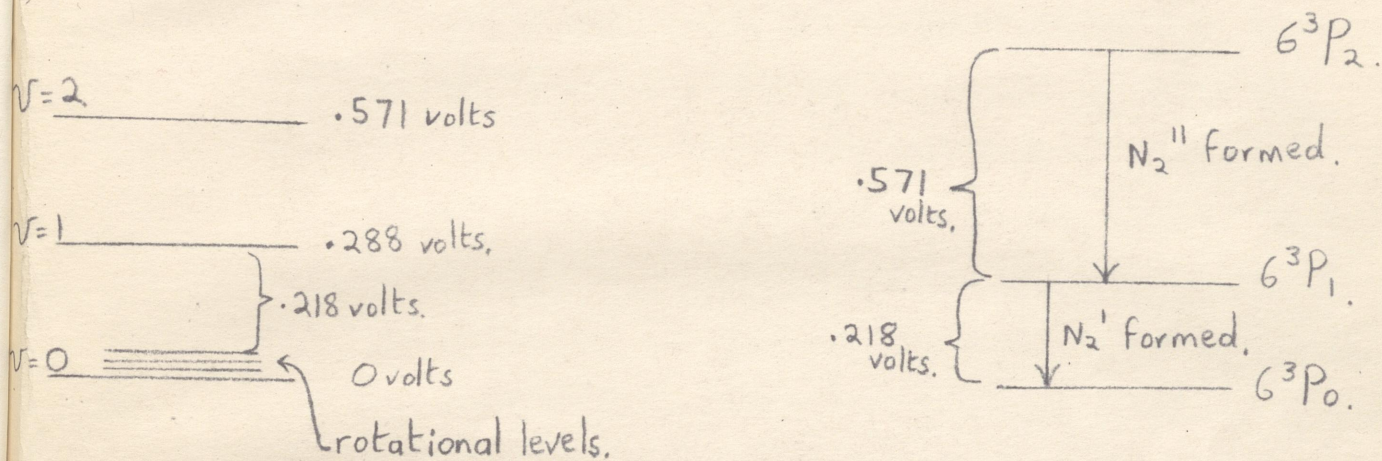
The decision to use the mercury isotope lamp was made after it was found that results from the 100 watt lamp showed considerable change after a time interval of 9 months, there being a 50% increase in relative intensity of the 4358 Angstroms line, and a 100% increase in intensity of the 4047 Angstroms line with respect to the 5461 Angstroms line. This does not affect the values given in the tables however, as these were all taken within a comparatively short time of one another.

This time variation in output of the 100 watt mercury lamp is thought to be due to the presence of nitrogen in the lamp gas filling, with the initial result that the 4047 Angstroms line was reduced in intensity and the 5461 Angstroms line was increased in intensity with respect to the 4358 Angstroms line. The carrier gas used in the 100 watt mercury lamp is according to the makers (The General Electric Company Limited) commercial argon, which

contains a small percentage of nitrogen. This gas is remarkably efficient in enhancing the intensity of the green line (Wood, 1934) and of diminishing the intensity of the violet line. The enhancement of the green line is probably due to the fact that the nitrogen diatomic molecule has a vibrational level exactly equal to the difference in energy of the 6^3P_2 and 6^3P_1 mercury levels (Pool, 1931) this fact being illustrated in figure 29. It is probable that an unexcited nitrogen molecule suffers a collision of the second kind with a mercury atom in the 6^3P_2 state, becoming raised to the second vibrational level as a result, the mercury atom being transferred to the 6^3P_1 level. The green line is hence affected by self-absorption to a lesser degree.

It can also be seen from figure 29 that the nitrogen molecule has a first vibrational level nearly equal to the difference in energy between the 6^3P_1 and 6^3P_0 mercury levels. A collision of the second kind between a nitrogen molecule and a mercury atom in the 6^3P_1 excited state is therefore possible, with a resultant transference of the mercury atom to the metastable 6^3P_0 level. Such a transition would result in a diminution of the intensity of the violet 4047 Angstroms line. Evidence of such a transition does exist (Berberet and Clark, 1955).

Subsequently the nitrogen cleans up, forming solid cyano products with organic compounds present in the heater



Nitrogen Molecule Ground
State Σ_g Vibrational Levels.

Mercury Atom
Energy Levels.

Figure 29.

