

FINE STRUCTURE SEPARATIONS  
in LANTHANUM I

By

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THESIS AND ABSTRACT APPROVED:

  
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I am greatly indebted to Dr. A. V. Pershing who supervised the research work and offered criticisms and suggestions on the writing of this thesis.

## TABLE OF CONTENTS

	Page
Introduction	1
CHAPTER I	
Theory of the Concave Grating Spectrograph	3
CHAPTER II	
Light Sources	7
CHAPTER III	
Alignment and Focusing of the Spectrograph	9
CHAPTER IV	
Photographing the Spectrogram	11
CHAPTER V	
The Determination of Wave Length	13
Conclusion	15

## INTRODUCTION

Lanthanum, which was discovered by Moslander in 1839, was first found in cerite in Sweden. It was one of the first rare earths to be discovered and today it is one of the more plentiful and better known rare earths. Lanthanum has a metallic like luster and like iron is ductile and malleable; like magnesium it burns in air. Since it was first found, it has been located in many places including the leaves of hickory trees growing over pegmatite veins. It combines with oxygen to form sesquioxide and also with nitrogen, chlorine and sulfur to form colorless astringent salts. Unlike most of the rare earths known, it does not give an absorption spectra.<sup>1</sup>

Lanthanum given by the symbol La I, has an atomic number of 57, atomic weight of 138.92 and its valence as 3.

This work on the investigation of some of the Lanthanum transitions is directed towards the comparison of theoretical values to the experimental values. There are some hundred or more lines present in the spectrum of Lanthanum, but the lines that are measured are confined to some of the strong multiplets along with a few prominent singlets.

The Cenco Grating Spectrograph No. 87102 used in the experiment is constructed to photograph the first order spectrum throughout the wave-length range of 2350A to 7000A. To extend the range outside of either of these limits the grating can be rotated about its vertical

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<sup>1</sup> Cutting, Theodore A, Manual of Spectroscopy, p. 130.

axis without any appreciable change in the focus of the instrument. The grating in this instrument is of the replica type, ruled with 15,160 lines per inch and masked to give maximum resolution at 106 cm., the radius of curvature of the grating.

## CHAPTER I

THEORY of the CONCAVE GRATING  
SPECTROGRAPH

Theory of the diffraction grating was formally developed and presented by Rowland in 1882 when he showed that a spherical concave mirror ruled with parallel equally spaced lines and equally spaced along a chord of its arc would produce a spectrum of sharp focus on a circle whose diameter is equal to the radius of curvature of the mirror.

The optical formulas that were worked out for a plane grating were then shown by Rowland to hold true in the case of a concave grating. The theory<sup>1</sup> given here will only be considered for a section through the grating in the plane of the Rowland circle. Referring to Figure 5, representing a section of the grating between two consecutive rulings and this distance being equal to  $s$ ; the grating space. The source of light is placed at  $S$ ; the center of curvature of the grating is at  $C$ . Let two light rays  $SA$  and  $SB$  of wave-length be incident upon the grating at angles  $i$  and  $i + di$ , then they will be diffracted at the grating at angles  $\theta$  and  $\theta + d\theta$ , coming to focus at the point  $P$ . By extending  $SB$  to  $G$  so that  $SG = SA$  and extending  $PB$  to  $F$  so that  $PF = PA$ , the condition for the rays  $SA$  and  $SB$  to reinforce each other at point  $P$  is that their light paths differ by integral wave-lengths. Hence, the fundamental grating equation for the position of the diffracted images is obtained:

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<sup>1</sup> Sawyer, Ralph A., Experimental Spectroscopy, pp. 126-132.

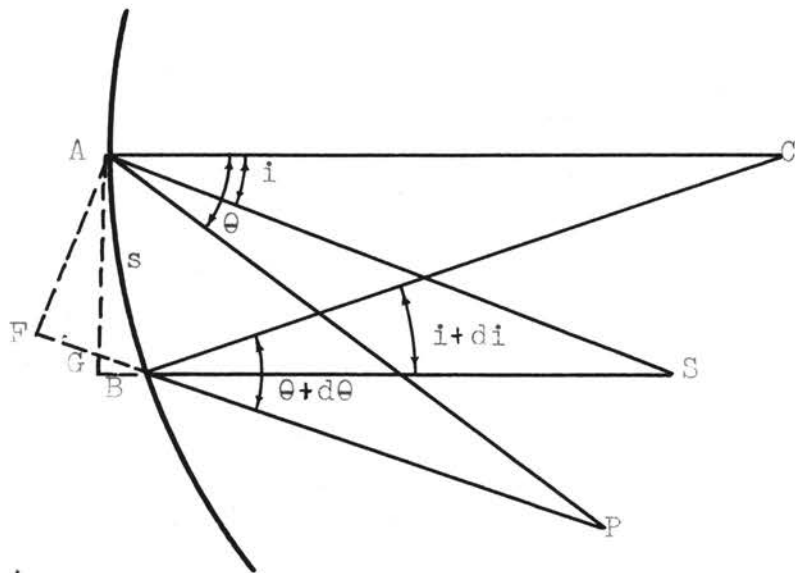


FIGURE 5

Diffraction by a Concave Grating



$$\begin{aligned}
 m\lambda &= (SA + AP) - (SB + BP) = (SG + FP) - (SE + BF) = EG + BF \\
 &= AB \sin i + AB \sin \theta \\
 &= s (\sin i + \sin \theta)
 \end{aligned} \tag{1}$$

where  $m$  is the order number. Now referring to Figure 6, where  $i$  is the angle of incidence and  $\theta$  the angle of the diffracted wave front having wave-length  $\lambda$ . Positive orders are taken to be those that fall on the side of the optic axis opposite the angle  $i$ . Both angles  $i$  and  $\theta$  are measured from the optic axis.

