SPECTROMETRY.

MAUDE FAILYER.

# OUTLINE.

## SPECTROMETRY.

I. DESCRIPTION AND ADJUSTMENT OF SPECTROMETER.

II. CALIBRATION OF PRISM.

a. Measurement of Angle of Prism.

b. Measurement of Minimum Deviation.

c. Construction of Curve.

d. Use of Curve in Determination of Unknown Substances.

e. Absorption Spectra.

III. MEASUREMENT OF WAVE LENGTHS BY USE OF DIFFRACTION GRATING.

a. From Fraunhofer Lines.

b. From Bright Line Spectra.

By methods which need not be given here it has been satisfactorily proven that light is a form of energy resulting from the rapid vibration of the molecules composing the luminous object. It can also be shown that light is propagated in straight lines by means of transverse waves in the ether which pervades everything.

The change in direction of propagation of the waves of light when passed into a more dense medium depends on their less velocity in the denser than in the rarer medium. White light consists of all wave length within a considerable range and when it is passed through a prism,we find that the waves which give rise to the sensation of the color red are not changed in direction so much as are those which produce the sensation of violet color. It follows that the waves producing the red coler move less slowly in glass than do those producing the violet and that,since the velocity varies directly as the wave length, violet light consists of waves of less length than does red light.

A spectrometer is an instrument fitted for observing a spectrum, having in addition a graduated circle and vernier by means of which the deviation of the emergent light is measured.

It consists of a circular table with a graduated circle and vernier which may be leveled by three leveling screws. To the circle are attached two tubes called the collimator and the telescope. These are cylindrical tubes which have their axes parallel to, and directed over the center of the graduated circle. The telescope,with a vernier attached, turns around the circle.

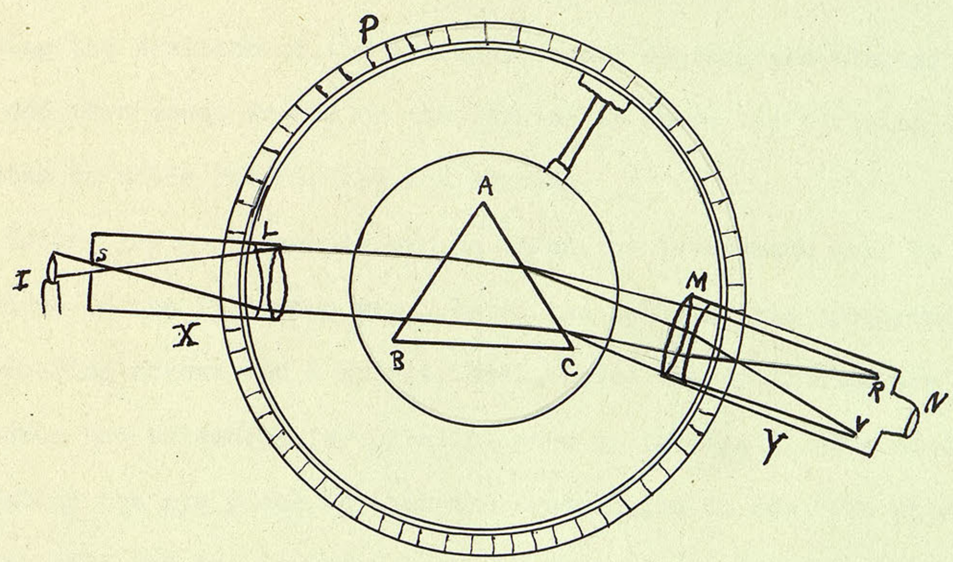



*Fig. 1.*

Let I (Fig. 1) be the source of light, X the collimator, Y the telescope, and P the graduated circle. S is the slit, adjusted by a screw, through which the rays of light pass. L is an achromatic lens focused on S so that the distance L S is equal to the focal length of the lens, hence the rays of light emerging from it form a parallel beam of light. A B C is the prism with refracting edge A. A beam of parallel rays of equal refrangibility remain parallel after being refracted at plane surfaces so that all the red rays will emerge from the prism parallel to each other, as will also the violet, and the yellow, etc. M, the object glass of the telescope, also an achromatic lens, focused to receive parallel rays, brings the sets of parallel rays to foci, the red at R, the violet at V, and the other colors at points between the two. The telescope is fitted with cross hairs and an eye piece ( N).

The main scale of the spectrometer is divided into three hundred and sixty degrees, with division lines marking every twenty minutes, so that each small division on the main scale is twenty minutes. Thirty nine divisions on the circle equal forty divisions on the vernier, therefore a change of one division of the vernier equals one fortieth of the whole, or one fortieth of one division of the circle, or one fortieth of twenty minutes, which is thirty seconds. In determining the position of the telescope,count degrees and minutes shown on the circle, and then count from 0 on the vernier to where the division lines of circle and vernier coincide for minutes and seconds.

