The Spectrum of Bromine Part I
Line and Band Spectra, Lines of Arc and Spark Types and the Relations between the Lines

By

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(Received Oct. 20, 1919)

The Spectrum of bromine is not yet thoroughly studied. Structures of lines, Zeeman effect, regularities in the line spectrum, etc., are quite unknown. Berndt[1] attempted to investigate the Zeeman effect on the lines of this element, but he got no definite result owing to the faintness of the light emitted by his tube. Multiplicity of the spectrum was already noticed by Goldstein[2] and Nutting[3], but their results were only fragmentary. The writer examined the spectrum of this element more minutely, and the result obtained will be given in the following pages. The present paper will deal chiefly with the line and the band spectra, lines of arc and spark types and certain relations among the lines. As to the structure of the lines and the Zeeman effect of certain lines including complex lines, a discussion will be offered in a separate paper.

One of the chief difficulties met with in this research was the preparation of a sufficiently intense source of light. As bromine vapour when ionized becomes very active, and electrodes are easily attacked, an ordinary Geisler tube could not be used. In the study of the spectrum of iodine[4], tubes having outer tinfoil electrodes were

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1 Ann. Phys. (4) **8**, 625, (1902).

2 Verh. Deutsch. Phys. Ges. **9**, 321, (1907).

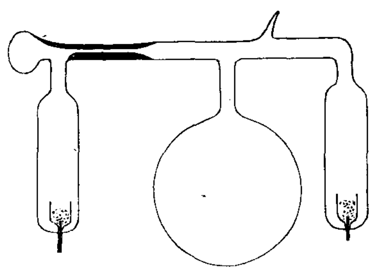
3 Astrophys. J. **19**, 239, (1904).

4 Astrophys. J. **46**, 183, (1917).

constantly used, and similar tubes were tried for bromine. This gave a fairly good result, but the intensity of the light emitted by such a tube was not sufficient for the present purpose. Next, tubes provided with thick platinum electrodes were tried. A carefully dried bromine was sealed in a very fine glass capillary having a very thin wall, and this was put in the discharge tube near one of the electrodes. The air was then thoroughly pumped out, and it was sealed off. A heavy discharge was then sent through the tube, which broke out the sealed capillary containing the bromine and filled up the tube with this vapour. The tube thus prepared was used as a bright source of light, but it was not easy to obtain a tube containing a proper amount of bromine. Besides this difficulty, the glass surrounding the electrodes was soon attacked by the active gas and the tube was soon spoiled.

Lastly, tubes provided with a bromine salt as electrodes were tried. A small quantity of a salt such as sodium bromide, potassium bromide, cadmium bromide, mercury bromide and silver bromide was put in a small glass cup having a platinum wire at bottom, and this was again sealed in an outer tube as shown in Fig. 1. Among the salts examined, silver bromide, owing to its relatively low melting point, gave a proper amount of bromine vapour, when an electric discharge was sent through. On the other hand, sodium bromide and potassium bromide gave a relatively small quantity of the vapour. Now, when tubes provided with such salt electrodes were sealed off from the pump, the vapour pressure of bromine was gradually increased as the discharge was going on, and the light emitted from the tube suffered a corresponding change. To reduce this change a one litre flask was connected to the main tube in order to increase the whole volume of the tube and this proved to be satisfactory. The form of the tube finally adopted is of the form shown in Fig. 1, in which the capillary part had a diameter about 0·2–0·3 mm. and 2 cm. in length. As salt electrodes, silver bromide was generally used, but in some cases sodium bromide and potassium bromide were employed. These tubes were excited by a 20 cm. induction coil, and an exceedingly bright light was obtained in an end-on direction.

Fig. 1.



The colour of this light varied with the vapour pressure and the current density. With a very low pressure, a bluish green light was emitted from the capillary part, while the wide part of the tube was filled up with a glow of a chamois yellow colour. When the vapour pressure was made to increase, the latter changed to a pink glow, and at the same time, a deep pink light took the place of the bluish green light in the capillary. The light emitted from the capillary portion consisted chiefly of the line spectrum of bromine, and the glow of chamois yellow in the wide tube gave up a mixture of lines and bands.