The dispersion<sup>2</sup>  $D$  of a spectrograph is a measure of the amount of separation of the lines according to wave-length. From the general expression for the position of the diffracted images (1), the equation for angular dispersion can be found by differentiating the equation (1); that is

$$m d\lambda = S \cos \theta d\theta$$

Whence: 
$$D = \frac{d\theta}{d\lambda} = \frac{m}{S \cos \theta} \tag{2}$$

Equation (1) shows that there may occur overlapping of spectra<sup>3</sup> of different orders. As can be seen, from fixed values of  $i$  and  $\theta$ , if a wave-length  $\lambda$  is observed for  $n = 1$ ; there will also appear at the same  $\theta$ , wave-lengths of higher order. This shows the relation  $\lambda_1 = 2\lambda_2 = 3\lambda_3 \dots N\lambda_N$  or that  $\lambda_2 = \lambda_1/2$ ;  $\lambda_3 = \lambda_1/3 \dots \lambda_N = \lambda_1/N$ .

These overlappings of orders can be eliminated by placing filters that will pass only certain wave-lengths between the grating and photographic plate. Sometimes however, this effect is advantageous since known wave-lengths in one region may be used to determine wave-lengths in another region.

<sup>2</sup> Technical Literature from Central Scientific Company, Chicago.

<sup>3</sup> Sawyer, Ralph A., Experimental Spectroscopy, pp. 126-132.

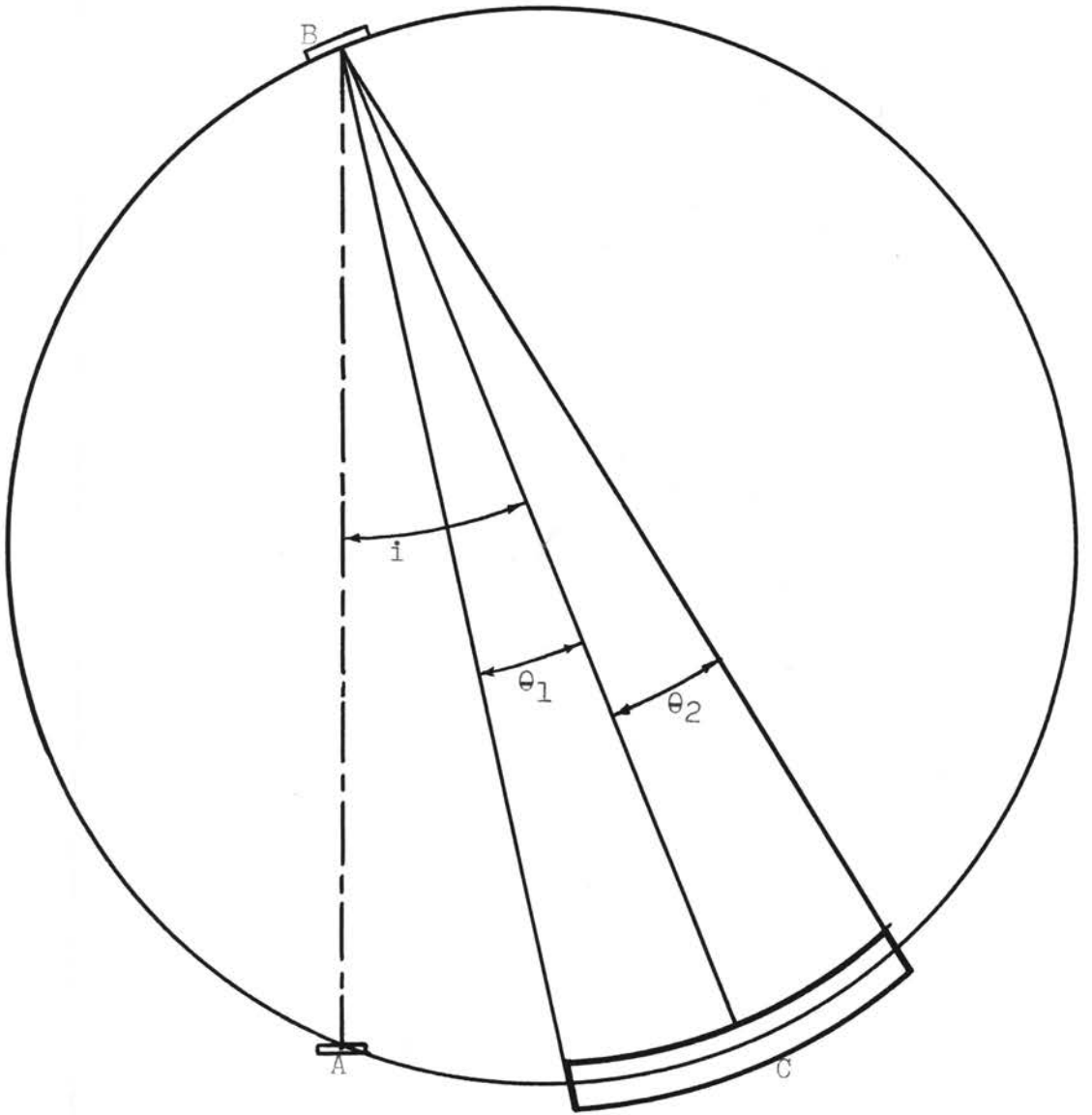


FIGURE 6  
The Rowland Circle

By putting  $x = CP$  in Figure 6, the expression for linear dispersion may be obtained:

since  $\theta = \frac{x}{r}$  and  $\frac{d\theta}{d\lambda} = \frac{1}{r} \frac{dx}{d\lambda}$

and  $\frac{d\theta}{d\lambda} = \frac{m}{s \cos \theta}$  from equation (1)

the linear dispersion is given as  $\frac{dx}{d\lambda} = \frac{mr}{s \cos \theta}$  (3)

where  $dx$  is the distance in centimeters on the film at wave-length corresponding to a spectral width of  $d\lambda$  and  $r$  is the radius of curvature of the grating. In most experimental work, the plate factor is used to measure the dispersion. The plate factor for the Cenco Spectrograph used in this experiment was found to be:

$$\begin{aligned} \frac{d\lambda}{dx} &= \frac{s \cos \theta}{106 \text{ cm}} = \frac{1.675 \times 10^{-4} \times 10^{-8}}{106} \\ &= 158 \text{ \AA/cm} = 15.8 \text{ \AA/mm} \end{aligned}$$

The angle of incidence  $i$  can be calculated from equation (1) by substituting the required constants:  $\lambda = 4800 \times 10^{-8}$ ,  $m = 1$ ;  $s = 2.54/15,160$  and  $\theta = 0$ .