Before any measurements can be taken,the instrument must be adjusted. This is done in the following way. Level the table of the spectrometer by means of the leveling screws and a spirit level. Level the collimator and the telescope .Focus the telescope for parallel rays by turning it on a distant object and adjusting the eye piece so that the cross hairs do not move with respect to the object when the eye is moved back and forth, i.e. the two images are coincident. Put the collimator and telescope on a line with each other and focus the lens in the collimator.

## To Find Angle of Prism.

The first thing to determine when working with the spectrometer is the angle of the prism to be used. This is done in the way which is now explained.

Put in the prism so that the light falls on both faces. Move the telescope until the image of the slit reflected from the right hand face coincides with the cross hairs. Clamp, and then take reading of this position of the telescope. Unclamp, turn to left side, and take reading of position of the telescope when the image of the slit from this side is on the cross hairs. In order to be accurate change the position of the prism slightly, and take readings as before. After several trials find the average angle between the two readings or the two reflected rays. This angle can be proven,by the following method, to be twice the angle of the prism.

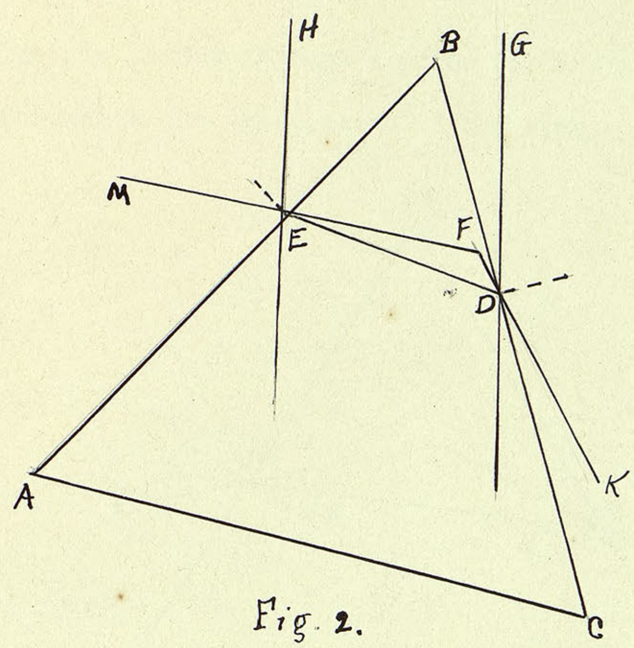



Fig. 2.

In Fig. 2-

$\angle B + \angle BEF + \angle FED + \angle BDF + \angle FDE = \angle F + \angle FED + \angle FDE$

(1). $\therefore \angle F = \angle B + \angle BEF + \angle BDF$

$\angle GDB = \angle CDK = \angle BDF$

$\angle HEB = \angle AEM = \angle BEF$

$\angle GDE = \angle HED = 2$ rt$\angle$s $= \angle B + \angle BED + \angle BDE$

$\angle GDB + \angle HEB = \angle B$

(2) or $\angle BDF + \angle BEF = \angle B$

$\therefore \angle F = 2\angle B$ (Subst. from (2) in (1) ).

The following data was obtained from the prism used:-

| | Reflected ray to right. | Reflexion to left. | Difference | Angle of prism. |
|---|---|---|---|---|
| 1st trial | 139° 54' 30" | 20° 1' 30" | 119° 53' | 59° 56' 33" |
| 2nd trial | 134° 3' | 14° 8' | 119° 57' | 59° 57' 30" |
| 3rd trial | 134° 4' | 14° 6' | 119° 58' | 59° 59' |
| 4th trial | 144° 41' | 24° 35' | 120° 6' | 60° 3' |
| 5th trial | 141° | 21° 1' 30" | 119° 59' 30" | 59° 59' 46" |

Mean angle of prism - - - - - - - - - - - - 59° 59' 46 "

When light is passed through a prism for any angle of incidence there is another value for which the deriviation is the same.

