THE EFFECTS OF CHANGES IN POTENTIAL AND FREQUENCY ON THE LINE SPECTRUM OF CERTAIN GASES

By James A. Swindler

Abstract

Using a Hilger quartz spectrograph, size C, spectrograms were made from electrodeless tubes containing helium, hydrogen, nitrogen, neon, xenon, krypton, mercury and chlorine. High frequency peak voltages were computed from the equation $E=KI\sqrt{d\lambda/C}$, where K is a constant depending upon the velocity of light and the cycles per second of the generator. An electroscope was constructed and calibrated for measuring the potential over the secondary of a 25000 volt transformer. Increasing the potential over the tube for either the 60 cycle or high frequency currents seemed merely to intensify the lines. Changes in frequency from 0.58×10^6 to 1.91×10^6 produced no changes in spectra. When the potential was kept approximately constant, marked differences were obtained, however, between the 60 cycle spectra and the high frequency spectra (1) of a chlorine tube containing nitrogen as an impurity, (2) of a helium tube containing nitrogen as an impurity and (3) of a helium tube containing mercury as an impurity.

SEVERAL experimenters[1,2] have called attention to differences that have occurred in line spectra as a result of the manner in which the luminosity of the gas has been excited. When such excitation is produced by high frequency currents it is claimed that the nature of the spectrum depends upon the capacity, the inductance and the potential of the oscillating circuit. It is also claimed that such a spectrum is modified greatly by changes in the pressure and temperature[3] of the gas. Since changes in inductance or capacity are, in most cases associated with changes in frequency, it would be interesting to know what part, if any, frequency plays in the production of spectra.

In order to make a study of the latter problem, E. O. Hulburt[4] compared the spectra obtained from an oscillating tube circuit capable of variations in frequency ranging from 3×10^6 to 0.43×10^7 cycles per second with that obtained from a 25000 volt transformer actuated by a

[1] Merton, Proc. Roy. Soc. **A89,** 447 (1912); Twyman, Wave-length Tables, Adam Hilger, Ltd., London; McVicker, Marsh and Stewart, J. Chem. Soc. (England) **124,** 642 (1923).

[2] Foley, Proc. Ind. Acad. Sci. **34,** 185 (1924).

[3] Robertson, Phys. Rev. **19,** 470 (1922); Wachsmith and Winawer, Ann. d. Physik **42,** 585 (1913); Dunoyer, Comptes Rendus **173,** 350 (1921); J. de Physique et le Radium **3,** 261 (1922).

[4] Hulburt, Phys. Rev. **20,** 127 (1922).

60 cycle alternating current and failed to find any differences in spectra resulting from the employment of different exciting frequencies. Since it is known, however, that high frequency spectra[5] do differ from those obtained by other methods of excitation, a further study of the problem seemed worth while. It is the object of this investigation, therefore, to determine, if possible, what effect changes in frequency or changes in potential have upon the spectrum of a gas at low pressure.

In the present investigation the spectrum of helium, hydrogen, nitrogen, neon, xenon, krypton, mercury and chlorine were studied. Most of the tubes were of the electrodeless dumbbell type, 12 cm in length with cylindrical bulbs 2 cm in diameter and 4 cm in length having inner diameters of approximately one-half millimeter. These tubes were pumped, filled and sealed by the late Sir William Ramsey, being a portion of the six dozen used by Dr. A. L. Foley[2] in his investigation on the stability of matter. There were equal numbers of glass and of quartz tubes in the allotment. In addition to these, eight tubes were purchased from the Hilton-Davis Company of Cincinnati, Ohio. These tubes were all electrode tubes, but were used as electrodeless tubes in all cases, by coating the outside terminals heavily with paraffine and then wrapping tin foil around each bulb.

A Hilger quartz spectrograph, size C, was used, giving a photograph 20 cm in length between λ2100 and λ8000. Near λ6000 this instrument is capable of resolving lines differing in wave-length by approximately 2A, while in the neighborhood of λ3000 the resolution is increased to differences of 0.12A. A cylindrical quartz lens was used in focusing light from the capillary of the tube upon the slit.