Solving gives:  $4800 \times 10^{-8} = \left( \frac{2.54}{15,160} \right) \sin i$

$$i = 16.66^\circ$$

In Figure 3, the values of  $\theta_1$  and  $\theta_2$  for lines at either end of the spectra is obtained by substituting the above value for  $(i)$  in equation (1) from which  $\theta$  is found to be approximately equal to  $6^\circ$ . Near the normal where the dispersion should be equal to one and checking the cosine  $6^\circ$  which is .9945, the uniformity of the dispersion over the whole spectrum is seen.

The mathematical expression for the resolving power  $R$  of the spectrograph is given by  $\lambda/d\lambda$  where  $d\lambda$  is the wave-length interval of two reasonably close lines of approximately equal intensity that can just be resolved by the instrument at wave-length  $\lambda$ . Or that is, two lines of equal intensity that can be just distinguished as two when the maximum of one falls on the minimum of the other. If the critical state is reached when  $\lambda_1$  and  $\lambda_2$  differ by  $\Delta\lambda$ , then  $\Delta\lambda$  may be given as:

$$\Delta\lambda = \left( \frac{d\lambda}{d\theta} \right) \Delta\theta \quad (4)$$

but 
$$\Delta\theta = \frac{\lambda}{a} \quad (5)$$

where  $a$  is the effective aperture. However, from Figure 7 it is seen that  $a = S \cos \theta$  and upon substitution in equation (5) gives:

$$\theta = \frac{\lambda}{S} (\cos \theta)^{-1} \quad (6)$$

and by substitution of (2) and (5) in (4) the result for  $\Delta\lambda$  is given as:

$$\Delta\lambda = \left( s \cos \theta / m \right) \left( \lambda / S \cos \theta \right) = s \lambda / m S \quad (7)$$

and solving for  $R$  gives:  $R = m S / s = m N \quad (8)$

where  $N$  is the total number of lines on the grating.

The resolving power as seen depends only on the number of lines on the grating and the order: the greater the number of lines the greater the resolving power. From equation (2) it can be seen the closer the lines the greater the dispersion. One of the chief defects of the concave grating is astigmatism which can however be nearly eliminated by making the rulings on the grating parallel to the slit.

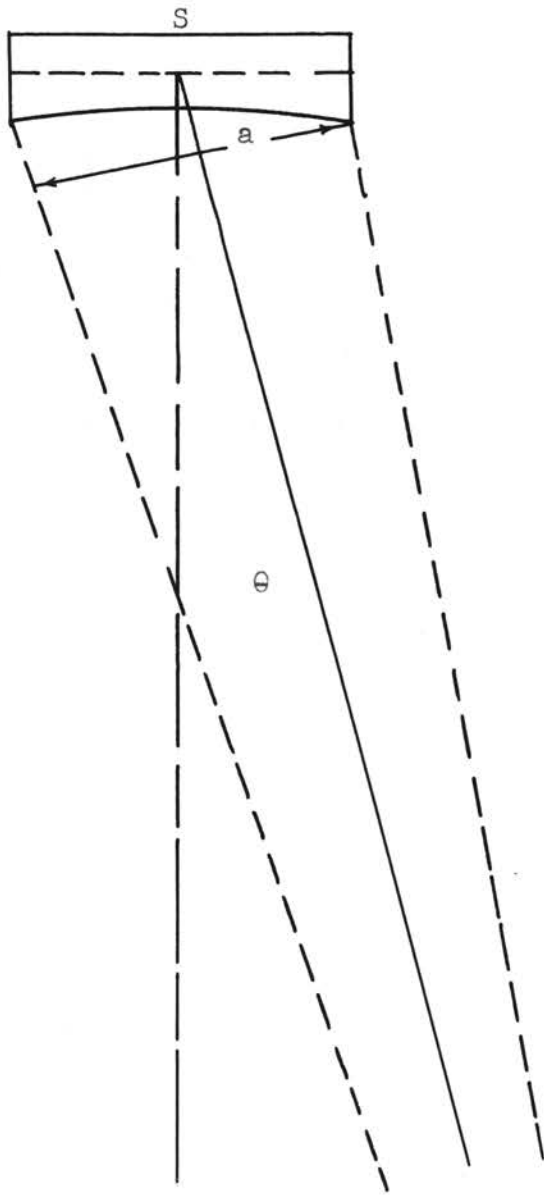


FIGURE 7

## CHAPTER II

## LIGHT SOURCES

For most work in spectroscopy four main types of light sources are used;<sup>1</sup> (a) arc sources, (b) spark sources, (c) thermal radiation, and (d) discharge tubes. In choosing the type of source to be used, the wave-length region that is to be examined is the determining factor. For work in the infrared and visible regions where the atomic or molecular energy transitions are the greatest in excitation, the thermal emission sources are used. For work in the visible and near ultra-violet region, the arc sources are used. Discharge tubes and sparks are used for the visible ultra-violet and extreme ultra-violet regions. Since this work is on the study of atomic structure a source such as a carbon arc which emits line spectra is used. Confining the discussion now to the carbon arc for this particular case; the lower electrode is made the positive crater since in D. C. arcs, the maximum intensity occurs in the positive electrode. For preparation of the electrode, a 1-1/4 inch carbon pole is used which is cored to a depth of 1-1/4 centimeters with a 1/16 inch drill. The two compounds in powdered form are then lightly packed in the core. It should be noted here that the shape of the two electrodes is critical so to help eliminate the jumping of the arc. The positive electrode should be shaped up to a point as much as possible and the negative electrode should be rather rounded to a point. This is to eliminate a large surface area. Also in accurate spectroscopy, the carbon electrodes

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<sup>1</sup> Candler, A. C., Practical Spectroscopy, p. 166.

that are used should be those made available for this particular type of work; that is, they should be chemically pure.