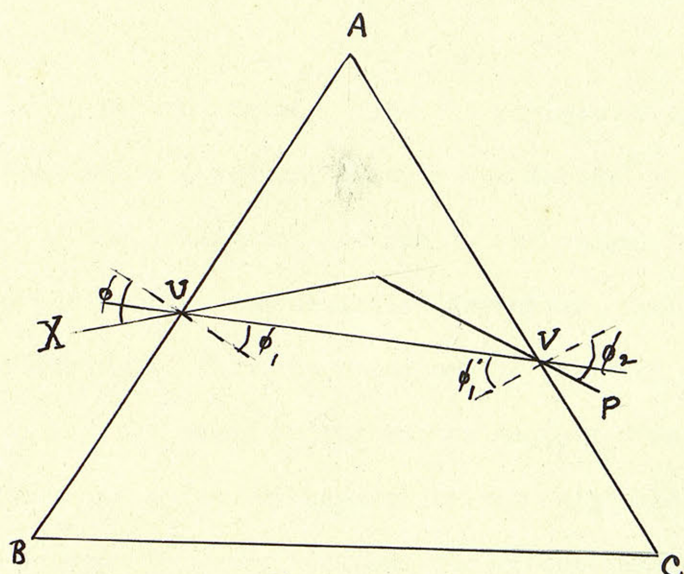



*Fig. 3.*

This can be easily seen by passing light through a prism in the direction XUVP (Fig. 3), with angles of incidence at the two faces $\phi$ and $\phi'$, and angles of refraction $\phi_1$ and $\phi_2$. The deviation, $\delta$, is the difference in direction between the incident and the emergent rays, XU and VP. Pass the light through in the direction PVUX and the deviation remains the same. Let i and i' be values of the angles of incidence which have the same deviation. Then as the angle passes from i to i' the deviation varies but finally resumes its original value, so it must pass through either a maximum or a minimum. Take such values for i and i' that their difference becomes smaller and smaller and the point where $\delta$ remains constant in the change from i to i' must correspond to the point where i equals i', or $\phi_1$ equals $\phi_2$. That $\delta$ is not a maximum but a minimum may be shown analytically although a simpler method is by experiment in which the direction of the incident ray is varied.

## To Measure Angle of Minimum Deviation.

To measure the angles of minimum deviation it is necessary to use light of one wave length, as the deviation depends upon the color or wave length of the light.

First of all, by several trials, find the correct reading for the direct image of the slit. Next place a sodium flame, if the deviation of sodium light is to be found, in front of the collimator and put in the prism. Determine which way the prism must be turned so that the deviation decreases, then rotate the prism in this direction, following it with the telescope. A position will be reached where no matter which way the prism is turned the deviation is increased. This is the position of minimum deviation. By several trials determine this position with accuracy. The angle between this position and the direct image is the angle of minimum deviation, or $\delta$. It is well to next let the incident light fall on the other face of the prism and find $\delta$ from the other side and then take the average value.

| | Direct image | $\delta$ to right | $\delta$ to left. |
|---|---|---|---|
| 1st trial | 88° 59' | 33° 15' 30" | 144° 45' |
| 2nd trial | 89° | 33° 15' | 144° 45' |
| 3rd trial | 89° | 33° 14' 30" | 144° 44' 30" |
| Mean | 88°59' 40" | 33° 15' | 144° 44' 50" |
| Angle of Deviation - - - - | | 55° 44' 40" | 55° 45' 10" |
| Mean angle of Deviation - - - - | | 55° 44' 55" | |

The law of refraction was first derived by Snell in 1620, and stated by Decartes in this form ,-" The incident and refracted rays are in the same plane with the normal to the surface, they lie on opposite sides of it, and the sines of their inclinations bear a constant ratio to one another." This constant ratio, as light passes from air into the substance, is called the refractive index of the substance. The refractive index, or $\mu$, equals the sin of the angle of incidence divided by the sin of the angle of refraction.

To find index of refraction.

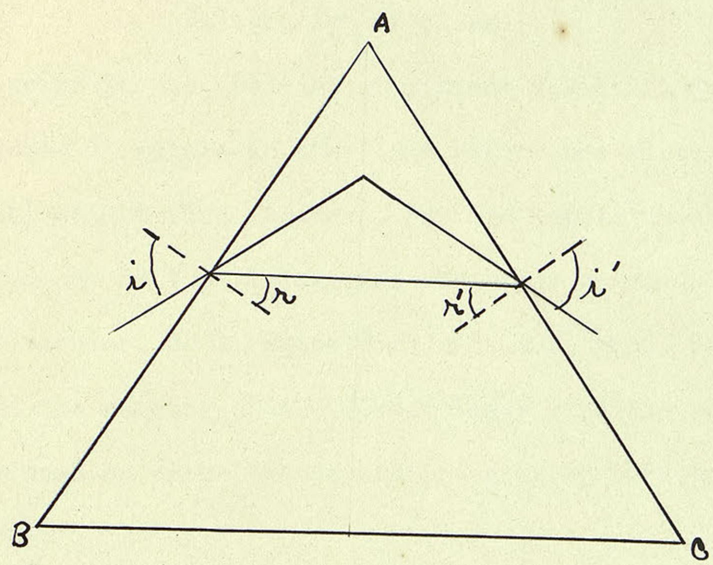



*Fig. 4.*

When the prism is placed in the position of minimum deviation for any particular ray of light -

$i = i'$ and $r = r'$.

$\delta = i - r + i' - r' = i + i' - (r + r')$.