Line and Band Spectra

As shown above the light emitted from the capillary portion of the tube suffered a change in colour from a bluish green to a deep pink, when the vapour pressure was made to increase. This change was studied with a spectrograph having a good replica grating; the dispersion on a photographic plate being 0·033 mm. at λ 4900 A. in the first order spectrum. The photographic plates used were the Wratten panchromatic and exposures of about twenty minutes were given to obtain good negatives. If a change in the colour of the discharge was noticed at the end of the exposure, the plate used was rejected. Photographs thus obtained are reproduced in Fig. 2 and Fig. 3, PL. I. It will be observed that the spectrum of the pink discharge consists of a much greater number of lines than that of the bluish green, and further that the former contains almost all the lines of the latter.

The intense lines belonging to the blue spectrum lie under λ 480 $\mu\mu$, while in the pink spectrum a number of strong lines are distributed over the entire visible spectrum. A closer examination shows, however, that a few lines in the blue spectrum reduce their intensities as the spectrum changes to pink. The intense lines belonging to these spectra are given in Table I, where the wave lengths were taken from Kayser's Spectroscopy. It will be seen that four strong lines in a red region, i.e., $\lambda\lambda$ 6632, 6560, 6351, 6150, and two bright lines in blue $\lambda\lambda$ 4478, 4473 are characteristic lines of the pink spectrum. There are, however, a number of intense lines common to the both spectra, i.e., $\lambda\lambda$ 4930, 4928, 4817, 4785, 4767, 4743, 4720, 4705, 4679, 4623 and 4365, etc. Lines at λ 4508 and λ 4261, though not strong in the blue spectrum, disappeared entirely from the pink one.

Table I

Wave lengths	Relative Intensities in Blue Spectrum	Relative Intensities in Pink Spectrum (cap)	S ...... spark line A ...... arc line	* ...... Weakened by Spark	C ...... Complex line
6632·02	0	3	A	*	C
6582·52	0	1			
6560·17	0	5	A	*	C
6545·00	0	1			
6351·02	0	10	A	*	C
6149·95	0	10	A	*	C
5940·83	0	1		*	
5852·40	0	1		*	
5831·04	1	2			
5719·17	0	1			
5711·25	0	1			
5600·90	0	0			
5590·15	1	1			
5506·97	f	2			
5495·24	f	2			
5489·00	f	2			
5466·43	0	2	A	*	C
5450·28	0	2			
5442·55	0	1			
5435·30	0	1			
5425·21	0	1			
5423·01	0	2			
5395·69	0	3	A	*	C
5345·53	0	2	A	*	C
5335·30	0	1			
5332·49	2	8	S		
5304·31	1	6	S		
5272·89	0	1			
5263·68	0	1			
5238·47	2	8	S		
5227·91	0	1			
5194·07	0	2			
5182·57	3	8	S		
5164·56	1	5	S		
5143·63	0	0			
5054·85	1	3			
5038·96	0	1			
4979·95	1	5	A	*	C
4959·51	1	3			
4945·77	1	3			
4942·21	1	0			
4930·82	10	10	S		
4928·97	10	10	S		
4921·39	2	5			
4867·94 } 4866·85 }	2	4	S		
4848·99	5	5			
4845·20	1	3	S		
4816·90	10	10			C
4807·80	3	5			C
4785·64	10	10			C
4780·52	0	6		*	
4777·30	4	5	S		
4774·01	1	3			
4767·28	7	7	S		
4752·47	0	6		*	
4742·87	7	7	S		
4735·67	4	5	S		
4728·49	3	5	S		
4720·56	8	8	S		
4705·00	10	10			C
4693·48	4	5			C
4678·89	10	10	S		
4673·56	3	5			C
4652·18	3	4	S		
4644·17	3	5	S		
4629·66	3	3			
4622·99	8	8	S		
4614·86	0	5		*	
4605·90	2	4	S		
4575·95	2	6		*	
4543·12 } 4542·67 }	4	5	S		
4538·95	2	4			
4530·00	1	5		*	
4525·82	0	9	A	*	
4513·99	3	5		*	
4508·29	3	0	S		
4490·68	0	4		*	
4477·96	0	10	A	*	
4472·83	0	10	A	*	
4441·93	0	8	A	*	
4425·32	0	5	A	*	
4407·80	0	0			
4399·87	0	1		*	
4365·76	8	10	S		
4291·54	2	6	S		
4261·44	3	0	S		
4237·00	1	4	S		
4224·00	7	10	S		
4193·62	1	5	S		
4179·76	2	6	S		
4140·37	1	4	S		
4135·79	1	4	S		
4117·58			S		

Next, the colour of the glow in the wider portion of the tube varied also with the vapour pressure of bromine. With a small pressure the glow showed a chamois yellow colour, but it soon changed to a pink when the vapour pressure was made to increase above a certain point. The spectrum of this pink glow differs somewhat from that of the pink light in the capillary. To compare these, the lights coming from both portions of the tube were photographed with a small prism spectroscope, and spectrograms thus obtained were shown in Fig. 4, PL. I.