For constant illumination, the distance between the electrodes must be held constant and this is accomplished by a hand-fed device on the instrument and also by varying the resistance  $R$  of the circuit.

Since the arc tends to jump on the electrodes, changes in current are very noticeable and therefore to obtain stable operation, an iron-core inductance can be placed in series with the resistance.

A disadvantage<sup>2</sup> of using the carbon electrode is the prevalence of the cyanogen bands which are due to the molecule  $(CN)_2$ . These lines are especially strong when the sample material has burned down and they interfere with sensitive lines in various parts of the spectrum.

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<sup>2</sup> Ibid., p. 438.

## CHAPTER III

ALIGNMENT and FOCUSING  
of the  
SPECTROGRAPH<sup>1</sup>

For the purpose of alignment and focusing of the spectrograph, the mercury arc lamp is recommended in that it affords a constant light; which is not readily available with an iron or carbon arc. Not only does it give a constant light, but it also gives a fairly good spectrum over the range covered by the instrument.

The mercury lamp is placed in the position where the arc is shown in Figure 1; which is directly in front of the slit. To obtain maximum intensity for checking the light on the grating, the slit is opened approximately 1/2 mm. and then the beam of light is adjusted until even illumination is obtained on the grating. To view the spectrum, remove the plate which holds the film in the holder and in place of the film insert a piece of translucent paper or tracing cloth cut to the dimensions of the film. If the spectrum cannot be seen on the screen, it may be located by moving a piece of white paper in front of the film holder. If the spectrum is too high or too low it may be adjusted by screw F in Figure D. For horizontal spacing; screw D is used. With combination adjustments of these two screws, the spectrum may be located on the screen. To make the lines of the grating perpendicular to the film holder, use is made of screws H and F. Adjust screw F until just a small part of one of the lines at one end of the spectrum is showing; then check at the opposite end to see

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<sup>1</sup> Technical Literature from Central Scientific Company, Chicago.



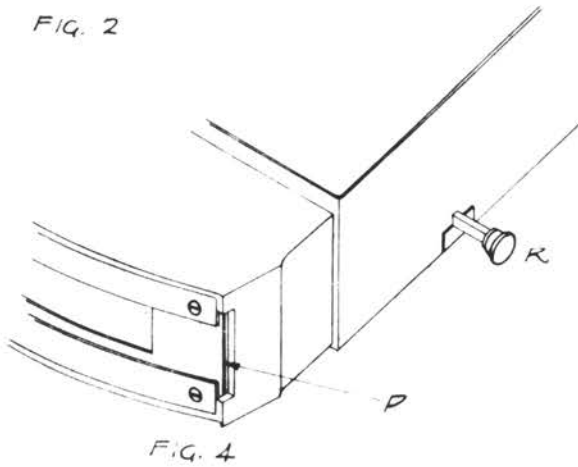
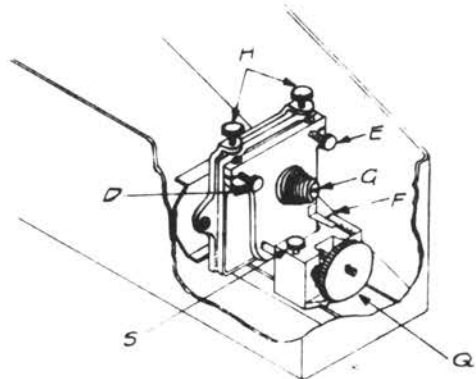
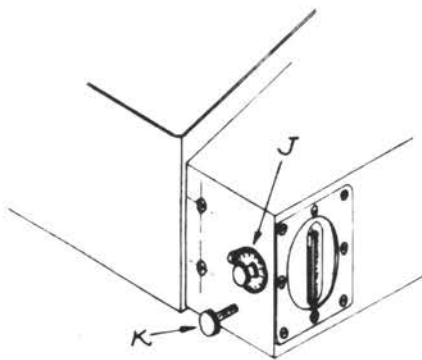
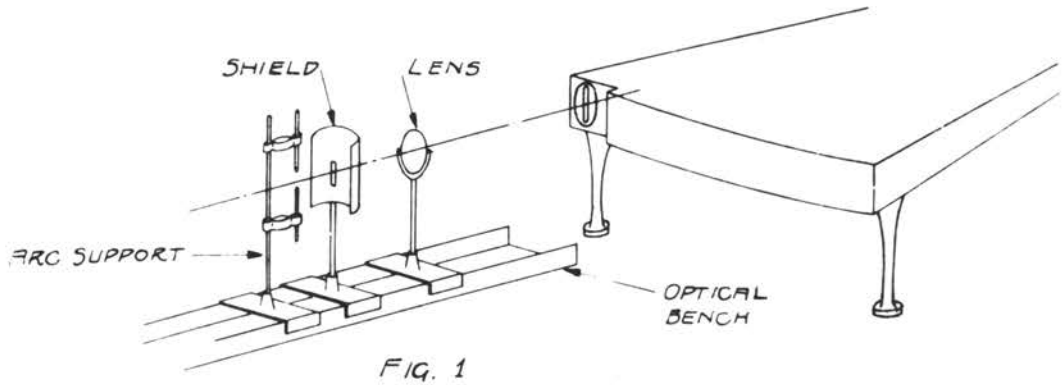