$r + r' + A \quad \therefore \delta = i + i' - A$

So that for minimum deviation

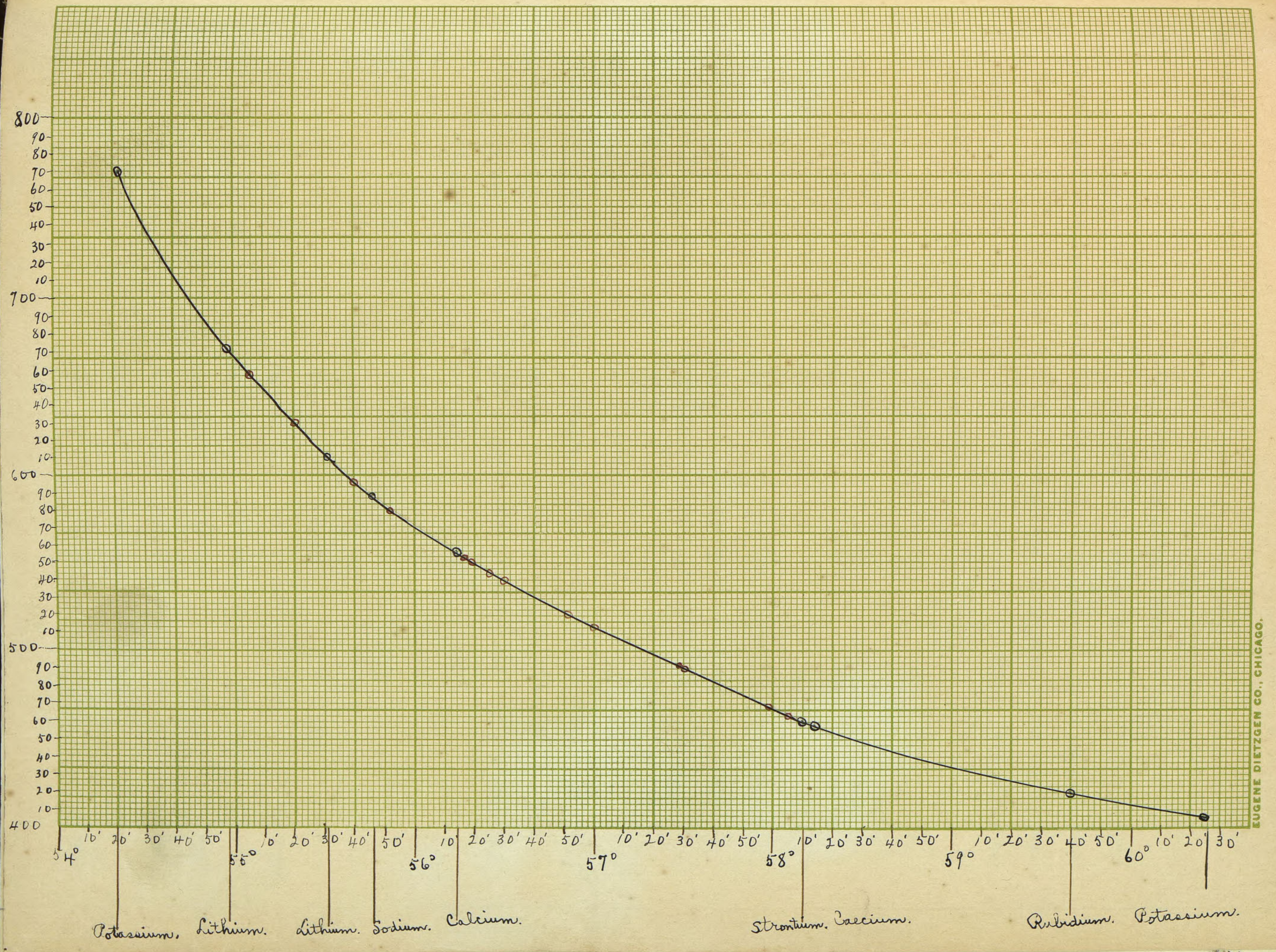
$A = 2r$ or $r = \frac{1}{2} A$

and $\delta = 2i - A$ or $i = \frac{1}{2}(A + \delta)$

Since the index of fefraction $\mu = \dfrac{\sin i}{\sin r}$ it is also equal to

$$\frac{\sin \frac{1}{2}(A + \delta)}{\sin \frac{1}{2} A}$$

In this way the refractive index of the prism was determined for sodium light or for light of any wave length.



800
700
600
500
400
54°
55°
56°
57°
58°
59°
60°
Potassium.
Lithium.
Lithium.
Sodium.
Calcium.
Strontium.
Caesium.
Rubidium.
Potassium.
EUGENE DIETZGEN CO., CHICAGO.

$\delta = 55^\circ\ 44'\ 55''$

$A = 59^\circ\ 59'\ 46''$

$$\mu = \frac{\sin \frac{1}{2}(A + \delta)}{\sin \frac{1}{2} A} = \frac{\sin\ (57^\circ\ 52'\ 21'')}{\sin\ (29^\circ\ 59'\ 53'')} = \frac{8468}{5000} = 1.693$$

Calibration of prism.

With the prism in the position of minimum deviation for sodium light, place successively a number of metals in the flame before the slit. Each metal produces its characteristic bright line spectrum. For the potassium light there is a bright line in the red and one in the violet. Set the cross hairs on each of these in turn and read the vernier. Do likewise with each substance. The differences between these readings and the reading of the direct image give the angles of deviation for the bands produced by each light, or their relative positions on a map of a continuous spectrum.