We see that there is a selective reduction of intensity in certain lines of the spectrum of the glow in the wide tube. Among these, the reduction of the intensity is especially strong in the following lines :

$\lambda\lambda$ 5332, 5304, 5238, 5183, 4931, 4929, 4868, 4867, 4743, 4623, 4543, 4542, 4292, 4237, 4140, 4136.

Thus the spectrum of the light emitted by the glow in the wide part of the discharge tube is much simpler than that of the light from the capillary. This seems to suggest that new centers of light emission were produced by the discharge as it passed from a wider part to the capillary, where both the electric field and the current density were stronger. We have thus three types of the line spectrum of bromine, one blue and two pink.

Beside these, we have a band spectrum emitted from the glow in a wide part of the tube. If the vapour pressure was sufficiently low, the colour of this glow was chamois yellow, the spectrum of which consisted of lines and bands. This band spectrum began nearly at λ 500 $\mu\mu$, and extended farther up to λ 660 $\mu\mu$ or more, and it showed a fluted appearance like that of the iodine band in a similar region. The heads of each band turned toward the violet side and more than twenty five of them could easily be seen on a photographic plate. This channelled band spectrum was always obtained whenever silver bromide or sodium bromide was used as electrodes, so that we should attribute the origin to bromine. A low vapour pressure and a small current density were necessary conditions for production of this band spectrum, and it disappeared almost entirely when the pressure exceeded a certain point.

The tube used for the study of this band spectrum had instead of a capillary, an ordinary tubing of a diameter of about 3 mm. and a length of 15 cm. and this was connected to a pump during exposure to a spectrograph to remove the excess of the bromine vapour produced by the discharge. The channelled spectrum emitted by such a tube was photographed with a three-prism spectrograph provided with a photographic objective of one meter focus, the time of the exposure being about five hours. The linear dispersion was not sufficient to separate the lines composing the band spectrum, and it was difficult to determine the wave lengths of heads as they were not so sharp to be measured.

The relation of this band spectrum to the absorption spectrum of bromine vapour was also studied with the same instrument. The light from the crater of a carbon arc was projected through a bulb containing bromine vapour on the upper half of the slit of the above spectrograph and the absorption spectrum was thus photographed. Then the lower half of the slit was illuminated from the light coming from the above tube and the emission band was thus recorded on the same plate. In this case, the difficulty was experienced of keeping the tube from cracking to the end of the exposure, more than a dozen plates being spoiled as the tube got cracks. The photograph reproduced in Fig. 5, PL. I is not a good one, but it will be sufficient to show the general features of both spectra. Here *a* and *b* were taken on one plate, and *c* on another.

Now, according to Eder and Valenta[1], lines in the emission band coincide closely enough with those of the absorption band determined by Hasselberg, but not exactly. The results obtained by the writer are not, however, in harmony with those obtained by them. As the writer is not able to consult their original papers, it is not certain that we are dealing with the same band but the plate shows that the emission and absorption spectra do not correspond even in general appearance. In the present experiment, as the dispersion was insufficient, the coincidence of line to line could not be examined, a further study on this point is necessary, and conclusion is reserved.

Lines of Arc and Spark Types

As described above we have, according to the conditions of the discharge, one blue and two pink spectra of bromine. The pink spectrum emitted by the glow in the wide part of the tube required less energy to be excited, because the current density and the poten-

1 Kayser. Spectroscopy V. p. 188.

tial gradient would both have smaller values in comparison with those in the constricted portion of the tube.

This will lead us to classify the stronger lines in this pink spectrum as lines of the arc type. Comparing this with the blue spectrum we see that certain stronger lines in the former have disappeared entirely from the latter, and at the same time a number of faint lines in the pink spectrum are enhanced in the blue. This difference in the spectrum will be due to the electric conditions in the corresponding glows, and it is evident that much energy will be required to excite the latter type of line. The insertion of a spark gap in the discharge circuit caused the pink glow in the capillary to change into the blue one. It is then natural to regard the lines enhanced in passing from the pink to the blue spectrum as lines of the spark type. The pink spectrum emitted from the capillary contains both kinds of lines, and shows an intermediate stage of the transition from one to the other.