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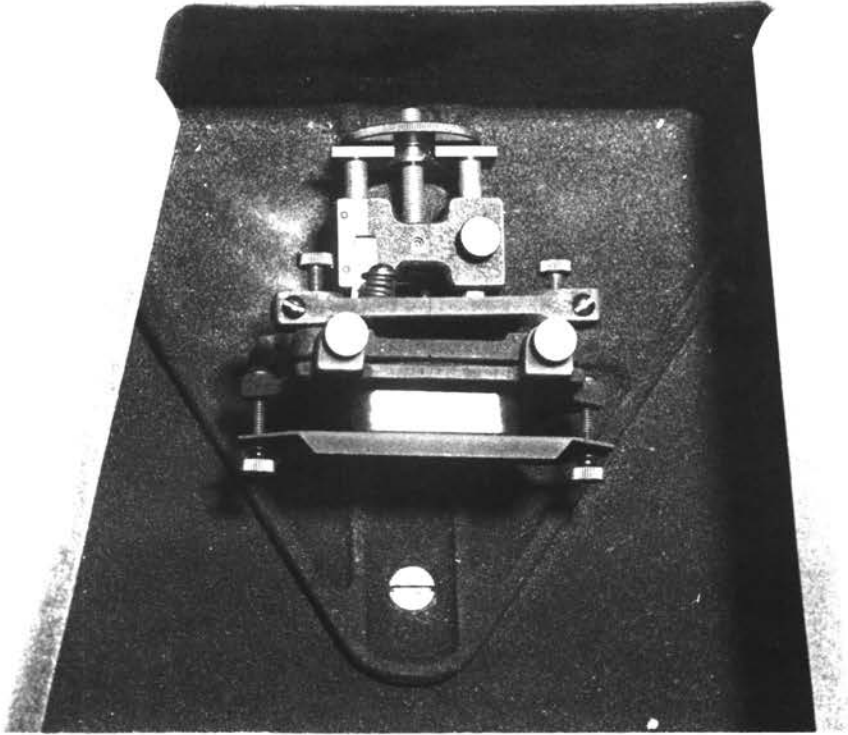
GRATING SPECTROGRAPH



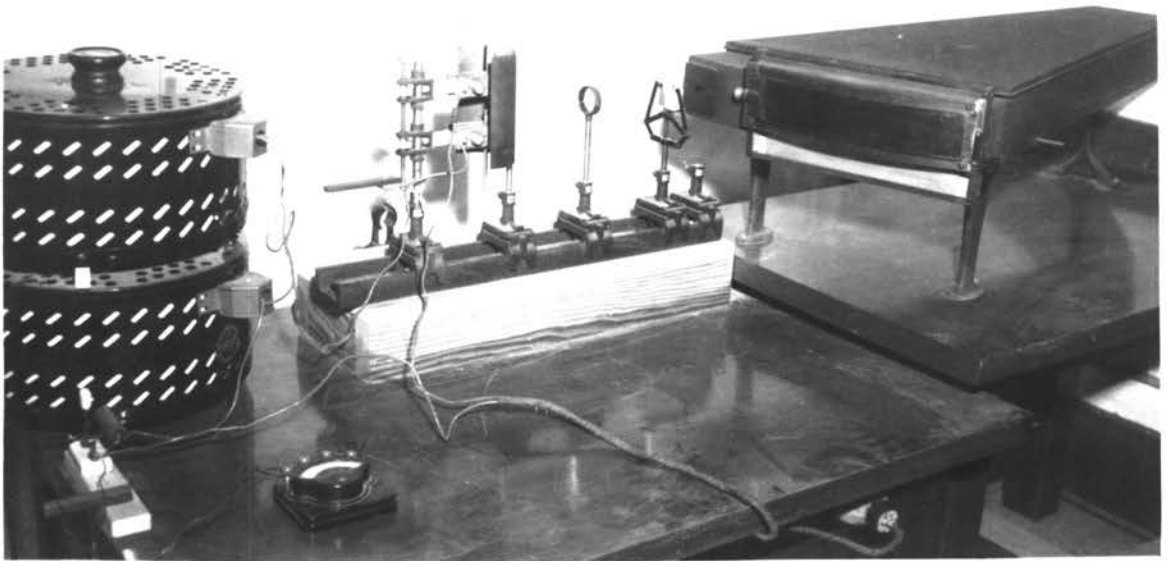
if the same amount of a line is showing. If they are both not visible by the same amount, adjust screw F; which rotates the grating, until even distribution of all lines is obtained. When the ends of the lines are all visible by the same amount along the slot, the lines of the grating will be at right angles to the holder. To make the lines as long as possible, adjust screw P which varies the width of the slot. To see if the slit is parallel to the rulings, observe some strong line while tilting the slit mounting by means of screw K. When the slit is parallel to the rulings, the lines of the spectrum will be exactly vertical.

For analysis of the spectrum of Lanthanum which has most of its strong lines in the visible and ultra-violet, it is well to rotate the grating about its vertical axis until the green mercury line (5461A) or a line of approximately this wave-length is aligned with a mark which is about  $2 \frac{3}{4}$  inches to the left of the center of the opening through which light strikes the film.

The final step in adjusting the spectrograph is the focusing of the spectrum. This is done by loosening the locking arm S (Figure 3) and moving the grating holder assembly back and forth by turning knob Q. If the instrument is out of focus to an excess, the whole assembly may be moved; however, since this is not the usual case, small adjustments may be made by turning knob Q. By observing the lines on the screen, the approximate position of focus may be determined. For a final check, a series of spectrograms may be taken, differing only by the position of the grating. From this film, the position of the grating giving the best focus is selected and the grating set and locked in this position.



Grating Holder Assembly



Cenco Grating Spectrograph

## CHAPTER IV

## PHOTOGRAPHING the SPECTROGRAM

Photographing the spectrum makes possible highly accurate quantitative analysis based upon the principle; high concentration makes brighter lines and brighter lines make denser spectrograms.