With these angles as abscissae and the wave lengths of the various metals as ordinates a curve is plotted. This curve begins with the red line of potassium as one limit and goes to the violet line of the same metal as its other limit.

Direct image - -269° _______ 89°

| Metal | Reading | Deviation | Wave length. |
|---|---|---|---|
| Sodium ( yellow) | 144° 45' | 55° 45' | 589 |
| Lithium (red) | 143° 57' | 54° 57' | 670.5 |
| " (orange) | 144° 31' 30" | 55° 31' 30" | 610 |
| Potassium (red) | 143° 22' | 54° 22' | 770 |
| " (violet) | 149° 25' 30" | 60° 25' 30" | 404 |
| Strontium (blue) | 147° 11 ' | 58° 11' | 461 |
| Calcium (green) | 145° 12' | 56° 12' | 556 |
| Calcium ( blue) 1st | 147° 14' | 58° 14' | 459 |
| Calcium (blue) 2nd | 147° 22' | 58° 22' | 455 |
| Barium (green) 1st | 145° 13' 30" | 56° 13' 30" | 531 |
| " " 2nd | 145° 59' | 59° 59' | 524 |
| " " 3rd | 146° 28' | 57° 28' | 513 |
| Rubidium (purple) | 148° 40' | 59° 40' | 420 |

To Name and Unknown Substance.

By means of this curve other substances can be determined. Put an unknown substance in the flame before the collimator, take the readings of the positions of the bright lines appearing in the spectrum and locate them on the curve. Their wave lengths can then be found and thus the substance identified. This method was followed to identify several substances.

1st Substance, a liquid.

Lines were

| | Reading | Angle | Wave length | Metal |
|---|---|---|---|---|
| In green | 145° 7' | 56° 17' | 553 | Barium |
| " " | 146° | 57° | 513 | Iron |
| " " | 146° 30' | 57° 30° | 488 | Barium |
| " " | 145° 7' | 56° 7' | 563 | Iron |
| " red | 144° 20' | 55° 20' | 628 | Iron. |

2nd Substance.

Gas in the Plücker tube, heated to incandescence by electric sparks.

| | Reading | Angle | Wave length | Metals |
|---|---|---|---|---|
| In red | 144° 4' 30" | 55° 4' 30" | 656 | Hydrogen |
| " blue | 146° 29' | 57° 29' | 490 | Tin |

3rd Substance.

Same as in second substance.

| | Reading | Angle | Wave length | Metals |
|---|---|---|---|---|
| In red | 144° 4' 30" | 55° 4' 30" | 656 | Hydorgen |
| " yellow | 144° 40' | 55° 40' | 597 | Iron |
| " " | 144° 52' | 55° 52' | 580 | Iron |
| " green | 145° 4' 30" | 56° 4' 30" | 565 | Iron |
| " " | 145° 19' | 56° 19' | 550 | Iron |
| " " | 145° 30' | 56°30' | 540 | Iron |

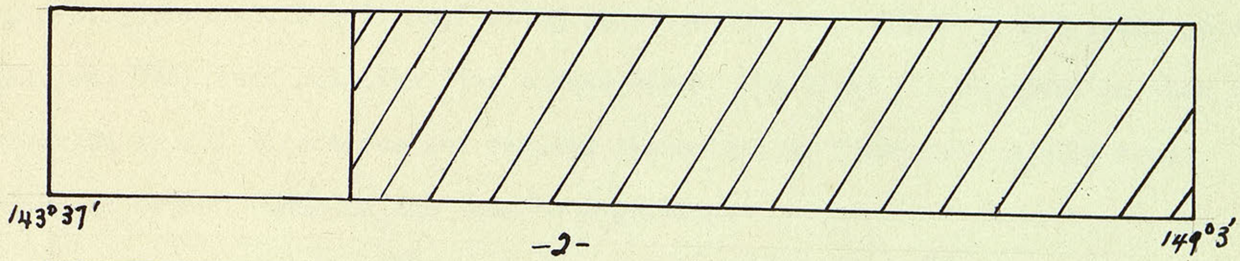
| | Reading | Angle | Wave length | Metals |
|---|---|---|---|---|
| In green | 145°51' | 56° 51' | 521 | Iron |
| " " | 145° 25' | 56° 25' | 545 | Iron |
| " blue | 146° 28' 30" | 57° 28' 30" | 490 | Iron |
| " purple | 146° 59' | 57° 59' | 468 | Hydrogen |
| " " | 147° 5' | 58° 5' | 463 | Hydrogen |

Authority, Landauer.

When sunlight is viewed through a prism its spectrum is not similar to the spectrum formed by a solid, a liquid, nor a gaseous earthy substance. The spectra of solid and liquid bodies are continuous bands of different colors overlapping and blending with each other, from the red to the violet. When a greatly heated gas is looked at through the spectrometer a number of bright lines may be noticed,some in the red, some in the yellow, and on to the violet. This is called a discontinuous spectrum of bright lines, and is characteristic of gases. The spectrum of sunlight consists of the spectrum colors spread out, with a great many fine black lines which seem to prevent the subrays from overlapping. These black lines are like missing notes in the solar key-board.