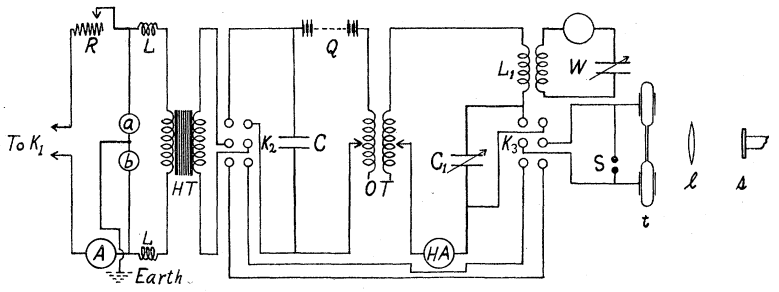


Fig. 1. Diagram of electrical connections.

Fig. 1 is a diagram of the oscillating circuit used in this investigation. The primary of a one kilowatt, 25000 volt transformer *HT* was subjected to a 60 cycle alternating current led in through K_1. The current through

[5] McVicker, Marsh and Stewart, loc. cit.

the ammeter A was controlled by the adjustable resistance R. The choke coils LL, grounded through the lamps a and b, were used to damp out any high frequency waves which might be carried over from the oscillating circuit. C was a two gallon Leyden jar having a capacity of 0.00124 microfarads. The oscillating transformer OT was a pancake coil consisting of about five turns on the primary and ten turns on the secondary. In series with each of these coils, tuning coils of heavy copper wire were inserted. The capacity C in some cases was a small Leyden jar of 0.000533 microfarad capacity, in other cases an adjustable oil condenser of similar average capacity. The current through the hot wire ammeter HA varied from 200 to 2000 milli-amperes depending upon conditions of the tube and circuit. The coil L_1 set up at approximately five feet from the oscillating circuit, consisted of two turns of wire. The diameter of these turns was about 10 cm. The wave meter W, which was found not to be in error by more than three percent of the correct wave-length, was used in measuring the frequencies of the oscillating circuits.

The order of procedure was as follows: After the circuit had been approximately adjusted to the wave-length desired, the coupling having been arranged to give the desired intensity, the ammeters A and HA were read and the wave-length and the decrement of the oscillation transformer secondary circuit recorded. The scale was first photographed, then the copper reference spectrum and then the tube spectrum. While making an exposure of the tube the slit was lengthened three times. This made possible the comparison of the intensities of lines having the same or different lengths of exposure. The total exposure varied from fifteen minutes in case of some of the tubes to as much as two hours in the case of others. The above procedure was repeated for one or two other frequencies. Then by use of switches K_2 and K_3 a sixty cycle frequency direct from the transformer was impressed upon the tube.

Theory of High Voltage Determinations

In the earlier part of this investigation a spark gap S, placed parallel with the tube, gave an estimation of the potential across its terminals; later this potential was computed in the following manner.

Voltage determination at high frequency. At the moment the discharge over the terminals of the condenser begins, letting I_0 be the initial current amplitude, E_0 the initial voltage over the condenser terminals, C the capacity and ω the frequency factor $2\pi n$, we have

$$I_0 = \omega C E_0. \tag{1}$$

Assuming that all the energy of each train of waves is dissipated before the next one begins, letting T be the period of a train of waves, in this

case 1/120 of a second, W_1 the energy dissipated in each train, then, since these two energies must be equal

$$RI^2T=\tfrac{1}{2}LI_0^2, \tag{2}$$

where L is the inductance of the circuit. Since d the decrement of a damped wave may be written $d=Rt/2L$, solving for R/L and substituting in the above equation gives

$$I_0^2=4dTI^2/t \tag{3}$$

Writing t in terms of λ, the wave-length, and combining Eqs. (1) and (3) gives, providing C is kept constant

$$E_0=KI\sqrt{d\lambda}. \tag{4}$$

In Eq. (4) K then becomes $(1/\pi C)\sqrt{T/V}$, where V is the velocity of the electric waves.

