

WAVE-LENGTH MEASUREMENTS IN SPECTRA FROM 5600 Å TO 9600 Å

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I. INTRODUCTION

During the past 30 years the spectra of the chemical elements have been quite thoroughly investigated in the wave-length region to which ordinary photographic plates are most sensitive—that is, from 2000 Å to 6000 Å (Å = angstrom = 0.0000001 mm). This was made possible by Prof. Rowland's invention of the concave grating and the establishment of his system of standard wave lengths. Since 1904 a new system of wave-length standards—the international system—has been established and the wave lengths from 2000 Å to 6000 Å of many spectra have been re-measured in international Angstroms.

The long waves have never been so extensively or carefully investigated, because of the great difficulty in photographing them. Measurements of the wave lengths of some of the strong lines in

the red and adjacent infra-red regions of the spectrum have been made by using radiometers or phosphoro-photography to detect the waves. These methods, however, are difficult and yield results which are not in very good agreement. It is generally conceded that nothing can compete with direct photography for the accurate determination of the structure and wave lengths of spectral lines.

The photographic work on long wave lengths has been done principally with ordinary photographic plates which have been specially treated with dyes to make them sensitive to these long waves. Such dyes as alizarin, nigrosin, cyanin, and dicyanin have been used for the purpose. Up to the present, however, comparatively few spectra have been investigated by this method. In most cases photography with stained plates has not registered waves much longer than 8000 Å, although it is possible to reach much longer waves by this method. Furthermore, such work has been done chiefly with the low dispersion of prisms or concave gratings with small radius of curvature, and very few long wave lengths have been measured in international angstroms. By using the photographic method with interferometers or with larger gratings, accurate information concerning the spectra of the elements can be extended to regions beyond 9000 Å without much difficulty.

II. PURPOSE

Some work on spectroscopic analysis at the Bureau of Standards led to a photographic investigation of the spectra of some of the elements in the region of longer wave lengths. The photographic sensitizers dicyanin and dicyanin A were used and found to be of great value in photographing spectra between the wave-length limits 5600 Å to 9600 Å. This work was begun with the plan of studying the longer waves of the spectra of elements commonly found in iron as impurities, such as nickel, cobalt, chromium, manganese, copper, titanium, vanadium, silicon, calcium, and carbon. The success in photographing these led to the photography of the spectra of the following elements in addition to those mentioned: Lithium, sodium, potassium, rubidium, caesium, beryllium, strontium, barium, and magnesium. Thus the arc spectra of 20 of the chemical elements were photographed from 5600 Å to 9000 Å or beyond.

Accurate measurements of wave lengths to 8824 Å in the arc spectrum of iron have been made with interferometers by Burns.¹

¹ Burns, *Journal de Physique* (5), 3, p. 457; 1913.

Similar measurements have been made to 8210 Å in the barium-arc spectrum by Werner.² These spectra do not contain a sufficient number of evenly distributed and sharp lines in this region to recommend them as entirely satisfactory for standards. A photographic survey of the spectra of the elements may disclose a more satisfactory source for long-wave standards.

Some of the spectra which were photographed, notably those of cobalt, nickel, titanium, vanadium, manganese, and chromium, were found to have sharp lines whose wave lengths can be more accurately obtained with interferometers than from the grating photographs made in this work. Furthermore, the number, distribution, and intensity of lines in this part of the cobalt-arc spectrum were found to be more satisfactory than in the iron-arc spectrum.

If the sharpness of these cobalt lines be examined with the interferometer, the cobalt arc may be found superior to the iron arc as a source of long-wave standards. The wave-length measurements in these sharp-line spectra will, therefore, be postponed until the interferometer is applied.

Many elements, especially the alkali metals, have spectra the greater part of whose lines are broad, diffuse, reversed, or unsymmetrical. A careful study of the long-wave spectra of some of these elements has been made.

* The wave lengths have been measured in international angstrom units, and the results are probably as accurate as the structure of the lines will permit. These results are of special interest because of the regularities and series relationships which exist in the spectra of the II and III groups of elements in the periodic system. The apparatus and method used in photographing and measuring these spectra are described in this paper, and the results are given for lithium, sodium, potassium, rubidium, caesium, copper, beryllium, calcium, strontium, barium, and magnesium.

III. APPARATUS

The spectra were photographed in the first-order spectrum of a concave grating ruled by Dr. J. A. Anderson at the Johns Hopkins University. The grating has a radius of curvature of 640 cm and the ruled surface is 7.5 cm by 13.3 cm with 299 lines per millimeter, or 39 800 lines in all. The mounting is shown in Fig. 1.

²Werner, *Ann. d. Physik*, 44, p. 289; 1914.

An image of the arc A was magnified about three diameters and focused by the lens L on the slit S of the spectrograph. The light passing through the slit S filled a concave mirror M , which sent out a parallel beam to the grating G , which was placed close beside the slit S . The grating G focused the spectra on the photographic plate P . The grating was fixed at one end of a webbed steel beam, and the camera was movable along the other end of the beam. The camera could be rotated by sliding this end of the beam along a double track, rotation taking place about a vertical axis through the center of the grating. The grating focused the spectra in a circle with its center at the grating and radius equal to the focal length of the grating. This spectrograph gave a dispersion of 10 angstroms per mm in the first order, so that a spectrum length of 2000 Å could be photographed on a 20 cm plate. The focal surface was practically plane for this distance.

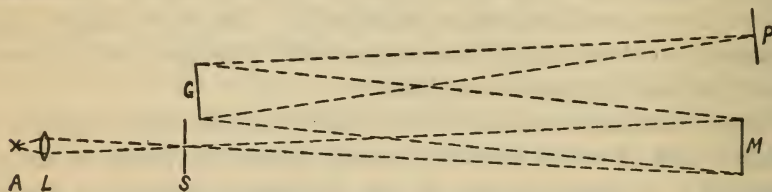


FIG. 1.—Plan of apparatus

After the camera was focused for a particular spectral region it was clamped to the double track. The whole apparatus was clamped to massive brick piers cemented to the thick concrete floor in a basement room where mechanical disturbances and temperature variations were small. A wooden house surrounded the entire apparatus and protected the camera from stray light.

The advantages of the grating mounted in parallel light, in addition to compactness and stability, are intensity of spectra and freedom from astigmatism. The intensity given by the so-called Rowland mounting is quadrupled by this mounting in parallel light. This is of great importance for the photographing of faint spectra and in regions where specially prepared plates must be used. The stigmatism of the slit images when the grating is mounted in parallel light allows the comparison spectrum, containing standards, to be photographed directly beside any other spectrum. This was accomplished by placing suitable diaphragms in front of the slit. An aperture was used which allowed light from an arc to cover 2 mm of the slit, and then this portion was

covered and 5 mm on either side was exposed to the iron arc. The slit width was usually about 0.02 mm.

IV. SOURCES

Arcs were made of metallic electrodes in all cases where it was possible. In the other cases the following salts were used in Acheson graphite electrodes: LiCO_3 , NaCl , KCl , RbCl_2 , CsCl_2 , BeCO_3 , SrCl_2 , and BaCl_2 . For calcium and magnesium arcs the lower electrode was of the metal and the upper one of graphite.

Direct current was supplied at a potential difference of 220 volts. The current strength was made to correspond roughly to the wave lengths to be photographed, i. e., 6 amperes were used to photograph from 6000 Å to 7000 Å, 7 amperes from 7000 Å to 8000 Å, etc. An exception was made in the case of magnesium. The metallic electrode would ignite with large currents, but burned quite satisfactorily with 3 amperes and 110 volts. Electrodes of Norway iron were used for producing the light of the comparison spectrum, and the arc was operated under standard conditions.³

In every case only light from the center of the arc was photographed, the light from the electrodes being screened from the slit by the diaphragm.

There is an important difference between so-called chemically pure substances and substances which are spectroscopically pure. In spite of the great skill and care taken in preparing the material, chemists seem unable to produce elements in an absolutely pure state. The use of impure materials for sources has naturally led to frequent mistakes in assigning spectrum lines to the proper element. Some of the long waves which have been wrongly identified by others will be pointed out in the results of this work. It is possible that some errors of this kind still remain.

Spectroscopic analysis of the Acheson graphite showed the presence of sodium, calcium, and barium. All the lines photographed were measured, but the wave lengths due to impurities were separated from the others and will be found in Table I I. This table shows the impurities in the "chemically pure" salts used in this work.