Since the exposure time for the Lanthanum and Carbon spectrums is not known, a series of exposures must be run at different time intervals. The adjustments on the spectrometer to be made when using mercury should be exposed about 4 seconds or less.

After the electrodes are replaced for the mercury arc, they are oriented with the lens until with the slit opened; maximum intensity covers the grating. Since the carbon arcs burn away so fast, it is best before each exposure to open the slit and adjust the electrodes as to their proper height.

When packing the electrodes with the compounds of La, it is very easy for the compound to absorb moisture. Since the La atoms are not easily excited with this moisture present only the cynogen bands are revealed. To eliminate this; run the arc for several minutes before the exposures are made to evaporate the moisture. In the exposures, the arc is operated at 175 volts and 7.5 amps. With this type of spectrograph, the entire length of the slit should be illuminated in order to make several exposures.

Two spectrograms are desired: one containing alternate spectrums of  $\text{LaNO}_3$  and  $\text{LaCl}$  and the other containing the spectrums of

Fe, Hg,  $(CN)_2$ ,  $LaNO_3$  and  $LaCl$ . The positive which is shown in Plate II gives the order in which they are taken. The alternate spectrums of  $LaNO_3$  and  $LaCl$  are exposed for a small fraction of a second. However, since no timing device is available to measure such a small time, it is very difficult to obtain even densities of all the spectrograms. The mercury was exposed for less than 4 seconds; the iron exposure was 2 seconds and to make the cyanogen bands show readily, a heavy exposure is recommended. This is so as not to confuse any of the lines in the other spectrums with the cyanogen band lines.

For best results, Kodak Tri-X Panchromatic film is recommended since it is sensitive in the red through the visible and ultra-violet. This is a fast film and gives good contrast. For focusing the instrument when the mercury arc is used, Kodak Commercial film is suitable.

Using both types of film in DK-60A developer at 20 degrees Centigrade about five minutes is sufficient for the development time and 10 minutes was enough time in the fixer. Unless time is an important factor, the film should be washed for about thirty minutes.

## CHAPTER V

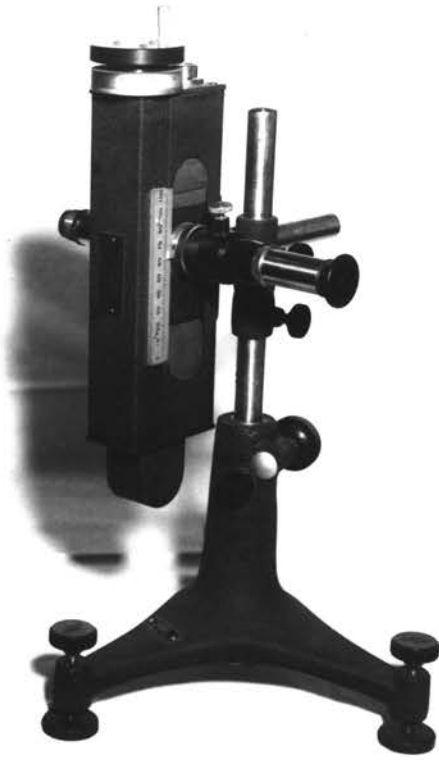
## THE DETERMINATION OF WAVE LENGTH

The wave-length of the La lines are measured in two ways. First, the spectrogram containing the alternate spectrums of Hg, Fe,  $\text{LNO}_3$ ,  $\text{LiCl}$  and  $(\text{CN})_2$  is placed on a viewing light and after the prominent Hg lines have been labeled, a scale with 40 divisions per inch can be used to read the values of the lines. The particular scale used here was divided so that 1 small scale division is equal to 10 microns. By viewing the spectrogram through a small magnifier and remembering that the instrument gives a dispersion of approximately  $10 \text{ \AA}$  per division, it is possible to determine to within about  $2 \text{ \AA}$  the wave-length of any line present by reading directly from the scale. Since the dispersion is not linear over the complete region, measurements of more than  $100 \text{ \AA}$  from the standard will not give satisfactory results at all; so in selecting lines care should be exercised that they are not separated too far from the standard.

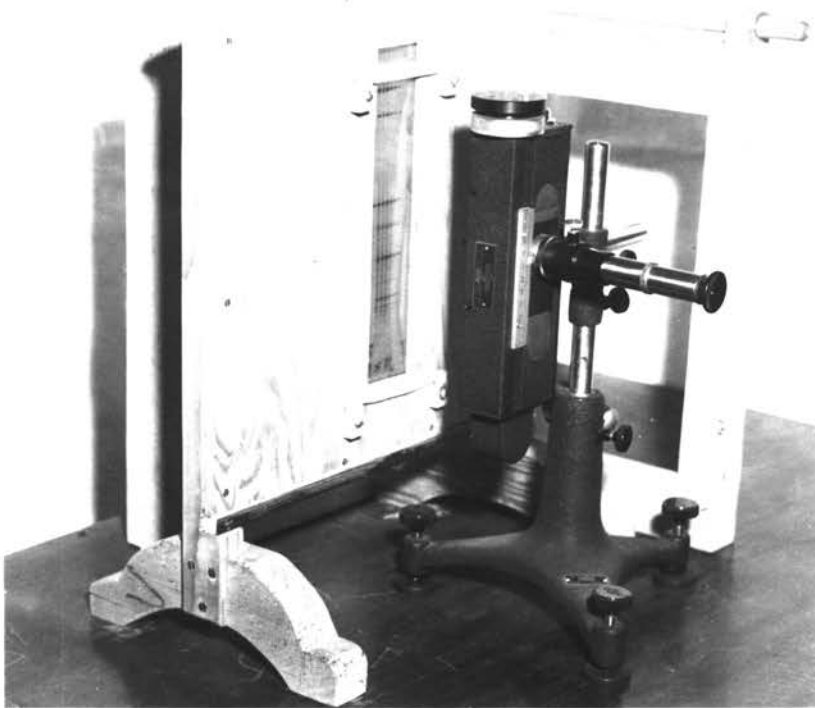
When more accurate results are desired, use is made of the cathetometer which is essentially a traveling microscope operating in a vertical plane. This instrument and the film holder are shown in Plates III and IV. The film is placed in the film holder and the data for the following formula is tabulated:

$$\lambda = \lambda_1 + \frac{\lambda_2 - \lambda_1}{d_2 - d_1} (d - d_1) \quad (9)$$

where  $\lambda_1$  and  $\lambda_2$  are two wave lengths of two known lines, and  $d_1$  and



Cathetometer



Film Holder and Cathetometer

$d_2$  the respective readings on the cathetometer for these two lines. The value of  $d$  is obtained from the reading for the unknown line  $\lambda$ .