The decrement of the wave-meter was determined by the ordinary method[6] of reducing the root-mean-square value of the current to one-

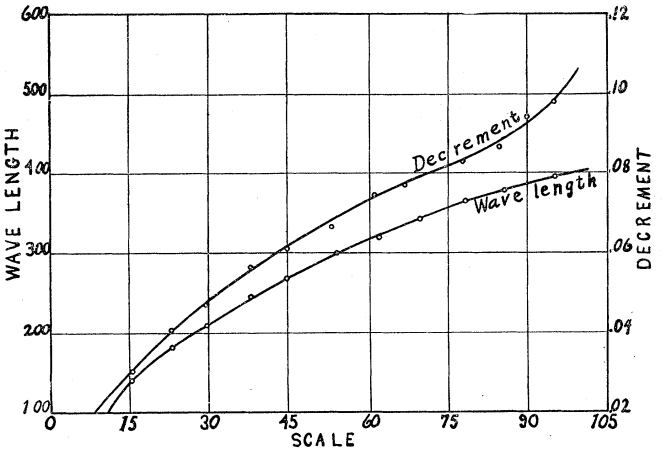


Fig. 2. Calibration curves for wavemeter and decremeter.

half value. In doing this two values of the capacity were found, one on either side of the resonance value. Under conditions of loose coupling the decrement is then given by the equation

$$d_1+d_2=\pi(C_2-C_1)/(C_2+C_1),$$

where d_2 is the decrement of the wave-meter and d_1 the decrement of the sending circuit. If the wave-meter is tuned to a continuous wave sending circuit, d_2 is obtained directly. As the decrement of the wave-meter

[6] Ramsey, Proc. Ind. Acad. Sci. for 1922, pp. 223–226.

was found to vary with the frequency, curves were plotted showing the relation between decrement and wave-length for the coils used. With d_2 known the above equation gave the values of the decrement of the tube circuit.

When the capacity was kept constant and the inductance varied,the potential over the terminals of the condenser remained practically constant, providing the current through the hot wire ammeter was not altered. A number of photographs were taken in which a high frequency spectrum at resonance under moderately close coupling could be com-

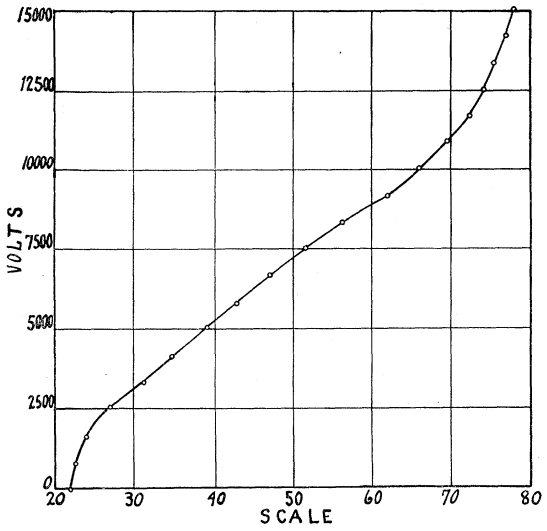


Fig. 3. Calibration curve for electroscope.

pared with one in which the frequency in the primary circuit had been lowered, all other factors in both circuits being left undisturbed. As the wave-meter showed practically no change in wave-length, thus indicating impulse excitation, the author concludes that whatever change took place in the spectrum was the result of a change in potential alone.

Voltage determination at 60 cycles. Assuming that the ratio of the voltages of the primary coil to that of the secondary coil remains constant for all potentials, an electroscope was constructed and calibrated having a range of from 0 to 15,000 volts Fig. 3. Peak voltages were obtained by multiplying by $\sqrt{2}$. Voltages computed in this way are shown in Table I.