Fraunhofer was the first to take particular notice of the missing notes, but although he located many of the most important ones he found no satisfactory explanation of their presence. It was Kirchoff who finally explained this peculiar phenomenon. By various experiments he deduced the following law.- When light from a solid or liquid incandescent body passes through a gas, the gas absorbs precisely those rays of which its own spectrum consists; so that the result is a spectrum marked by black lines occupying exactly the same positions which would be held by the bright lines in the spectrum of the gas alone. His conclusion was that the luminous surface of the sun is composed of solid or liquid matter producing a continuous spectrum, and that the black lines are produced by the

-1-

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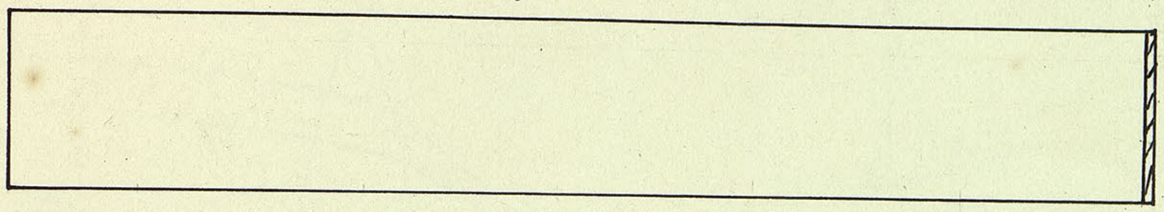

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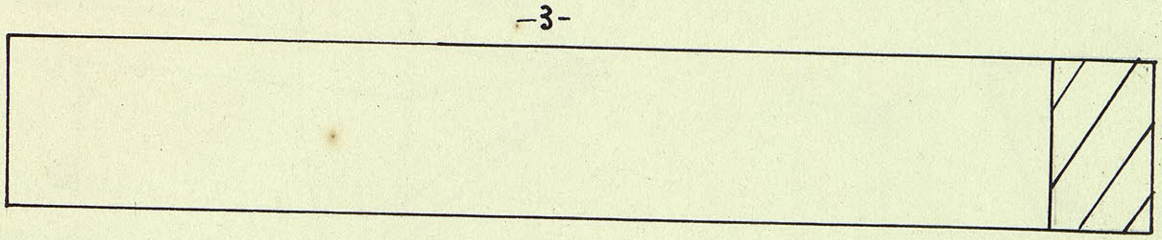

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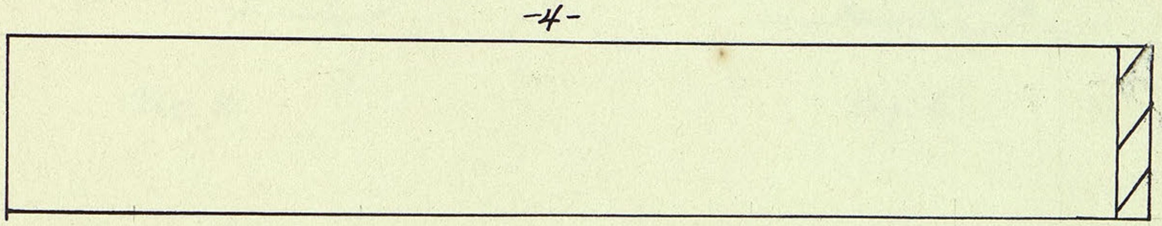

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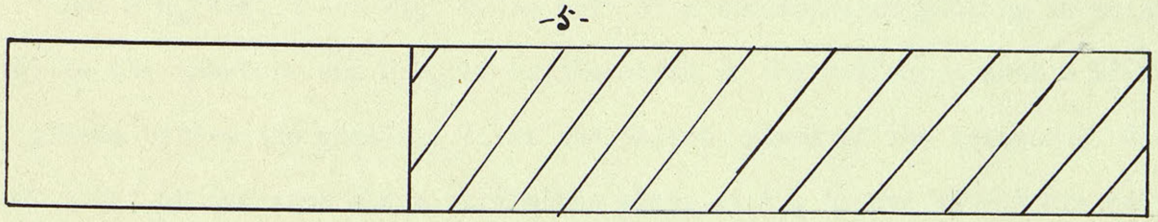

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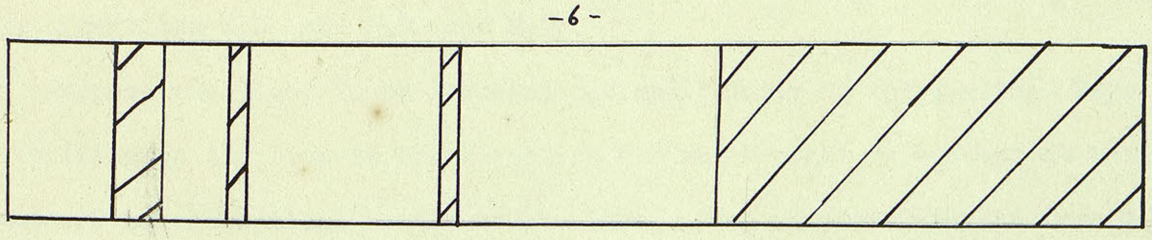

transmission of light through an enveloping atmosphere.