The above Table I gives some of the strong lines of the arc and spark types.

Certain Relations in the Lines of the Bromine Spectrum

Lines belonging to the arc type have very interesting properties. If the wave lengths of these lines are plotted on a coordinate paper, it will be observed that they are divided into a system of groups. If the wave numbers are used instead of the wave lengths, the relation becomes more evident. They arrange themselves in a nearly equal interval with a roughly equal width.

Counting from the red, three lines at $\lambda\lambda$ 6560, 6351 and 6150 form the first group having the width of 1017, in the scale of $1/\lambda$, the second group seems to be missing, the third one comes between λ 5423 and λ 5144, the fourth between λ 4980 and λ 4752, the fifth within λ 4615 and λ 4408, and the sixth lies between λ 4291 and λ 4118. The widths of the above groups are 1017, 1002, 961, 1018 and 984 in the scale of $1/\lambda$, and the distances between the first lines of each group are 2×1598, 1641, 1589, 1633 and 1619 respectively in the same scale. Here the first line of a group denotes the line lying at the red end of the group.

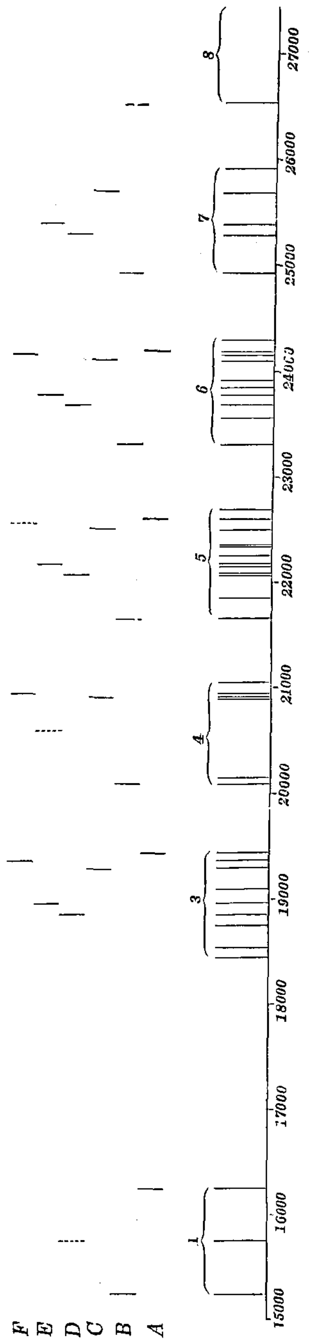


FIG. 6

As the lines recorded in our plates ended nearly at λ 4100, we could not proceed farther, but the two lines at λ 4103 and λ 3857 having an interval of 1004 may be found in the table of the wave lengths given by Eder and Valenta[1]. The first of them is situated at a distance of 1601 from the corresponding one of the sixth group. Further, one line at λ 3770 may be selected at a distance of 2×1610 from the first line of the sixth group, suggesting that this is the corresponding line of the eighth group. The table of the above authors ceases at λ 3685, so that we can not proceed farther.

The grouping of the line is illustrated in Fig. 6, and their wave lengths are given in Table II.

These groups of lines may also be analysed into systems of lines having approximately constant frequency differences, and they are given in Table III.

Lastly, it is desirable to note that the following pairs of lines having constant frequency differences may be picked out from the table.