RESULTS

Chlorine. The tube used in making Plates 125 and 128 (Figs. 4 and 5) was one marked Chlorine *B*, an electrodeless quartz tube. The pressure

in this tube was exceedingly low. Few if any of the lines shown in these spectrograms are due to chlorine. In photographs of the 60 cycle frequency, a great many nitrogen bands appear between λ2800 and λ4100. All photographs of the 60 cycle show similar results, the only difference being that increasing the potential seems to intensity the spectrum. When frequencies of 1.5×10^6 and 1.1×10^6 cycles per second were impressed upon the tube the appearance of the spectrum was almost completely changed. All the nitrogen bands were more or less suppressed and the so-called cyanogen band at λ3884 came out with maximum intensity, extending almost to λ3700. This would seem to throw some doubt upon the opinion held by some,[7,8] that this band is due to the N_2 molecule. It at least suggests a different carrier from that of the other nitrogen bands. The silicon lines at λ2881.7 and 2479.8 were brought out strongly in the high frequency spectra but did not show at all in the 60 cycle spectra. Since the potential over the tube for the 60 cycle frequency was equal to or greater than that of the high frequency spectra, the author believes that these lines were brought out as a direct result of the more rapid vibrations of the high frequency waves.

Helium. Photographs were made from six different helium tubes and from one hydrogen-helium tube. All of these tubes except one, a quartz tube, were obtained from the Hilton-Davis Company and were new tubes. The pressures in these different glass tubes at the time when they were sealed varied between 1 mm and 6 mm. The tube used in making Plate 129 (Fig. 6) had a pressure of 1 mm. A number of lines due to mercury and other impurities appear (See Table I, Plate 129, Fig. 6). The main differences in spectra seem to be that the mercury lines λ5460, 4358 and 4046 of the sharp series, as well as the diffuse triplet λ3663, 3655 and 3650, are greatly intensified by high frequency waves. The quartz tube used in making Plate 132 (Fig. 7) had a very low pressure. Most of the lines and bands shown in the photograph are due to nitrogen. Voltages and frequencies are given in Table I. In the spectrogram of the 60 cycle frequency many nitrogen bands appear, which become less intense as high frequency excitation is impressed upon the tube. At the same time the cyanogen band 3884 comes out brilliantly and lines due to the walls of the tube appear in the ultra-violet. Plate 116 (Fig. 8) shows these changes in a remarkable way. All tubes filled with pure helium at pressures between 1 mm and 6 mm showed no changes in spectra when the frequency was changed from 60 to 1,000,000 alternations per second.

[7] Runge and Grotrian, Phys. Zeits. **15,** 545 (1914).

[8] Sommerfeld, Atomic Structure and Spectral Lines, p. 429; Campbell, Series Spectra, Camb. Phys. Ser., Chap. XV, p. 105.

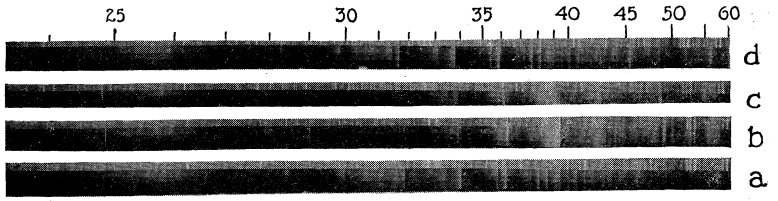


Fig. 4. Plate 125. Chlorine B. Electrodeless quartz tube. Explanation given in Table I.

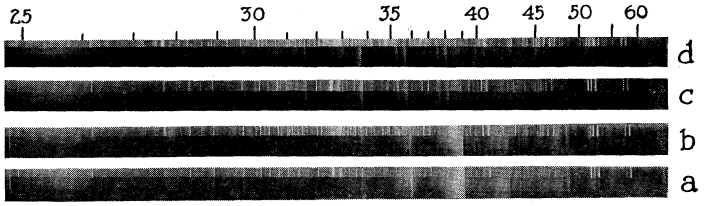


Fig. 5. Plate 128. Chlorine B. Electrodeless quartz tube. Explanation given in Table I.