When large quantities of salts are used in graphite electrodes the spectrum of carbon is quite effectively suppressed. If only small quantities are used the thousands of lines due to carbon become very troublesome. Electrodes of copper, cored and filled

³ *Astroph. JI.*, **39**, p. 93; 1914.

with salt, may be recommended for work in the region of long wave lengths, for the copper spectrum has very few strong lines in this region.

V. PHOTOGRAPHY OF RED AND INFRA-RED SPECTRA

Among the various photographic sensitizers which have been used to photograph red and infra-red spectra, the most efficient and convenient is probably dicyanin. Eder,⁴ Geiger,⁵ Burns,⁶ and others have used it successfully, and it is regrettable that its use has not become more universal.

Photography with stained plates is generally thought to be difficult, troublesome, and uncertain. Perhaps some have tried dicyanin without success because their dye was inferior or worthless. This dye is quite easily decomposed by the action of light or heat, after which its value as a photographic sensitizer is lost. If stored in a cool, dark place it may be kept months without decomposing. The process of staining plates is probably thought to require special apparatus and technique. It is possible, however, to obtain satisfactory results with a very simple procedure.

The most efficient staining bath was found to be the one recommended by Burns.⁶ It consisted of a mixture of water, alcohol, ammonia, and dicyanin in the following proportions: About 4 cc of a stock solution of 1 part dicyanin to 1000 parts alcohol were added to 50 cc distilled water, 50 cc ethyl alcohol, and 5 cc of strong ammonia. Ordinary photographic plates, like Seed 27 or Graflex, were soaked in such a bath from 3 to 5 minutes, rinsed in alcohol 30 seconds, and dried by a current of air from an electric fan. Plates treated in this manner were found to be quite sensitive to wave lengths between 6000 Å and 9000 Å. The strong lines between 7500 Å and 8500 Å in the spectra of the alkali metals were photographed with exposures of 1 minute or less. In the barium-arc spectrum a line of wave length 9370 Å was registered with an exposure of 20 minutes, while an exposure of 60 minutes on a plate stained with dicyanin A showed the line of wave length 9608 Å quite strongly. (See Fig. 7.) The exposures were usually limited to 30 minutes in length, so as to be reasonably sure that no displacements had taken place in the spectrograph. With these half-hour exposures the spectrum of the iron arc has been photographed to 9118 Å, the chromium arc to 9290 Å, the vana-

⁴ Eder, *Kaiser. Akad. d. Wiss.*, **123**, p. 2289; 1914.

⁵ Geiger, *Ann. d. Phys.*, **39**, p. 752; 1912.

⁶ Burns, *Journal de Physique*, (5), **3**, p. 457; 1913.

dium arc to 9087 Å, the nickel arc to 8968 Å, the cobalt arc to 8926 Å, and the titanium arc to 8734 Å. In the region 5600 Å to 7600 Å the exposure times ranged from 1 to 15 minutes.

A few typical spectrum photographs as made with the dicyanin-stained plates are reproduced in Figs. 3, 4, 5, 6, and 7. These photographs are enlargements of three diameters made from copies of the original spectrum plates. They show the first-order spectrum of some element bounded on either side by the arc spectrum of iron as photographed in the second order. An exception to this arrangement is found in the last two spectra on Fig. 3. In these cases the first-order spectrum of iron is shown below that of Caesium. The wave lengths of the strong lines in the middle spectrum are indicated by the accompanying numbers.

VI. WAVE-LENGTH MEASUREMENTS

The plates were measured with the excellent measuring machine at the Johns Hopkins University. This machine has a screw which is nearly perfect throughout its entire length of more than 50 cm. The pitch of the screw is 1 mm. The head has a diameter of 25 cm and the circumference is divided into 1000 parts. One division thus corresponds to 1μ along the axis of the screw or to 0.01 Å on a spectrum photograph with 10 Å per mm.

Turning the head moved the microscope along ways which were parallel to the screw. The spectrum plate was clamped firmly to a shelf fastened to the ways. A five-fold magnified image of a part of the plate was then visible in the field of the microscope with the cross-hair images superposed. The microscope contains two pairs of cross hairs, as shown in Fig. 2. Readings were made when the cross-hair intersection b_1 was on a spectrum line and again when b_2 was on the same line. The mean of these two readings was used for the position of the line on the plate. The positions of the standards in the comparison spectrum of iron were obtained from readings when the cross-hair intersections a_1 and a_2 were on the lines. After the two spectra were completely measured from short to long wave lengths, the plate was reversed and remeasured from long to short wave lengths. Thus each determination of

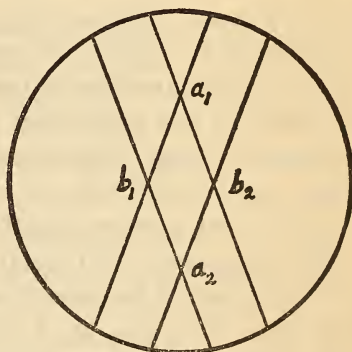


FIG. 2.—Cross hairs

wave length is based upon four independent observations of the position of a line with respect to the neighboring standards.

The scale of the plate, assuming normal dispersion, was obtained by dividing the difference in wave length by the measured distance between the first and last standards measured on the plate. All the other measurements were then reduced to wave lengths on this basis. The deviations from standard values of the values thus obtained for the iron lines were plotted as a function of wave length and a curve was drawn through these points. From this curve the correction required to express any other wave length on the international scale was obtained.

Interference measurements of wave lengths in the iron spectrum by Burns, Meggers, and Merrill⁷ were used as standards. These standards contain the 85 international secondary standards from 3233 Å to 6750 Å, together with 318 other iron lines compared with the international standards by the interferometer method. This set of standards contains chiefly the sharpest iron lines, of different intensities, consistent with regularity of distribution throughout the spectrum. The average distance between these standards is less than 9 Å. Eighty-six per cent of the 85 international secondary standards are lines of intensity 4 to 6, inclusive, while only 47 per cent of the additional 318 lines have these intensities, the remainder being distributed among fainter and stronger lines. These facts make this set of standards very convenient for the measurement of wave lengths.

The comparison iron spectrum from 3300 Å to 4800 Å was usually photographed in the second order of the grating, when long waves, from 6600 Å to 9600 Å of other spectra were photographed in the first order. Orders overlapping on the first order spectrum were removed by placing a screen of Jena red glass in front of the slit. The first-order spectrum of iron was photographed beside the shorter waves of the other spectra. On a few plates the first-order spectrum of iron was used to 8600 Å and Burns's values were then used for the standards longer than 6750 Å.

VII. RESULTS

The results are contained in the following tables. The first column of each table gives the wave lengths as measured in international angstroms. The second column indicates the intensity and character of each line. The strongest lines are called intensity

⁷ This Bulletin, 13, p. 245; 1916.

10. Faint but measurable lines are called intensity 1. The character or appearance of a line is represented by letters which have the following meanings:

b=broad.

d=perhaps double.

h=hazy.

H=very hazy.

l=shaded to red.

L=much shaded to red.

R=broadly reversed.

rs=narrow reversal, red component stronger.

Sb=very broad.

The third column indicates the probable error of the measurement of each wave length. The letters have the following significance:

A=probable error 0.000 Å to 0.010 Å.

B=probable error 0.010 Å to 0.020 Å.

C=probable error 0.020 Å to 0.030 Å.

D=probable error >0.030 Å.

E=only one determination.

A and B also indicate that the line was measured more than twice. In fact most of the stronger lines were measured on three to six plates. The lines marked "E" are generally faint and show only on the longest exposures. Their wave lengths are not very accurate, but they are all included in the table to show how many of them have been recorded by comparatively short exposures of the dicyanin-stained plates. In the following tables I. A. indicates that the wave lengths are given in international angstroms. The others are based on Rowland's system of standards.

The tables contain also the results of others who have photographed in this region with stained plates. The only investigations of this kind embracing more than one spectrum are those of Lehmann,⁸ Hermann,⁹ Saunders,¹⁰ Lorensen,¹¹ and Eder.¹² Among these, Eder's results are the only ones expressed in International Angstrom units.¹³ Lorensen used the Hartmann¹⁴ values for the iron lines as standards. For purposes of comparison, the

⁸ Lehmann, *Ann d. Phys.*, (4), 5, p. 633, strong line 1, weak line 4; 1901.

⁹ Hermann, *Ann d. Phys.*, (4) 16, p. 684; 1905.

¹⁰ Saunders, *Astrophys.*, JI., 20, p. 188; 1904.

¹¹ Lorensen, *Dissertation*, Tübingen; 1913.

¹² Eder, *Sitzungsber. d. k. Akad. d. Wissensch.*, Wien. 123, p. 2289, strong line 100; 1914.