1 Kayser's Spectroscopy V.

TABLE II

Group No.	λ	$\frac{1}{\lambda}$	Group widths.	Group distances.
1.	6560·17	15243·5	1016·8	3196·4 =2×1598·2
	6351·02	15745·5		
	6149·95	16260·3		
3.	5423·01	18439·9	1001·6	1640·6
	5395·69	18533·3		
	5332·49	18751·1		
	5304·31	18852·6		
	5272·89	18964·9		
	5238·47	19089·5		
	5182·57	19295·4		
	5164·56	19362·7		
	5143·63	19441·5		
4.	4979 95	20080·5	961·2	1588·6
	4959·51	20163·2		
	4785·64	20895·8		
	4780·52	20918·2		
	4774·01	20946·7		
	4752·47	21041·7		
5.	4614·86	21669·1	1018·0	1632·6
	4575·95	21853·4		
	4530·00	22075·1		
	4525·82	22095·4		
	4513·99	22153·4		
	4508·29	22181·4		
	4490 68	22268·3		
	4477·96	22331·6		
	4472·83	22357·2		
	4441·93	22512·7		
	4425·32	22597·2		
	4407·80	22687·1		
6.	4291 54	23301·7	984·4	1619·2
	4237·00	23601·6		
	4224·00	23674·2		
	4206·23	23774·3		
	4193·62	23845·7		
	4179·76	23924·8		
	4151·52	24087·6		
	4140·37	24152·4		
	4135·79	24179·2		
	4117·58	24286·1		
7.	4012·70	24920·9	1003·6	1601·4
	3955·50	25281·2		
	3939·86	25381·6		
	3891·79	25695·1		
	3857·36	25924·5		
8.	3770·41	26522·3		

TABLE III

SERIES A

Line Number	λ	$\frac{1}{\lambda}$	Differences.
1.	6149·95	16260·3	1594·0
2.	5600·90	17854·3	1587·2
3.	5143·63	19441·5	3155·7 =2×1577·9
4.	——	——	
5.	4425·32	22597·2	1582·0
6.	4135·79	24179·2	

SERIES B

Line Number	λ	$\frac{1}{\lambda}$	Differences.
1.	6560·17	15243·5	4837·0 =(3×1612·3)
2.	——	——	
3.	——	——	
4.	49799·5	20080·5	1630·8
5.	46059·0	21711·3	1590·4
6.	42915·4	23301·7	1619·2
7.	40127·0	24920·9	1601·4
8.	37704·1	26522·3	

SERIES C

Line Number	λ	$\frac{1}{\lambda}$	Differences.
1.	——	——	
2.	——	——	
3.	5182·57	19295·4	1622·8
4.	4780·52	20918·2	1594·5
5	4441·93	22512·7	1574·9
6.	4151·52	24087·6	1607·5
7.	3891·79	25695·1	

SERIES D

Line Number	λ	$\frac{1}{\lambda}$	Differences.
1.	—	—	
2.	—	—	
3.	5304·31	18852·6	
4.	—	—	3222·5 =(2×1611·2)
5.	4530·00	22075·1	
6.	4224·00	23674·2	1599·1
7.	3955·50	25281·2	1607·0

SERIES E

Line Number	λ	$\frac{1}{\lambda}$	Differences.
1.	—	—	
2.	—	—	
3.	5274·89	18964·9	
4.	4860·19	20575·3	1610·4
5.	4508·29	22181·4	1606·1
6.	4206·23	23774·3	1592·9
7.	3939·86	25381·6	1607·3

SERIES F

Line Number	λ	$\frac{1}{\lambda}$	Differences.
1.	—	—	
2.	—	—	
3.	5164·56	19362·7	
4.	4774·01	20946·7	1584·0
5.	4431·13	22567·6	1620·9
6.	4140·37	24152·4	1584·8

TABLE IV

Pairs having Constant Frequency Differences		
λ	$\frac{1}{\lambda}$	Differences
4151·52 3891·79	24087·6 25695·1	1607·5
4224·00 3955·50	23674·2 25281·2	1607·0
4860·19 4508·29	20575·3 22181·4	1606·1
4206·23 3939·86	23774·3 25381·6	1607·3
4224·00 3955·50	23674·2 25281·2	1607·0
6149·95 5600·90	16260·3 17854·3	1594·0
4780·52 4441·93	20918·2 22512·7	1594·5
4508·29 4206 23	22181·4 23774·3	1592·9
5600·90 5143·63	17854·3 19441·5	1587·2
5164·56 4774·01	19362·7 20946·7	1584·0
4431·13 4140·37	22567·6 24152·4	1584·8