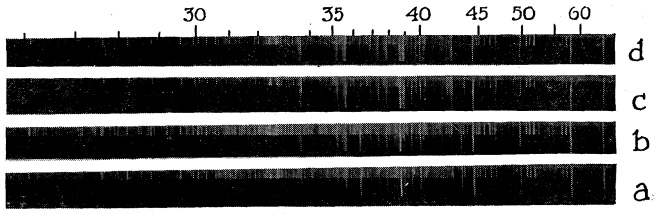


Fig. 6. Plate 129. Helium. Electrodeless glass tube. Explanation given in Table I.

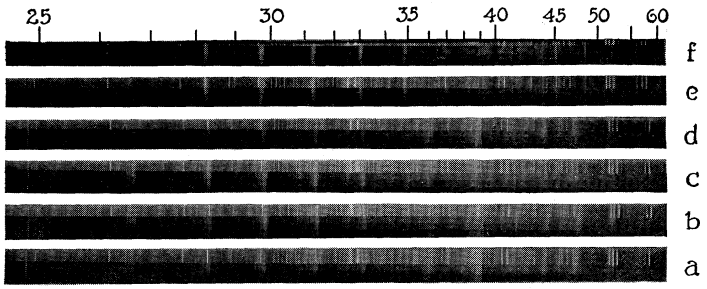


Fig. 7. Plate 132. Helium. Electrodeless quartz tube. Explanation given in Table I.

TABLE I

Conditions under which the spectrograms of Figs. 4, 5, 6, 7 were taken.

Position on scale	Exposure on tube in seconds	Current through secondary of transformer in amperes	Frequency	Capacity in OT primary circuit in microfarads $\times 10^{-6}$	Decrement of wavemeter	Decrement of sending circuit	Scale of electroscope	Potential over tube in volts
			Plate 125 Quartz electrodeless, Chlorine B					
a	30, 20, 10	Small	60	...	.....	.....	....	.....
b	15, 10, 5	0.67	1.11×10^{6}	350	0.266	0.072	....	14180
c	15, 10, 5	0.73	1.50×10^{6}	350	0.181	0.091	....	14950
d	60, 40, 20	Small	60	...	.....	.....	....	.....
			Plate 128 Quartz electrodeless, Chlorine B					
a	15, 10, 5	0.71	0.93×10^{6}	350	0.0594	0.654	....	15630
b	15, 10, 5	0.72	1.48×10^{6}	350	0.0660	0.460	....	10500
c	60, 40, 20	Small	60	...	.....	.....	61.4	12870
d	30, 20, 10	Small	60	...	.....	.....	73.5	17270
			Plate 129 Helium glass, electrodeless					
a	10, 5, 5	0.30	1.45×10^{6}	350	0.0475	0.1465	....	7900
b	10, 5, 5	0.30	1.03×10^{6}	350	0.0667	0.1273	....	8760
c	20, 10, 10	Small	60	...	.....	.....	44.7	8760
d	10, 5, 5	Small	60	...	.....	.....	67.0	14500
			Plate 132 Helium quartz, electrodeless					
a	15, 10, 5	0.78	1.17×10^{6}	570	0.0588	0.0624	....	9160
b	15, 10, 5	1.21	0.91×10^{6}	927	0.0762	0.0524	....	9080
c	15, 10, 5	0.80	0.58×10^{6}	681	0.0842	0.0427	....	9260
d	15, 10, 5	0.77	1.91×10^{6}	500	0.0360	0.0780	....	9270
e	60, 40, 20	Small	60	...	.....	.....	46.1	9190
f	30, 20, 10	Small	60	...	.....	.....	74.0	17600

Neon. A quartz electrodeless tube gave spectrograms showing no changes in spectra for slight changes in frequency, i.e., from 0.4×10^6 to 1.5×10^6 alternations per second. Marked differences were shown, however, when compared to the 60 cycle spectrum. A great many lines appeared in the violet and ultra-violet end of the high frequency spectrum which either did not appear at all in the 60 cycle spectrum, or appeared with reduced intensities. Two new neon tubes, which had not been used previously and which had pressures of approximately 6 mm at the time they were sealed, indicated no changes in spectra when the frequency was changed from 60 to 1,000,000 alternations per second.