¹³ Science Abstracts, 20, Abs. 223, 1912, briefly describes "Researches and Measures of Wave Lengths in the Red and Infra-red Regions of the Spectrum," by K. W. Meissner, whose work is published in *Ann. d. Physik*, 50, p. 713, 1916. Dicyanin-stained plates were used to investigate the spectra of Cs, Fe, Na, K, Rb, Al, Ca, Ag, Cu, Cr, U, S, O. It has been impossible to obtain a copy of Meissner's publication. This explains the absence of his results in the following tables.

¹⁴ Hartmann, *Physik. Zeitschr.*, 10, p. 123; 1909.

results based upon Rowland's standards may be changed to the international scale by subtracting the following quantities:

0.22 A from 5500 to 6050
.21 A from 6050 to 6500
.22 A from 6500 to 6570
.23 A from 6570 to 6750
.24 A from 6750 to 6850
.25 A from 6850 to 7000
.26 A from 7000 to 7200
.27 A from 7200 to 7400
.28 A from 7400 to 7700
.29 A from 7700 to 8000
.30 A from 8000 to 8200
.31 A from 8200 to 8300
about .35 A from 8300 to 8800

For the proper discussion of series relationships among the lines in these spectra, the wave lengths should be reduced to vacuum. This can not be done accurately at the present time because the dispersion of air has never been determined for waves longer than 6800 A. For this reason an investigation on atmospheric dispersion in the region of long wave lengths has been begun. The frequency differences of pairs of lines which appear in doublet series in some of the spectra will not be affected appreciably by the dispersion of the atmosphere. Such frequency differences, as determined from my wave-length measurements, will be given below. The oscillation frequency used here is the reciprocal of the wave length or the number of waves per centimeter. This number is proportional to the absolute frequency or number of waves per second and is more convenient and in wider use than the latter.

TABLE 1.—Lithium

Meggers			Eder		Saunders	Lehmann		Kayser and Runge ¹⁵	
λ I. A.	Notes	p. e.	λ I. A.	Notes	λ	λ	Notes	λ	Notes
6103.53	10b	E						6103.77	10R
6707.85	10R	B	6707.85	100R	6240.3			6708.2	10R
8126.52	10	B	8126.27	10b	8127.0	8127.34	1		

The arc was produced between graphite electrodes containing lithium carbonate. The impurities present were sodium, potassium, calcium, and barium.

The spectra of the alkali metals have attracted much attention because of their similarity. They all contain definite sequences

¹⁵ Kayser and Runge, Wied. Ann., 41, p. 302; 1890.

or series of lines, and the members of each series possess the same spectral character. In general three types of series exist in each of these spectra. The intense and easily reversed lines constitute the so-called principal series. Most of the other lines are broad and diffuse. They may be arranged in two subordinate series, the lines of the first subordinate series being broadened by shading toward the red. In the spectra of sodium, potassium, rubidium, and caesium all the series consist of doublets, but the lines in the lithium spectrum have generally been measured as single. The lines are, no doubt, very narrow pairs, and King¹⁶ has recently found the line 6707 double under certain conditions. Two components for this line have also been observed by others. The separation is about 0.15 Å.

TABLE 2.—Sodium

Meggers			Eder		Kayser and Runge ¹⁷		Saunders	Hermann	
λ I. A.	Notes	p. e.	λ I. A.	Notes	λ	Notes	λ	λ	Notes
5682.97	8	E			5682.90	7ur			
88.61	10	E			88.26	8ur			
5889.97	10R	E			5890.19	10R			
95.94	8R	E			96.16	9R			
6154.40	4	E			6154.62	8ur			
60.96	5	E			61.15	8ur			
							7369.4		
							77.4		
							7410.0		
						Lehmann	18.3		
8183.30	8rs	C	8183.35	100R	8184.33	1	8184.5	8183.74	2
								8188.17	0
8194.82	10rs	C	8194.92	100R	8194.76	1	8196.1	8195.33	3

Sodium chloride was used in graphite electrodes for the arc. The impurities present were potassium, strontium, lithium, calcium, and barium. When a large amount of sodium chloride was used in the arc the lines 8183 and 8194 showed narrow reversals displaced from the centers of the lines toward shorter wave lengths. The wave lengths given are from measurements on these reversals. When unreversed the lines are shaded to the red, and the measured wave lengths are then usually from 0.1 Å to 0.2 Å larger. These two lines are the first pair of the first subordinate

¹⁶ King, *Astrophys. J.*, 44, p. 169; 1916.¹⁷ Kayser and Runge. See note 15.

series and their frequency difference is 17.2, which is identically the frequency difference of the first pair of the principal series, 5889 and 5895. The lines 6154 and 6160 are the first pair of the second subordinate series, and their frequency difference from these measurements is 17.3. The frequency difference of the second pair, 5682 and 5688, in the first subordinate series, is 17.4. The range in frequency differences for these four pairs of lines is little more than 1 part in 100 000 in the actual number of waves per centimeter, and this is of the same order of magnitude as the errors in the wave-length measurements.

TABLE 3.—Potassium

Meggers			Eder		Kayser and Runge ¹⁵		Saunders	Hermann		Lehmann	
λ I. A.	Notes	p. e.	λ I. A.	Notes	λ	Notes	λ	λ	Notes	λ	Notes
5782.60	2h	E			5782.67	5u R					
5801.96	4h	E			5802.01	6u R					
12.52	2h	E			12.54	6u R					
5832.09	2h	E			5832.23	7u R					
6911.30	10	A	6911.31	5	6911.2	7	6911.8				
38.98	10	A	39.07	6	38.8	8	39.5				
							6966.3				
7664.94	10R	A	7664.95	150R	7665.6	10u R	7664.91	7665.29	8	7668.54	1
99.01	10R	A	99.02	100R	99.3	10u R	99.08	99.32	6	7701.92	1
							7931.8				

Potassium chloride was used in graphite electrodes. The impurities in the spectrum were sodium, rubidium, calcium, barium, and lithium.

The lines 7699 and 7664 are the first pair of the principal series and their frequency difference from these measurements is 57.74. The next pair, 6938 and 6911, are the first lines of the first subordinate series. Their frequency difference is 57.72, or identically that of the first pair of the principal series. The lines 5801 and 5782 are the second pair in the first subordinate series and their frequency difference is 57.71. The pair 5832 and 5812 belong to the second subordinate series. The difference in waves per centimeter for this pair is 57.73. The above measurements thus give exactly the same frequency difference for these four pairs.

¹⁵ Kayser and Runge. See note 15.

TABLE 4.—Rubidium

Meggers			Eder		Eder and Valenta ¹⁹		Saunders	Lehmann	
λ I. A.	Notes	p. e.	λ I. A.	Notes	λ	Notes	λ	λ	Notes
6070.95	2l	E	-----	-----	6071.30	3	6071.1	-----	-----
6159.84	5l	E	-----	-----	6160.20	4	6160.0	-----	-----
6206.48	8l	E	-----	-----	6206.74	6	6206.7	-----	-----
98.50	10l	E	-----	-----	98.85	8	98.8	-----	-----
					7060.09	1	-----	-----	-----
7280.22	10l	C	-----	-----	7280.53	1	7280.3	7277.01	4
7408.37	10l	C	7408.49	1l	7408.71	1	7408.5	7406.19	4
7619.12	8l	C	7619.17	2b	7619.7	1	7619.2	7626.66	3
7757.80	8l	B	7757.70	2b	-----	-----	7757.9	7753.58	3
59.58	1	C	-----	-----	7759.6	1	59.5	-----	-----
7800.29	10R	A	7800.30	100R	7800.3	4R	7800.2	7805.98	1
7947.64	8R	A	7947.63	50R	7947.7	2R	7947.6	7950.46	2
			8521.21	3u	-----	-----	-----	8513.26	4

Rubidium chloride was used in graphite electrodes. The arc spectrum showed sodium, potassium, caesium, calcium, barium, and lithium as impurities.

The line 7060 observed by Eder and Valenta is due to barium. The line measured as 8521 by Eder and 8513 by Lehmann belongs to caesium.

The lines 7947 and 7800 are the first pair of the principal series. Their frequency difference is 237.7. Lines 7757, 7619, and 6298, 6206 are the first two pairs of the first subordinate series. Their frequency differences are 234.5 and 235.4. Lines 7408, 7280, and 6159, 6070 are the first two pairs of the second subordinate series. Their frequency differences are 237.5 and 237.7. Thus it appears from these measurements that the frequency differences of pairs in the second subordinate series are identical with that of the first pair of the principal series, while those of the first subordinate series are about 1 per cent smaller. This is also true for the succeeding pairs.