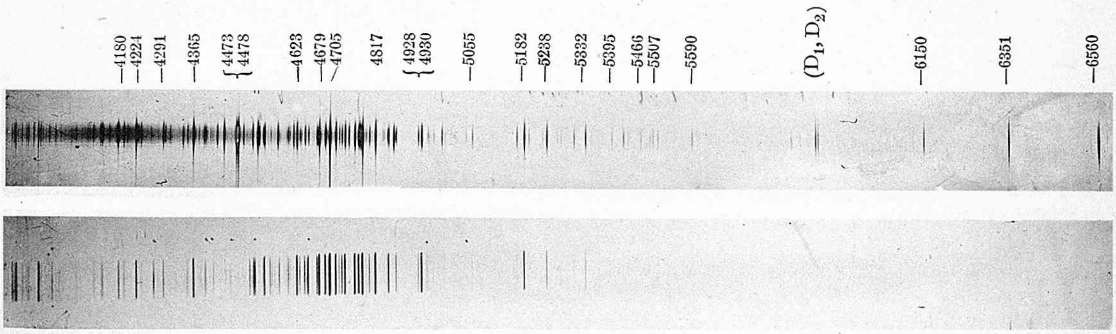
Summary

1. Sources of light giving bright line spectrum of bromine were described.
2. Bromine emits the light in blue and pink glows, and the corresponding spectra were studied.
3. The relation of the emission band to the absorption spectrum was discussed.
4. Lines in the spectrum of bromine were classified into the arc and the spark types.
5. Among the arc lines, certain relations were found.
6. Pairs of lines having constant frequency differences were found.

In conclusion, the writer wishes to express his thanks to Prof. T. Mizuno for the interest he has taken in this work.

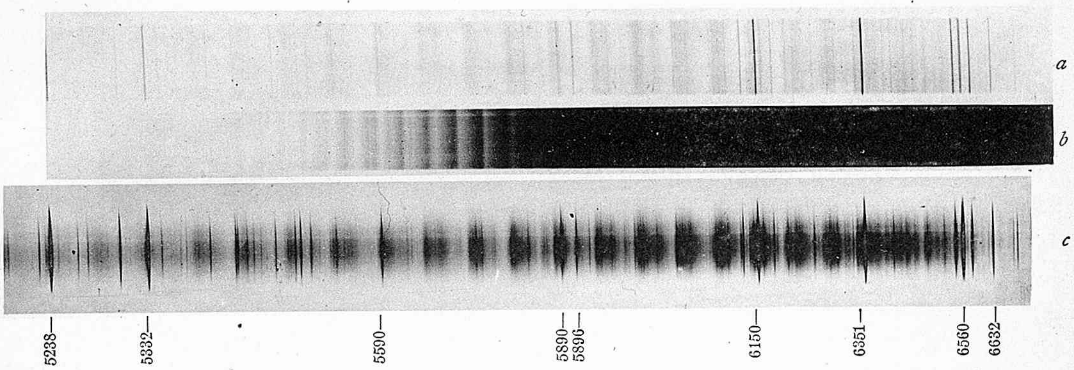
Plate I.

Fig. 2 (Pink discharge)



Magnification: 1.7 Fig. 3 (Blue discharge)

Fig. 5 (Bromine Band Spectrum)



Magnification: 2.

(Na)

a
c > Emission
b Absorption

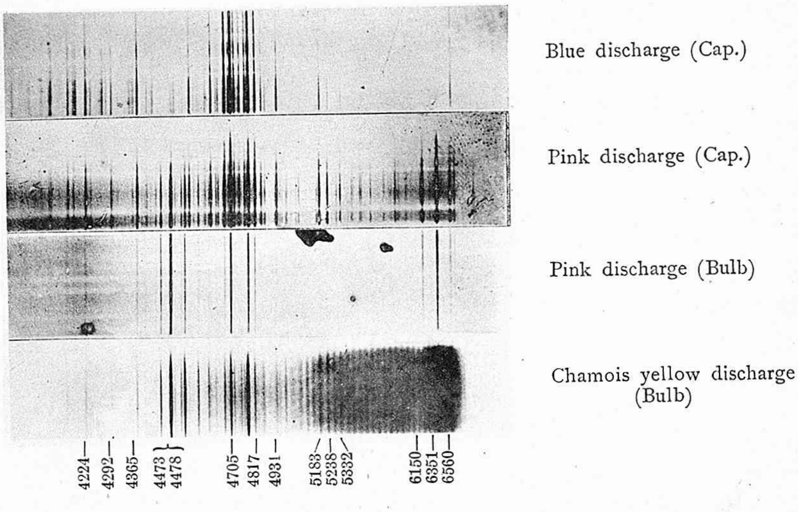


Fig. 4 Magnification: 3.5