## Absorption Spectra.

Between an electric light, which by itself gave a continuous spectrum, and the slit in the collimator different solutions of aniline were placed. Results were as follows .

| | |
|---|---|
| Limits of continuous spectrum | 143° 37'<br>149° 3' |
| **1st ,-Red** | |
| Limit of bright red band. | 143° 37'<br>144° 44' |
| **2nd. -Yellow** | |
| Bright band | 143° 37'<br>149° 1' |
| **3rd. Pale yellow** | |
| Bright band | 143° 37'<br>148° 35' |
| **4th Red liquid.** | |
| Bright band | 143° 37'<br>148° 53' |
| **5th Brown liquid.** | |
| Bright band | 143° 37'<br>145° 12' |
| **6th Solution of Chlorophyll** | |
| Limits of spectrum | 143° 37'<br>146° 53' |
| 1st black line (dark) | 143° 55'<br>144° 10' |
| 2nd black line (faint) | 144° 30'<br>144° 39' |
| 3rd black line (faint) | 145° 25'<br>145° 34' |

A diffraction grating is a piece of highly polished glass or metal ruled with very fine, parallel lines, leaving narrow, equal, equi-distant, and rectangular apertures. The lines act like fine opaque wires. The light incident on them is reflected in all directions and refused transmission. There are usually from 20,000 to 40,000 lines to the inch on a grating.

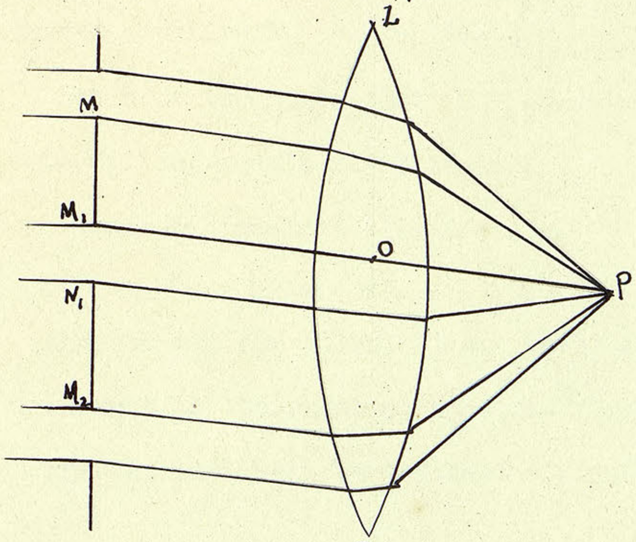


Fig. 5.

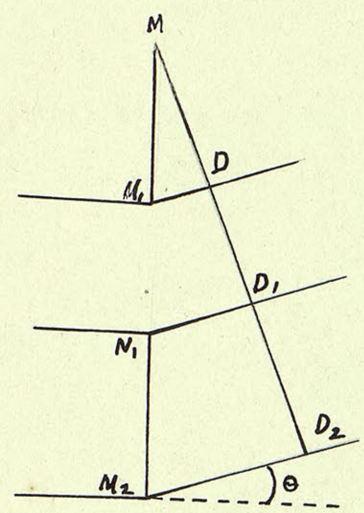


Fig. 6.

Let M $M_2$ (Fig. 5 and Fig. 6) be part of a transmission grating in which $M_1N_1$(a) is the aperture and $N_1M_2$(b) is the width of the ruling. A lens L L'(Fig. 5) is placed before the grating. It is the object glass of the telescope. Parallel rays of light of the same phase strike the glass at $M_1$, $N_1$ and $M_2$ and are refracted in the directions $M_1D$ and $N_1D_1$ and $M_2D_2$.

Suppose the light to be incident perpendicularly to the grating. Rays of light light falling on the lens in the direction O P are brought to a focus at the point P, where O is the optical center of the lens. Drop a perpendicular from $M_1$ to the line $M_2$ $D_2$. Each stream is propagated from this line to the point P in the same length of time. But since the incident wave front was parallel to the grating, each stream reaches the grating in the same phase, so that the stream at the first edge of the second aperture reaches P just as much behind that at the first aperture as the length of $M_2$ $D_2$.

If the retardation $M_2D_2$, is an even number of half wave lengths the light from $M_2D_2$ reaches P in the same phase as that from $M_1D$ and it reinforces that light, making a bright spot if monochromatic light is used. If, however, $M_2D_2$ is an odd number of half wave lengths, the two streams reach P in different phases and interference occurs, making a spot more or less dark. This will apply to each successive aperture in the grating .