¹⁹ Eder and Valenta, *Atlas Typischer Spektren*, Wien, 1911.

TABLE 5.—Caesium

Meggers			Eder		Lehmann		Saunders
λ L. A.	Notes	p. e.	λ L. A.	Notes	λ	Notes	λ
5663.8	H	D					
5844.7	H	D					
6010.33	7b	C					
							6034.8
6212.87	8b	C					6213.1
6217.27	1b	E					6217.6
							6325
6354.98	4b	C					6353.3
							6359
							6434
							6475
							6587.3
6586.94	5i	D	6587.11	6i			6588.0
							6630.5
6723.18	10b	A	6723.28	20			6723.7
							6826.9
							6872.6
6973.17	10b	A	6973.35	20R			6973.1
83.37	5b	A	83.39	3b			6983.8
7228.5	L	E			7227.46		7228.8
7279.7	L	E					7280.5
7609.13	5i	B	7609.28	2i	7616.58	3	7609.7
			7800.11	2b			
			7941.1	1u			
7944.11	6b	C					7944.7
8016.2	10L	D			8019.62	3	8007.7
8016.9							
8079.1							
8079.8	10L	D			8082.02	3	
8521.12	10R	A			8527.72	1	
8761.35	5b	B			8766.10	2	
8943.46	8R	A			8949.92	2	
9172.23	2b	A			9171.38	3	
9208.40	1b	A			9211.86	3	

Caesium chloride was used in graphite electrodes. The arc spectrum showed sodium, potassium, rubidium, lithium, calcium, and barium as impurities. The line 7800 measured by Eder is due to rubidium. The line 8079 and the line 8016 are very unsymmetrical. The photographic maximum is therefore dependent on the duration of the exposure for its position, and the measurements on this maximum vary between the limits indicated.

The following lines belong to series:

		Meggers	Kayser
		$\Delta\nu$	$\Delta\nu$
First pair of principal series.....	$\left\{ \begin{array}{l} 8943.46 \\ 8521.12 \end{array} \right\}$	554.1	546.9
First pair of first subordinate series.....	$\left\{ \begin{array}{l} 9208.40 \\ 8761.35 \end{array} \right\}$	554.2	552.0
Second pair of first subordinate series.....	$\left\{ \begin{array}{l} 6973.17 \\ 6923.18 \end{array} \right\}$	533.2	533.8
Third pair of first subordinate series.....	$\left\{ \begin{array}{l} 6212.87 \\ 6010.33 \end{array} \right\}$	542.2	543.0
Fourth pair of first subordinate series.....	$\left\{ \begin{array}{l} 5844.7 \\ 5663.8 \end{array} \right\}$	546.5	547.0

Kayser²⁰ suspected that accurate measurements would show these frequency differences to be constant. Although my measurements show the frequency differences to be identical for the first pairs of the principal and subordinate series, the frequency differences for the next three pairs of the first subordinate series show the same deviations from constancy as the older measurements.

TABLE 6.—Copper

Meggers			Aretz ²¹		Hasbach ²²	
λ I. A.	Notes	p. e.	λ I. A.	Notes	λ I. A.	Notes
6415.18	1	E	6415.155	1		
27.57	1	A	27.564	2		
			52.287	0		
			56.672	1u		
74.20	3	A	74.176	5u	6474.2	1u
85.18	2	D	85.142	5u		
			6504.051	0	6485.15	1
			06.142	2u		
			31.437	1		
6544.51	1h	D	44.427	2u		
50.98	1	E	50.977	3		
65.54	3h	C	65.555	2u		
			83.542	2u		
			99.681	5		
6621.61	4	A	6621.623	1u	6621.59	1
29.67	1	C	29.730	1u		
72.23	3	A	72.234	5	72.2	1u
6741.42	7	A	6741.418	6	6741.4	1u
49.29	2b	E				
75.64	2b	C				

²⁰ Kayser, Handbuch der Spectroscopie, 2, p. 529.

²¹ Aretz, Zeitschr. f. wiss. Phot., 9, p. 256; 1910.

²² Hasbach, Zeitschr. f. wiss. Phot., 13, p. 399; 1914.

TABLE 6.—Copper—Continued

Meggers			Aertz		Hasbach	
λ I. A.	Notes	p. e.	λ I. A.	Notes	λ I. A.	Notes
6821.86	1h	C	81.869	0u		
35.46	1	E				
40.99	1h	A				
81.94	2	A				
89.92	2	C				
90.90	2	A				
6905.90	6	A	6905.937	3u		
20.09	4h	A	20.287	1u		
35.80	2h	C				
68.36	1	C				
7000.02	1h	E				
39.34	3	B				
7124.66	1	E				
54.29	1	E				
93.56	2h	A				
7427.26	1	E				
7570.09	5	A				
7771.98	4	A				
74.18	3	A				
75.41	2	A				
7848.55	1	C				
7911.95	1	C				
33.20	10	A				
54.23	2	B				
8006.27	2	B				
17.78	2	B				
71.06	2	C				
92.74	10	B				
8114.17	2	B				
78.96	2	B				
87.90	1	E				
8216.22	1	C				
23.13	1	E				
42.27	1	E				
73.45	1	E				
8408.00	1h	E				
46.40	2	C				
8680.08	1	E				
83.17	1	E				

Copper rods 6 mm in diameter were used as arc electrodes. The D lines of sodium appeared in the spectrum. The work of Aertz and of Hasbach should be consulted for wave lengths shorter than 6621 Å. Aertz made exposures on Wratten & Wainwright plates for six hours and obtained lines below 6621 Å which were not recorded by the 15-minute exposures on my plates. The line 6599 which Aertz marked intensity 5 did not appear on my plates. It may represent an impurity.

The copper-arc spectrum also has a doublet system of series. The first pair of the principal series, 3247.550 Å and 3273.967 Å, according to Hasbach, has a frequency difference of 248.45. Lines 7933.19 Å and 8092.76 Å are the first lines of the second subordinate series and have a frequency difference of 248.55. The lines 5133.261 Å and 5220.083 Å have a frequency difference of 248.40. This pair belongs to the first subordinate series. The frequency differences of these three pairs representing three different series differ from each other by less than one part in 100 000 in the wave number.

Beryllium

Investigations in the arc spectrum of beryllium have thus far disclosed only 12 lines with certainty. The longest of these has a wave length of 4572 Å, which is in the blue part of the spectrum. Exposures of a half hour on my stained plates showed no traces of lines between 4572 Å and 9000 Å. Beryllium carbonate was used in graphite electrodes to produce the arc spectrum.

TABLE 7.—Strontium

Meggers			Eder		Hampe ²³	Lehmann		Eder ²⁴ and Valenta	Lorenser	
λ I. A.	Notes	p. e.	λ I. A.	Notes	λ I. A.	λ	Notes	λ	λ	Notes
6363.98	4	C			6363.932			6364.21	6364.19	5
70.00	5	C			69.959			70.20	70.18	6u
80.77	5	C			80.740			80.95	80.94	10s
86.57	7	C			86.507			86.76	86.76	9u
88.32	6	D			88.245			88.50	88.48	8u
6408.49	9	C			6408.465			6408.70	6408.69	15
46.70	1	C			46.676				46.91	3
65.78	1	C			65.788			66.08	66.10	2
6504.02	6	C	6504.01	6	6503.990	6504.07	1	6504.26	6504.26	12u
									16.07	1
21.29	1								21.53	1
46.82	4	B	46.79	4	46.785	46.27	4	47.09	47.06	8u
50.28	5	B	50.29	6	50.253	50.19	3	50.53	50.51	12u
6617.28	5	B	6617.27	4	6617.268	6616.92	3	6617.50	6617.54	10u
43.58	4	A	43.52	3	43.545	44.05	3	43.78	43.80	6u
						6708.10	4			
						54.21	4			
6791.08	5	A	6791.06	6	6791.046	6792.19	1	6791.30	6769.59	1
									91.35	10
									6803.55	1
6878.36	10	A	6878.36	7	6878.347	6880.69	1	6878.63	78.65	15v
92.62	6	A	92.62	4	92.598	93.37	3	92.83	92.86	8s
7070.15	10	A	7070.12	20R	7070.102	7070.34	2	7070.45	7070.53	20v
									88.90	1

²³ Hampe, Zeitschr. f. wiss. Phot., 13, p. 348; 1914.