Again precautions should be taken in the measuring procedure. The cathetometer should be leveled first and the film placed in the vertical holder and aligned as accurately as possible in the vertical plane of the cathetometer and  $xz$  and  $yz$  planes. In placing the film in the holder, be sure that it is flat against the plate all along the spectrogram. This is to keep the lines from being out of focus up and down the cathetometer scale. In measuring, the elevating mechanism should always be in the same direction; is measuring up on the spectrogram, always move up on the scale and when measuring down, move down on the scale. This is important so that no backlash occurs. Once the measuring has commenced, there can be no reversing of the screw therefore all lines to be measured and the standard lines should be distinctly marked.

Laborious calculations may be eliminated if the setting on the scale reads zero for  $\lambda_1$  and then equation (9) is reduced to a more simple form:

$$\lambda = A + B (d - d_1) \quad (10)$$

where  $A$  and  $B$  are constants determined by the reference lines.



CALCULATION OF WAVELENGTHS BY LINEAR INTERPOLATION

Table I

d (mm)	(d-d <sub>1</sub> ) (mm)	c(d-d <sub>1</sub> ) (mm)	λ(calc) A	λ(MIT) A	Error A	λ(calc) (cm <sup>-1</sup> )
18.609	0.474	7.444	3451.3	3451.1	0.2	28974.5
22.296	4.161	65.349	3509.2	3510.0	0.8	28496.5
22.486	4.351	68.332	3512.2	3512.9	0.7	28472.1
22.539	4.404	69.165	3513.0	3514.9	1.9	28465.6
26.407	8.269	129.865	3573.7	3574.4	0.7	27982.2

$$c = \frac{\lambda_2 - \lambda_1}{d_2 - d_1} = 15.705$$

Table II

d (mm)	(d-d <sub>1</sub> ) (mm)	c(d-d <sub>1</sub> ) (mm)	λ(calc) A	λ(MIT) A	Error A	λ(calc) (cm <sup>-1</sup> )
35.748	0.396	6.220	3600.8	3601.1	0.3	27771.6
36.324	0.922	14.481	3609.1	3609.2	0.1	27707.7
36.463	1.061	16.665	3611.3	3611.0	0.3	27690.8
36.491	1.639	25.744	3611.4	3611.4	0.0	27690.0
37.253	2.051	32.215	3620.4	3620.6	0.2	27621.2
37.571	2.169	34.068	3628.7	3628.9	0.2	27558.0
37.684	2.282	35.843	3630.5	3630.0	0.5	27544.4
38.037	2.635	41.388	3636.3	3636.7	0.4	27500.4
38.570	3.168	49.760	3644.7	3695.4	0.7	27437.1
38.833	3.431	53.891	3648.8	3649.5	0.7	27406.2
38.880	3.478	54.629	3649.3	3650.7	1.4	27403.5

$$c = \frac{\lambda_2 - \lambda_1}{d_2 - d_1} = 15.707$$

Table III

d (mm)	(d-d <sub>1</sub> ) (mm)	c(d-d <sub>1</sub> ) (mm)	λ(calc) Å	λ(MIT) Å	Error Å	λ(calc) (cm <sup>-1</sup> )
31.970	0.101	1.586	3661.1	3662.1	1.0	27314.1
35.266	3.402	53.418	3712.9	3713.5	0.6	26933.1
35.417	3.548	55.711	3715.2	3715.5	0.3	26916.4

$$c = \frac{\lambda_2 - \lambda_1}{d_2 - d_1} = 15.702$$

Table IV

d (mm)	(d-d <sub>1</sub> ) (mm)	c(d-d <sub>1</sub> ) (mm)	λ(calc) Å	λ(MIT) Å	Error Å	λ(calc) (cm <sup>-1</sup> )
39.536	3.652	49.466	3772.0	3773.1	1.1	26511.1
40.435	4.551	61.643	3784.8	3784.8	0.7	26426.3

$$c = \frac{\lambda_2 - \lambda_1}{d_2 - d_1} = 13.545$$

Table V

d (mm)	(d-d <sub>1</sub> ) (mm)	c(d-d <sub>1</sub> ) (mm)	λ(calc) Å	λ(MIT) Å	Error Å	λ(calc) (cm <sup>-1</sup> )
48.160	0.554	8.015	3935.5	3936.2	0.7	25409.7
48.903	1.297	18.765	3950.0	3949.1	0.9	25316.4
49.455	1.849	26.751	4041.3	4041.0	0.3	24744.5
51.082	3.476	50.291	4100.2	4101.0	0.8	24389.0

$$c = \frac{\lambda_2 - \lambda_1}{d_2 - d_1} = 14.468$$

Table VI

d (mm)	(d-d <sub>1</sub> ) (mm)	c(d-d <sub>1</sub> ) (mm)	λ(calc) Å	λ(MIT) Å	Error Å	λ(calc) (cm <sup>-1</sup> )
70.555	3.475	53.595	4123.2	4213.3	0.1	24311.7
73.480	6.400	98.707	4205.3	4204.0	1.3	23779.3