Krypton. It was noticed in the case of an electrodeless quartz tube, that, if resonance conditions were established in the oscillating circuits

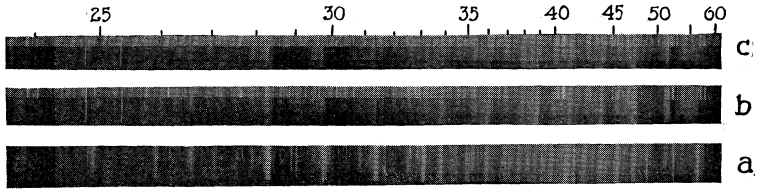


Fig. 8. Plate 116. Helium. Electrodeless quartz tube. (a) Freq. 60; exp. 10-20-30 min.; current less than 1 m.a. (b) Freq., resonance, 1.48×10^6; exp. 10-20-30 min.; current through tube 40 m.a. (c) Freq. in secondary, 1.48×10^6, in primary 0.91×10^6; exp. 10-20-30 min.; current through tube 15 m.a.

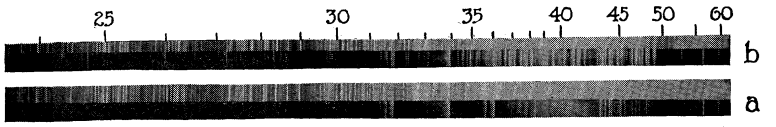


Fig. 9. Plate 109. Krypton. Electrodeless quartz tube. (a) Freq. in secondary, 1.70×10^6, in primary 0.84×10^6; exp. 40-20 min.; current through tube 25 m.a. (b) Freq., 1.70×10^6, resonance; exp. 16-14 min.; current through tube 75 m.a.

and the inductance of the tuning coil in the primary circuit changed gradually the color of the light given out changed from a bright blue to a pale yellow. The differences in spectra are shown in Plate 109 (Fig. 9). A number of plates were exposed each time with the same results. Upon closer inspection it was found, that, when conditions were such as to produce the yellow light, only two main lines appeared in the visible spectrum, the yellow line and the green line. In addition to these there were a few blue and violet lines, which appeared with greater intensity on the photographic plate than to the naked eye. As the inductance in the primary circuit was brought nearer its resonance value, line after line appeared in the violet and ultra-violet, while the yellow line and

green line, mentioned above, became somewhat weaker in intensity. At the same time the point of maximum energy was shifted toward the violet. As the wave-meter indicated that practically no change in frequency had occurred, the difference was attributed to a change in potential. At resonance the potential as indicated by the sparking distance was approximately four times as high.

Hydrogen, mercury and xenon. A few spectrograms were made from hydrogen and xenon tubes, but no changes worth mentioning were found. One mercury plate showed marked differences between the 60 cycle spectra and the high frequency spectra; but, as the tube had to be heated in order to get the discharge through it, little significance was attributed to these changes. It is known[2] that the spectrum of a heated mercury tube is quite different after heating from what it was before heating.

Conclusions

The results obtained from these experiments seem to warrant the following conclusions:

1. That the spectra of the gases, hydrogen, helium, neon, krypton, xenon, nitrogen, mercury and chlorine, in no case show differences in spectra for changes in frequency between 2×10^6 and 0.4×10^6 alternations per second, when the potential is kept approximately constant.

2. That the high frequency spectra and 60 cycle spectra of the gases studied appear to be identical for pressures between 1 mm and 6 mm.

3. That for low pressures high frequency spectra differ widely from the 60 cycle spectra in neon, krypton and in chlorine or helium tubes containing nitrogen.