Let θ be the angle that O P makes with the normal to the grating. Then $M_2D_2$, the retardation, equals sin θ times $M_1M_2$ or $M_2D_2 = \sin\theta\,(a + b)$.

Hence for maximum illumination

$$(a + b) \sin\theta = 2n\tfrac{1}{2}\lambda$$

and for minimum illumination $(a+b) \sin\theta = (2n + 1)\tfrac{1}{2}\lambda$

where n is the order of spectra.

Now let the light be incident obliquely,-

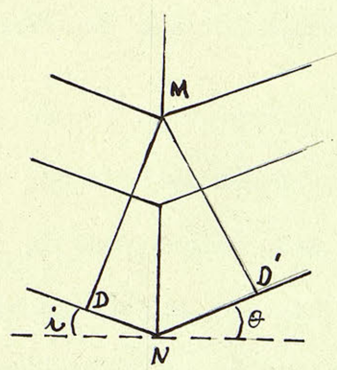


Fig. 7.

The light comes in the direction D N (Fig.7) and is refracted in the direction N D', making the angle of incidence i, and the angle of refraction θ, Draw MD perpendicular to N D and MD' perpendicular to ND'. In this case the retardation is ND + ND'.

But $ND = (a+b) \sin i$

and $ND' = (a+b) \sin\theta$.

so that the retardation $= (a+b) (\sin\theta + \sin i)$

Gratings of glass transmit the rays of light but those of metal reflect them. These streams of light regularly reflected from the polished intervals proceed from virtual images of the source, as if they came through the intervals from behind the surface. When sunlight is used a bright central or direct image of the slit is seen, on either side of which are spectral images richly colored, which increase in breadth and diminish in brilliancy as they recede from the center. When the metallic grating is placed so that the light is incident perpendicularly the same formula for retardation applies that did in the case of the transmission grating, but when the light is incident obliquely the retardation

or $n\lambda = (a+b)(\sin i \pm \sin\theta)$.

Gratings are used to determine the wave lengths corresponding to any part of the spectrum. This method of finding wave lengths is by far the most accurate one. It involves the measurement of the angle of diffraction of the ray under consideration and of <u>the width of the grating element</u>.

To find Wave Length of $D_1$ and $D_2$ Lines.

Place the grating in a position as nearly perpendicular to the incident ray as possible. Take readings of the vernier when the cross hairs coincide with the $D_1$ line in the second order of spectra on each side of the reflected image. The differences of these readings and the reading for the direct image subtracted from 180° give the angles of diffraction. By moving the grating avery little one way or the other, the angles of diffraction on each side can be made equal. When this condition is complied with the grating is in a position perpendicular to the incident light. In this case $n\lambda = (a+b)\sin\theta$.

Let $(a+b)$ be the width of an aperture and a ruling. If the number of lines is known, and also the total width of the grating, $(a+b)$ can be easily determined. If there are $(m+1)$ lines, then $(a+b)$ equals $\frac{1}{m}$ of the whole width of the grating. This must be in centimeters.

Results were as follows:

Width of grating - - - - - - - - - 2.54 cm.

Lines on grating - - - - - - - -14437.

(a+b) - - - - - - - - - - - - - -,.0001759

| | $D_2$ | $D_1$ |
|---|---|---|
| Reading to right - - - - - - - - | 226° 59' 30" | 226° 56' 30" |
| Reading to direct image - - - - - - | 89° 1' 30" | 89° 1' 30" |
| Difference - - - - - - - - - - - | 137° 58' | 137° 55' |
| Reading to left - - - - - - - - - | 131° 3' 30" | 131° 7' 30" |
| Direct image - - - - - - - - - - | 269° 1' 30" | 269° 1' 30" |
| Difference - - - - - - - - - - - | 137° 58' | 137° 54' |
| Angle of diffraction - - - - - - - | 42° 2' | 42° 5' 30" |
| $\lambda$ - - - - - - - - - - - - - - - | .00005889 | .00005894 |

Authorities give for the wave lengths of $D_2$ and $D_1$, .00005890 and .00005896. This spectrometer does not read angles closer than 30". The difference in wave length owing to a change of 30" in the angle of diffraction is . .0000000129, so that the mean wave lengths obtained are within the limits of possible error in reading.

With the grating in the same position place a sodium flame in front of the collimator and set the cross hairs on the bright lines formed in the spectrum. It was found that these bright lines in the sodium spectrum exactly coincided with the dark lines in the solar spectrum, so that the $D_2$ and $D_1$ lines in the solar spectrum are caused by the absopption of this light by the sodium in the solar atmosphere.

A few of the uses o f the spectrometer have been demonstrated. The spectrometer is very useful in the chemical analysis of unknown substances. The elements of which a solution is composed can be found by the observation of the lines in its spectrum. By means of spectrum analysis many elements have been detected in the sun and stars. Not only their chemical composition can be studied but also their physical composition. A great deal as to the nature of the phenomenon of light has been learned from using the spectroscope. There is a wide field open for investigation in this subject and many interesting as well as beneficial results may follow from such study.