$$c = \frac{\lambda_2 - \lambda_1}{d_2 - d_1} = 15.423$$

Table VII

d (mm)	(d-d <sub>1</sub> ) (mm)	c(d-d <sub>1</sub> ) (mm)	λ(calc) Å	λ(MIT) Å	Error Å	λ(calc) (cm <sup>-1</sup> )
80.347	1.268	13.495	4216.5	4216.6	0.1	23716.1
82.414	3.335	35.494	4237.6	4238.4	0.8	23598.6
83.473	4.394	46.765	4248.8	4248.3	0.5	23536.0
85.477	6.398	67.987	4270.0	4269.5	0.5	23419.0
87.328	8.249	87.794	4289.9	4289.0	0.9	23310.9
88.277	10.198	108.537	4310.6	4311.7	1.1	23198.7
88.387	10.281	110.464	4314.0	4315.9	1.9	23180.3
88.929	11.850	126.120	4326.2	4326.2	0.0	23114.8

$$c = \frac{\lambda_2 - \lambda_1}{d_2 - d_1} = 10.643$$

Table VIII

d (mm)	(d-d <sub>1</sub> ) (mm)	c(d-d <sub>1</sub> ) (mm)	λ(calc) A	λ(MIT) A	Error A	λ(calc) (cm <sup>-1</sup> )
91.813	2.586	26.768	4335.8	4335.0	0.8	23063.7
92.262	3.035	31.415	4340.5	4339.9	0.6	23039.0
92.325	3.098	32.067	4341.1	4340.7	0.4	23035.6
94.409	5.182	53.639	4362.7	4363.1	0.4	22921.7
94.638	5.411	56.009	4365.1	4364.7	0.4	22909.2

$$c = \frac{\lambda_2 - \lambda_1}{d_2 - d_1} = 10.351$$

## SAMPLE CALCULATION

$$\lambda_2 = 3971.327$$

$$d_2 = 52.196$$

$$d = 48.160$$

$$\lambda_1 = 3899.710$$

$$d_1 = 47.606$$

$$d_1 = 47.606$$

$$(\lambda_2 - \lambda_1) = 71.617$$

$$(d_2 - d_1) = 4.590$$

$$(d - d_1) = .554$$

$$\lambda = \lambda_1 + \frac{\lambda_2 - \lambda_1}{d_2 - d_1} (d - d_1)$$

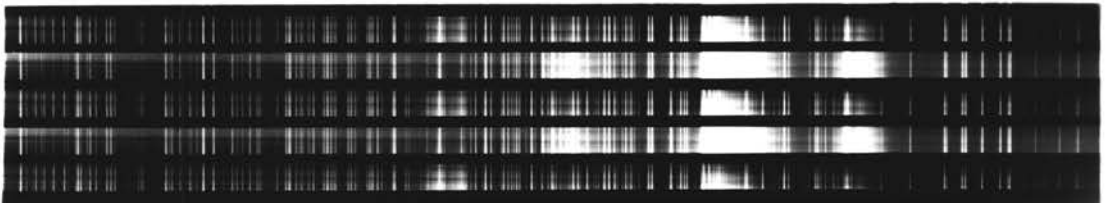
$$= 3899.710 + \frac{71.617}{4.590} (.554)$$

$$= 3899.710 + 50.291$$

$$\lambda = 3950.001 \text{ A}$$



Alternate Spectrums of  $\text{LaCl}$ ,  $\text{Fe}$ ,  $\text{Hg}$ ,  $\text{LaNO}_3$ ,  $(\text{CN})_2$ ,  $\text{LCl}$ ,  $\text{Fe}$  and  $\text{Hg}$ .



Alternate Spectrums of  $\text{LaNO}_3$  and  $\text{LaCl}$ .

## CONCLUSION

The results obtained in measuring the Lanthanum separations were found to be accurate within the order of  $2-0 \text{ \AA}$ . Since the dispersion curve is not linear over the whole spectrogram, the major factor introducing error is choosing the separation between  $\lambda_1$  and  $\lambda_2$  too large. This separation should not exceed 2.5 cm in the ultra-violet and 1 cm in the red region. It was noticed that the results obtained in the short wave-length region were those most accurate, which shows the irregularity in the dispersion curve. Another factor that permits error is the selection of the standard lines  $\lambda_2$  and  $\lambda_1$  in the Fe spectrum. A small size chart was used to locate these lines and if two lines are relatively close, a relative mistake can be made in reading the values for these lines from the chart.

With the instrument in focus for the mercury lamp, one would expect sharp lines such as those produced by the mercury; but it was noticed that the carbon arcs did not produce as sharp lines. Then when these lines are observed in the cathetometer, the exact center of the heavy lines is difficult to obtain. Experience in measuring will tend to reduce this error. As seen in the formula, an error of 0.1 mm in reading the value of  $d$  will give a difference in wave-length of  $1.5 \text{ \AA}$ . However the cathetometer measures to 0.01 mm and a high degree of accuracy should be obtained in recording the readings.

As was pointed out in Chapter IV, the electrodes had to be heated for several minutes to evaporate the moisture that may have collected in the Lanthanum compounds. In this process of drying, it was found

that with the current of 7.5 amps., the atoms tend to become ionized and give some of the spectrum lines for singly ionized Lanthanum (LaII). It might not be expected that the atoms would become ionized at such a small current, but the length of time that was necessary for drying is so long that the temperature becomes high enough to cause ionization. This effect can be reduced if the compounds are kept perfectly dry at all times or used as soon as possible when exposed to the moisture.

The wave-length precision of measurements may then be summarized as follows: (1) displacement on the spectrogram of the lines to be measured relative to standard lines, (2) displacement caused by blending with impure lines or bands, (3) determination of the exact center of the lines, (4) variations of wavelength with excitation conditions and (5) the errors in the reading of the cathetometer. For more desirable results, an instrument with a larger grating of more lines and longer radius of curvature should be used.

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