²⁴ Eder and Valenta, Atlas Typischer Spektren, Wien; 1911.

TABLE 7.—Strontium—Continued

Meggers			Eder		Hampe	Lehmann		Eder and Valenta	Lorenser	
λ I. A.	Notes	p. e.	λ I. A.	Notes	λ I. A.	λ	Notes	λ	λ	Notes
7153.08	4	A	7153.07	2				7153.24	7153.43	4s
67.24	6	A	67.29	5		7168.02	3	67.49	67.66	10u
7232.24	6	A	7232.20	4		7232.10	3	7232.53	7232.56	8u
						54.44	3			
87.44	1h	E	87.57	1					87.75	4
			89.25	1					89.19	2
7309.47	6	A	7309.46	10				7309.65	7309.70	12u
									48.72	1
									62.83	1
									7406.07	2
			7408.13	1					08.32	3
									38.53	2
7621.54	5	A	7621.55	3					7621.76	8
73.11	6	A	73.07	6					73.38	10
			8183.58	4						
			95.14	4b						

Strontium chloride in graphite electrodes was used for the arc. Lithium, sodium, calcium, and barium were found as impurities. The lines 8183 and 8195 observed by Eder are due to sodium. The unsymmetrical character of these two lines makes their measured wave lengths several tenths of an angstrom unit larger than when measurements are made on the reversals. The line 6708 measured by Lehmann is probably a lithium line. The line 7408 measured by Eder and by Lorenser may belong to rubidium.

TABLE 8.—Calcium

Meggers			Eder		Crew and McCauley ²⁵		Holtz ²⁶	Lehmann		Lorenser	
λ I. A.	Notes	p. e.	λ I. A.	Notes	λ I. A.	Notes	λ I. A.	λ	Notes	λ	Notes
6439.13	10	E			6439.086	9	6439.061			6439.31	20v
49.83	5	E			49.811	7	49.794			50.05	10
55.60	3	E			55.606	3	55.560			55.82	8s
62.62	10	E	6462.55	8	6462.576	9	62.550			62.82	20v
										64.93	2u
71.69	5	E	71.64	5	71.659	5	71.644			71.92	10
93.83	7	E	93.77	7	93.789	8	93.762			94.04	20v
99.67	5	E	99.64	5	99.648	4	99.624			99.94	10
					6508.742	1		6508.02	3		
6572.78	2	E	6572.78	4	6572.783	3	6572.71	71.93	2	6509.10	4s
										73.03	6s
										6656.1	1u

²⁵ Crew and McCauley, *Astrophys. J.*, **39**, p. 29; 1914.

²⁶ Holtz, *Zeitschr. f. wiss. Phot.*, **12**, p. 101; 1913.

TABLE 8.—Calcium—Continued

Meggers			Eder		Crew and McCauley		Holtz	Lehmann		Lorenser	
λ I. A.	Notes	p. e.	λ I. A.	Notes	λ I. A.	Notes	λ I. A.	λ	Notes	λ	Notes
6717.78	8	C	17.69	8	17.688	5	17.70	6666.98	2	65.6	1u
								6707.81	-----	6708.06	6u
										10.12	1
								6714.47	3	18.01	15v
										44.0	1u
										47.2	1u
								67.02	1	-----	-----
								82.85	4	-----	-----
										84.13	4u
										89.38	1u
7148.15	10	B	7148.14	6	7148.123	3	-----	6833.50	4	-----	-----
										6866.80	1u
										84.29	2
								7146.45	3	7148.49	15v
								99.83	1	7202.51	15v
								7322.95	2	7326.43	20v
										7468.69	3
										7521.22	1u
										34.75	2u
										66.08	3u
7202.21	8	A	7202.15	4	7202.161	2	-----	7600.74	4u	82.39	1uR
										87.79	2uR
										98.40	3uR
										-----	-----
										7602.78	4uR
										10.66	6uR
										45.25	1u
										7984.25	1u
										95.31	2u
										8153.13	2
7326.12	8	A	7326.10	5	7326.099	1	-----	-----	-----	-----	-----
8153.13	1	E	-----	-----	-----	-----	-----	-----	-----	-----	-----
8497.98	8	B	8498.11	4	-----	8498.32	00	8499.20	3	8498.35	3
8542.06	10	B	8542.25	1u	-----	8542.48	1	8543.08	1	8542.47	5
8662.10	9	B	-----	-----	-----	8662.42	0	8662.10	2	8662.50	3

An electrode of metallic calcium was used below and a graphite electrode above to produce the arc. Sodium, lithium, potassium, and strontium contaminated the spectrum. The line 6707 measured by Eder, Crew and McCauley, Holtz and Lorenser is due to lithium, although Eder insists that it is a calcium line. Woodward²⁷ has shown that this line is absent in the arc spectrum of pure calcium. By means of a 25-ampere arc and longer exposures

²⁷ Woodward, *Astrophys. J.*, **41**, p. 169; 1915.

Lorenser has found a number of new lines. Some of these may belong to band spectra and to impurities. Most of the lines become broad and unsymmetrical when the arc is operated with large currents. Crew and McCauley used the arc in a vacuum to get sharp lines.

TABLE 9.—Barium

[illegible]

²⁸ Burns, *Kayser's Handbuch der Spectroscopie*, 6, p. 934.

²⁹ Werner. See note 2.

²⁰ George, *Zeitschr. f. wiss. Phot.*, 12, p. 237; 1913.

Meggers			Lorenser		Eder		Burns	Werner	Lehmann		Hermann
λ I. A.	Notes	p. e.	λ	Notes	λ I. A.	Notes	λ I. A.	λ I. A.	λ	Notes	λ
			8329.17	3u							
50.64	1	E									
90.38	1	E									
8414.52	1h	E									
8514.23	2h	C	8514.50	1u					8518.24	4	
21.91	1	C									
			42.72	1u							
8559.90	10	B	8560.21	6u	8559.98	5			8563.92	1	8560.20
67.53	3h	B	68.08	3u R							
69.11	1	E	69.60	2u R							
			70.34	1u R							
82.04	4	B	82.66	3u					85.70	4	
93.40	1	E									
8654.02	4	B	8654.40	3					8659.38	4	8654.33
			59.65	1							
8710.74	1	A									
37.71	1	C									
99.70	2h	C							8806.22	4	8799.86
8860.96	4	B	8861.32	2					8868.50	4	8861.40
8914.96	4	A	8915.40	2					8921.04	3	8915.19
27.30	1	E									
37.85	1	E									
9091.15	1	E									
9133.70	1	E									
89.43	2	E									
9219.65	2	B									
9308.09	1	E									
24.53	1	E									
70.05	3	B									
9455.94	1	E									
9608.83	1	E									

The arc was operated with barium chloride in graphite electrodes. Lines belonging to sodium, lithium, potassium, strontium, and calcium appeared in the spectrum. The line 9370 was registered by the phosphoro-photographic method by Lehmann,³¹ who measured the wave length as 9367 Å. The line 9608 was detected by Randall³² with a thermopile, and this wave length was given as 9610.7 Å. Randall measured a line of wave length 9527.3 Å, which did not appear on my plates.

It is unfortunate that the line structures and wave lengths in the barium spectrum are so sensitive to the conditions under which the arc is produced. Werner used the arc in a vacuum in order to obtain sharp lines. Under atmospheric pressure many of

³¹ Lehmann, Ann. d. Phys., 39, p. 53; 1912.

³² Randall, Astrophys. J., 34, p. 1; 1911.

the lines begin to broaden. Lorensen used large quantities of barium chloride in a carbon arc fed by 30 amperes. Under these conditions nearly all of the lines are broad or unsymmetrical.

TABLE 10.—Magnesium

Meggers			Nacken ³³		Lorensen		Hermann	
λ I. A.	Notes	p. e.	λ I. A.	Notes	λ	Notes	λ	Notes
5528.49	10	C	5528.466	5				
5711.14	5	C	5711.127	1				
82.10	1	C						
6021.70	1	C						
6318.5	2d	D			6318.55	2u R		
					18.82	2u		
					19.08	1u		
					32.48	2s		
					47.27	4u		
					6457.03	1		
					64.51	2		
					6505.62	2		
					45.66	2u V		
					46.77	5u R		
7657.5	1h	D			7658.46	3		
8806.75	5	B			8807.20	5	8806.96	8
							8929.35	2
							9224.44	00

Metallic magnesium was used as a lower electrode and graphite as an upper electrode in the arc. It is difficult to burn such an arc in air because of the tendency of the magnesium to ignite and oxidize. Lorensen burned the arc in a vacuum.