Basis of interaction between Nitrogen Molecules
and excited Mercury Atoms.

coating used to initiate the discharge. An apparent reduction in intensity of the green line, and an increase in intensity of the violet line result from this cleaning up process. The mercury isotope lamp, however, is filled with spectrally pure argon and contains no heaters to initiate the discharge, so that it should be relatively free from any effects due to the presence of nitrogen.

Examining results obtained from the mercury isotope lamp, it is seen that the photomultiplier results are in good agreement with the photographic results but are more accurate being subject to a total variation of 4% as against 10% for the photographic method. This latter value is not unreasonable when it is considered that a 5% variation is possible due to calibrating difficulties (see section 3) and a further 2.5% variation is possible as a result of emulsion non-uniformity (see section 5.1).

It would also appear that there is a certain discrepancy between the results obtained on each spectrograph. This is probably due, in part, to errors in determining the dispersion curves for the instruments, there being an error of $\pm 3\%$ in the determination of the dispersion of the constant deviation spectrograph, and $\pm 1\%$ in that of the Littrow spectrograph. The smaller percentage error in the case of the Littrow spectrograph being due to the greater numerical value of its dispersion. The dispersion correction

as applied to the results obtained is only strictly applicable when, (a) The exit slit of the instrument is of negligible width, in terms of wavelength, or (b) If the exit slit is of appreciable width, then the calibrating spectrum must vary linearly over the wavelength range admitted.

In the case of the Littrow spectrograph the first condition is satisfied, but for the constant deviation spectrograph neither condition is satisfied, for reference to figure 3 (page 25) shows that the calibrating spectrum is non-linear over a wavelength range of 50 Angstrom units (the estimated slit width at 4,400 Angstroms). It is calculated that an error of 5% is introduced by this effect. The non-linearity of the spectrograph in the region of cut-off can introduce a similar error. It is for these reasons that the results obtained on the Littrow spectrograph are regarded as being more reliable than those obtained on the constant deviation spectrograph.

The intensities of the components of the mercury triplet 5461 : 4358 : 4047 were found to be in the ratio 1 : 0.54 : 0.16, as measured on the Littrow spectrograph. This is in poor agreement with the theoretical value of 1 : 1.18 : 0.52 (see section 2) although the low value of the ratio obtained here may in part be due to the absorption of the envelope of the lamp, and in part due to self-absorption effects. However, it is hoped that further investigation, in particular with a thermopile, will clarify further the experimental differences with theory.

(It may be noted that the presence of nitrogen is known to have little effect on the corresponding energy levels in cadmium and the measurements of Van Hengstrum and Smit (1956, Physica 22, 86) show fairly close agreement with theory for cadmium, while admitting experimental errors fully as great as those discussed here.)

10. Conclusion.

It is concluded that the photomultiplier method of determining intensity ratios is the most accurate of the methods tried, an accuracy of about 4% being achieved. This method, either direct, or with an interrupted beam technique, is also the most convenient method in practice. With the photographic method an accuracy of 10% is, in general, the best that can be obtained; this method also tends to be rather tedious to use. However, where intensities are to be compared simultaneously, the photographic method becomes the most convenient to use. This is also true when the intensities of two near spectrum lines are to be compared. In this case a calibrated step filter can be used and the accuracy obtainable, which is about 5%, approaches that of the photomultiplier method.

The Schwarz cell was found to be an unsuitable detector for the comparison of intensities. It appeared to be very suitable for the qualitative detection of light, but its rather long response time, and extreme sensitivity to temperature effects rendered it unsuitable for the quantitative determination of light energy.

In all methods, the prime source of inaccuracy would appear to be in the method of calibrating the apparatus in terms of light energy. The correction for dispersion represents another, smaller, source of error, whilst in the

case of the photographic method, variations in the emulsion sensitivity of approximately 2.5% give rise to further inaccuracies.

There seemed to be a lack of agreement between the experimental and theoretical values for the intensity ratios of the components of the mercury triplet. In this respect, the department is now obtaining a semiconductor type thermopile from Messrs. Hilger Limited, which will be suitable for either direct or interrupted beam methods. In the first instance it is proposed to use this thermopile directly, in conjunction with a specially designed magnetic amplifier, for the determination of the intensity ratios already discussed. It is hoped that this will assist in the more accurate determination of intensity ratios, and at the same time, enable the sources of errors in the existing methods to be more exactly determined.

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