Comparison with the tables of solar wave lengths, published by Capt. (Sir) W. de W. Abney,³⁴ brings out certain interesting facts. Aside from the telluric lines, a large percentage of the rays in the infra-red solar spectrum are due to iron, as would be expected from the character of the solar spectrum in the visible and ultra-violet regions. The strongest solar lines in the infra-red are due to calcium and magnesium. These are the lines X_I, X_{II}, X_{III}, and X_{IV} of Abney, the last and weakest being due to magnesium. Some of the strong lines of barium seem to show in the solar spectrum, as well as the strong lines of potassium (7664 and 7699), sodium (8183 and 8194), lithium (8126), and copper (7933).

³³ Nacken, *Zeitschr. f. wiss Phot.*, **12**, p. 54; 1913.

³⁴ Abney, *Phil. Trans.*, **177**, p. 457; 1886.

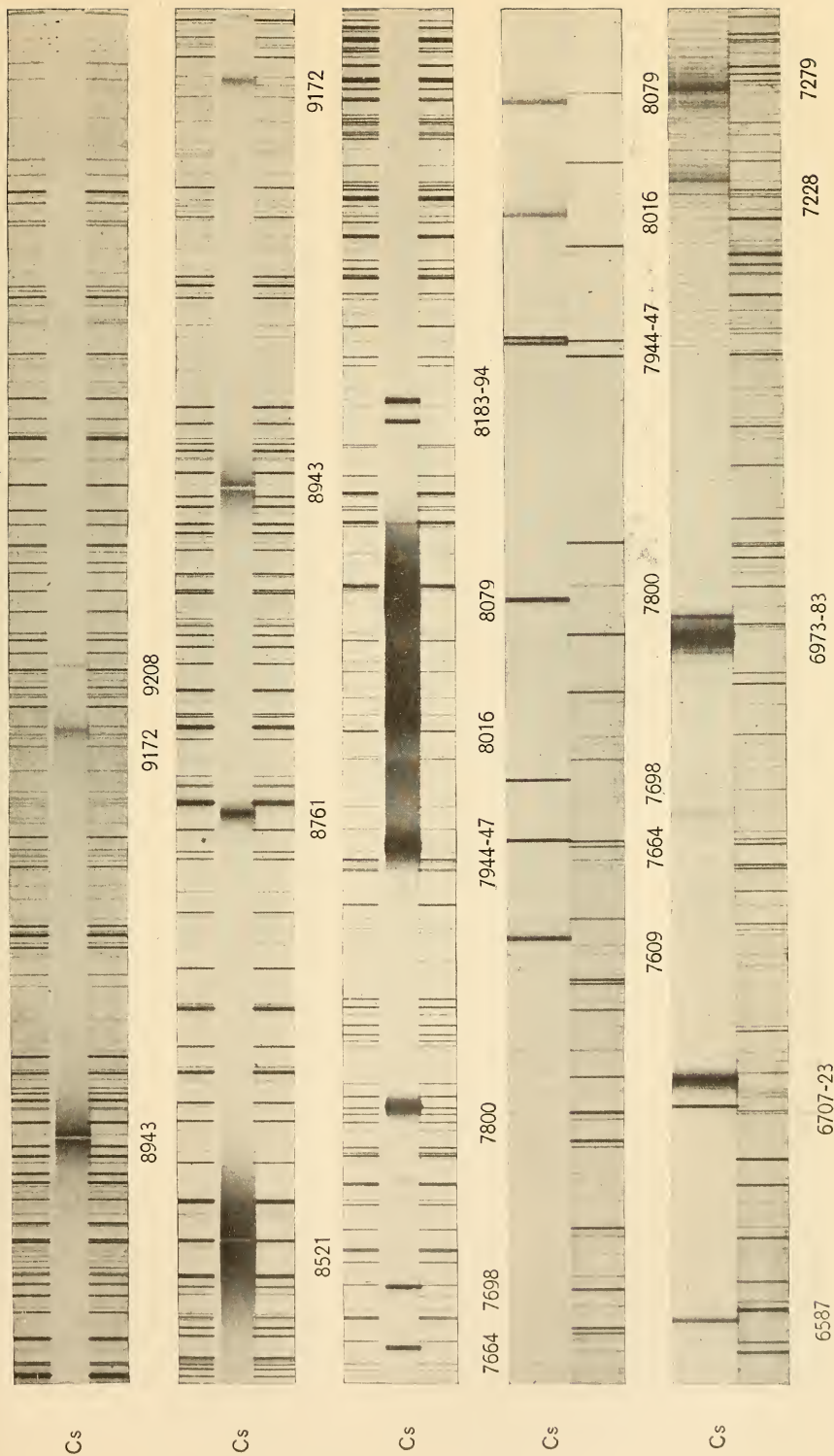


FIG. 3

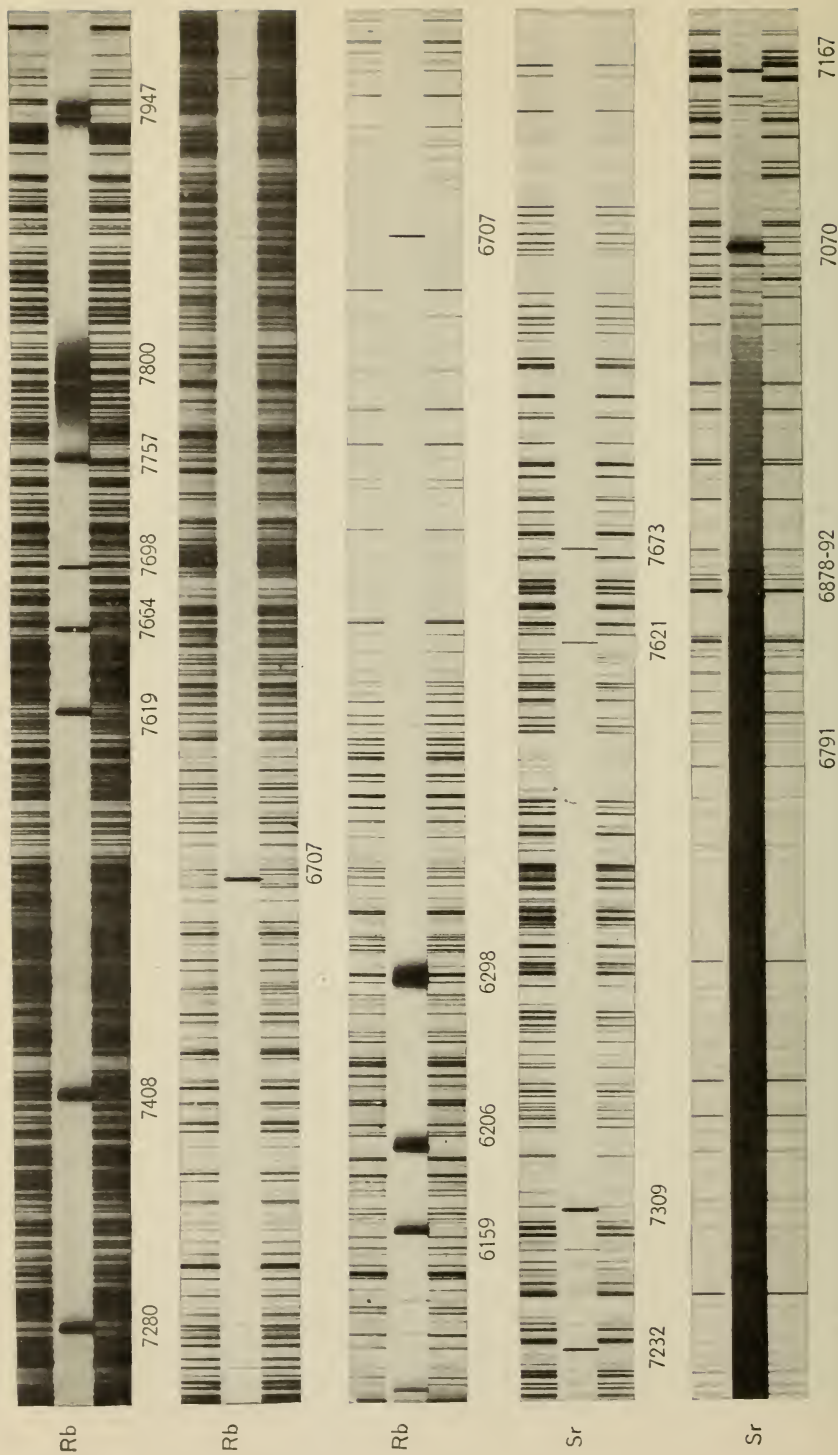


FIG. 4

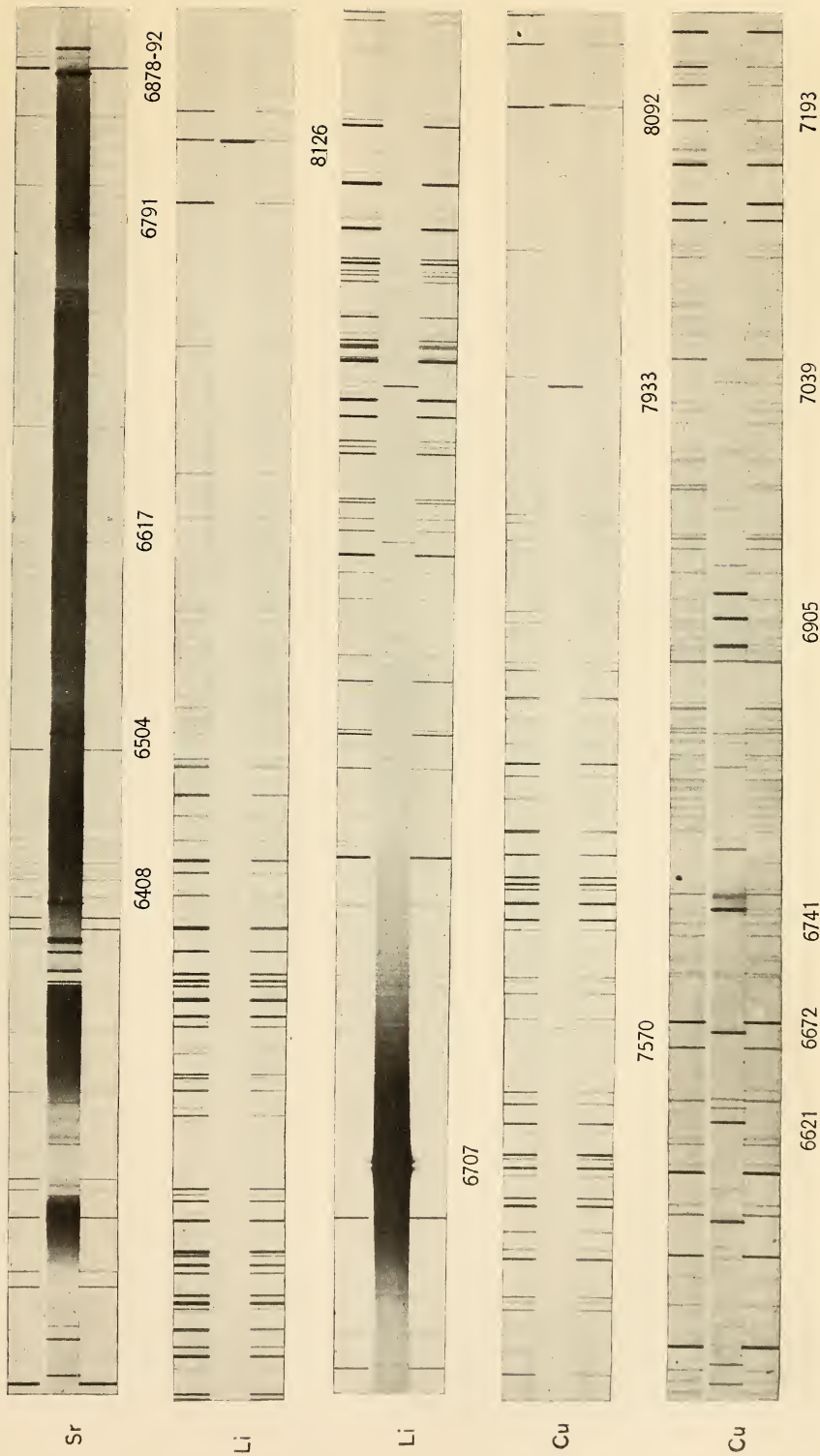


Fig. 5

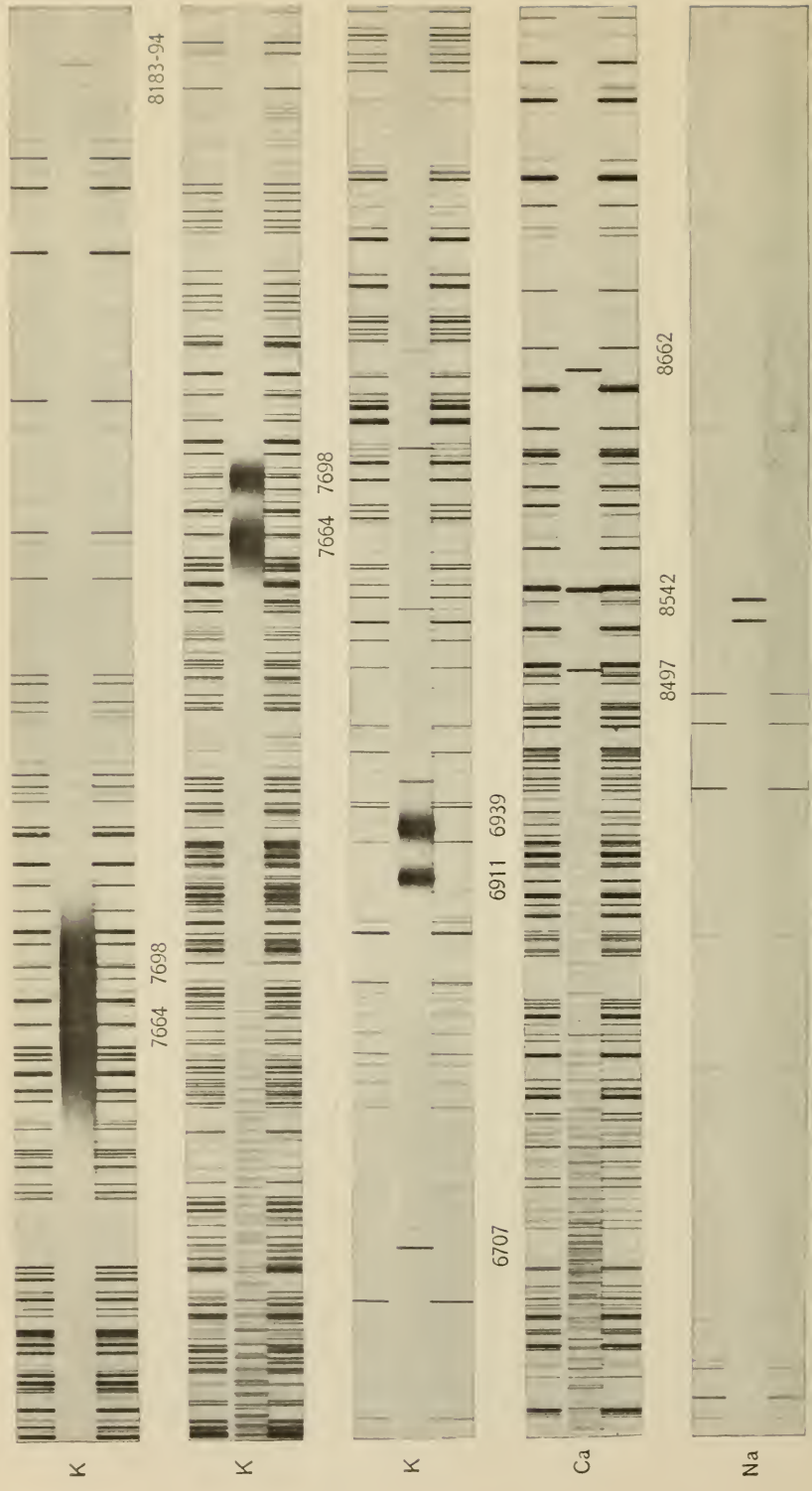


FIG. 6

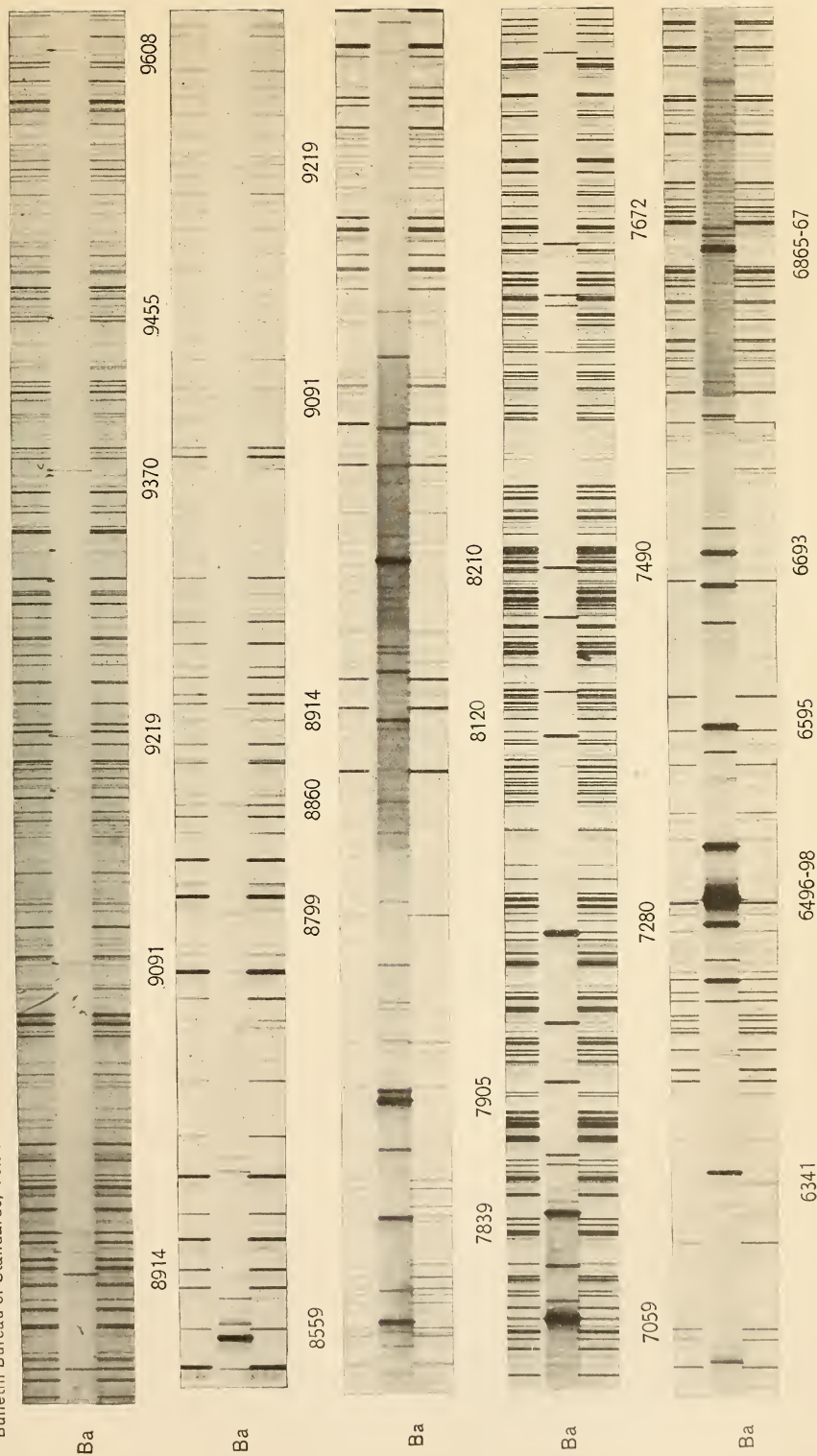


FIG. 7

TABLE 11.—Wave-Length Measurements of Impurity Lines in Spectra

	Li	Na	K	Rb	Cs	Cu	Ca	Sr	Ba	Mg
Li.....										
6707.85 10R		0.85 2A	0.81 4A	0.80 8E	0.84 8A		0.82 4A	0.83 E	0.84 2A	0.75 1A
5889.97 10R	0.96 3E		.96 10E	.98 10E	.97 10C		90.00 8E	90.01 4E	.97 2C	.97 3C
95.94 8R	.92 2E		.93 8E	.98 8E	.96 8C	0.96 2C	.97 6E	.94 3E	.94 2C	.95 2C
8183.30 8R			.49 4D	.26	.40 1A	.95 1C	.32 1E		.2 1E	.34 1E
				.56						
94.82 10R	.88 1E		95.06 5D	.94.95	.98 1B		.91 1E		.9 2E	.90 1E
				.95.14						
7664.94 10R	.91 3A	.92 5B		.93 10A	.94 8A		.92 1C		.92 2A	.9 1D
99.01 10R	98.95 3A	.98 4B		.98 8A	.99 6A		.99 1C		.99 2A	.9 1D
7800.29 10R			.32 2B		.34 10A					
7947.64 8R			.64 1B		.67 4A					
8521.12 10R				.09 3E						
6102.78 6		.70 1E	.76 1E	.76 2E				.77 1E	.76 1E	
22.30 8	.26 2E	.22 2E	.26 3E	.26 3E	.23 2C			.28 3E	.26 1C	
62.20 10	.20 2E	.14 2E	.18 3E	.21 4E	.16 3D			.23 4E	.20 2A	
6439.13 10	.07 2E	.08 2E	.10 2E	.11 3E	.13 1E			.10 1C	.07 2C	
62.62 10	.58 2E	.56 1E	.55 1E	.59 3E	.57 1E					
93.87 7	.78 1E	.78 1E	.80 1E	.82 1E				.84 1E	.57 2C	
7148.15 10	.16 2E	.16 3A	.17 1C	.14 1A	.10 1E			.23 1E	.16 2B	
7202.21 8	.16 1E	.16 2C	.23 1E	.15 1E				.22 1E		
7326.12 8		.12 2E								
8497.98 8	.90 1E								.95 1C	
8542.06 10	.09 2E		.07 1E	.01 1E	.08 1E				.07 4B	.03 1E
8662.10 9	.15 1E		.08 1E	.07 1E	.13 1E				.12 2A	.11 1E
6408.49 9									.44 1E	
6878.36 10							.40 2E		.39 2E	
7070.16 10		.12 2E					.17 1E		.16 2C	
6141.75 10	.75 1E	.68 1E	.70 1E	.73 2E	.71 1E			.77 2E		
6496.93 10			.99 1E	.92 1E				.92 1C		
7059.94 10	.94 1E	.94 1B	.94 1E	.92 1A						
7280.29 10		.30 1E								

Many of Abney's wave lengths are in error by several tenths of an angstrom, and further identification of these Fraunhofer lines with elements in the sun is difficult and uncertain. The solar spectrum from 6800 Å to nearly 10 000 Å has been photographed recently on dicyanin-stained plates, and it is hoped that the wave-length measurements will make more identifications possible.

VIII. SUMMARY.

Accurate measurements of wave lengths and determinations of the characteristics of the emission lines in the spectra of the elements are of importance in spectroscopic analysis and for the discussion of regularities in spectra. Securing such data about the long waves has been delayed chiefly by the insensitiveness of ordinary photographic plates to the red and adjacent infra-red spectral regions. More extensive use of photographic dyes is important for these spectral investigations.

Dicyanin is especially valuable and efficient as a photographic sensitizer for the long waves. The simple procedure of staining ordinary photographic plates in a mixture of dicyanin, water, alcohol, and ammonia renders the plates quite sensitive to wave lengths from 6000 Å to 9000 Å. Such plates were used to photograph the arc spectra of 20 of the chemical elements, including the alkali metals, the alkaline earths, and elements commonly found in iron as impurities.

The photographs were made in the first-order spectrum of a concave grating of 640 cm radius, the grating being mounted in parallel light. Exposures were usually limited to 30 minutes, and these sufficed to record waves longer than 9000 Å in many of the spectra. The second-order spectrum of the iron arc was photographed on either side of the first order and the long wave lengths were obtained from the standards in the iron spectrum. The wave-length measurements are given on the international scale for the arc spectra of the following elements: Lithium, sodium, potassium, rubidium, caesium, copper, calcium, strontium, barium, and magnesium. The wave lengths range from 5600 Å to 9600 Å, and the probable error is less than 0.02 Å for all lines measured more than twice. The broad and unsymmetrical character of some of the lines imposes a limit on the accuracy obtainable in the measurements.

Frequency differences of doublets in the spectra of sodium, potassium, rubidium, caesium, and copper are shown by these

wave-length determinations to be constant in most cases to one part in 100 000 in the number of waves per centimeter.

Comparison of the spectra made it possible to detect many impurities in the elements used for light sources. Still more extensive spectral investigations are required in the region of long wave lengths to identify all the lines with certainty.

In conclusion, I wish to express my thanks to Prof. J. S. Ames and to Dr. K. Burns for their interest and encouragement in this work.

WASHINGTON, March 20, 1917.