4. That mercury when existing as an impurity in a helium tube comes out more strongly when stimulated with Tesla frequencies than when stimulated with 60 cycle frequencies of equal potential. Especially is this true of the lines λ5460, 4358 and 4046 of the sharp series and the diffuse triplet λ3662.8, 3654.8 and 3650.1. Slight changes in frequency, however, seem to produce no differences in spectra.

5. That in chlorine tubes containing nitrogen, the nitrogen bands are brought out much more intensely by the 60 cycle currents than by high frequency currents with possibly one exception. The so-called cyanogen band at λ3884 is greatly intensified by high frequency currents. This would seem to throw some doubt on its being due to the N_2 molecule as suggested by Runge and Grotrian.[7]

6. That lines due to the walls of the tube are at the same voltage more easily brought out in high frequency spectra than in 60 cycle spectra. Especially is this true of the silicon lines λ2881.7 and 2479.8. These lines appear in the spectra of both quartz and glass tubes.

7. That the characteristic differences between 60 cycle spectra and high frequency spectra are not due to a change in potential but rather to some sort of a trigger action on the part of the high frequency waves which make possible the release in the atom of a greater variety of quanta.

In conclusion the author wishes to express his thanks to Dr. A. L. Foley of Indiana University, who suggested the problem and under whose direction the work was done. Thanks are likewise due Dr. R. R. Ramsey for many helpful suggestions on the electrical side of the problem, and to John G. Moorhead, with whom the author was associated in the earlier part of this work.

WESTMINSTER COLLEGE,
NEW WILMINGTON, PA.
July 24, 1926.

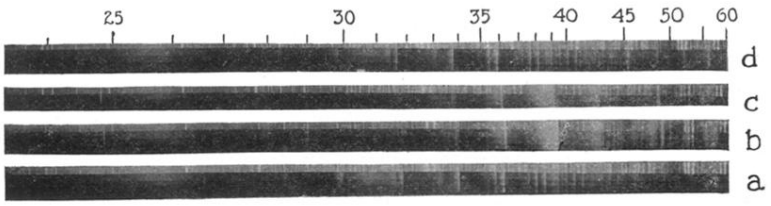
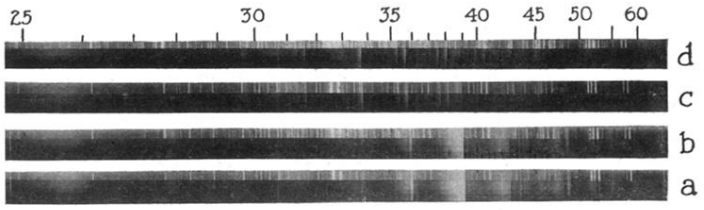


Fig. 4. Plate 125. Chlorine B. Electrodeless quartz tube.
Explanation given in Table I.



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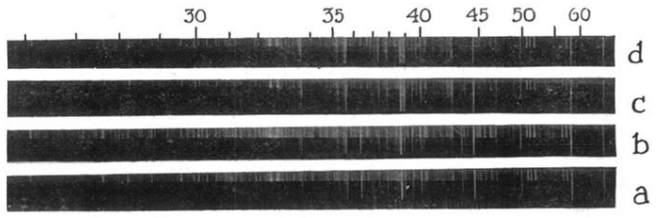
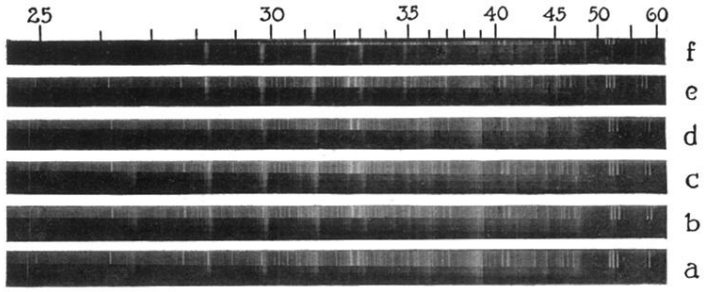


Fig. 6. Plate 129. Helium. Electrodeless glass tube. Explanation given in Table I.



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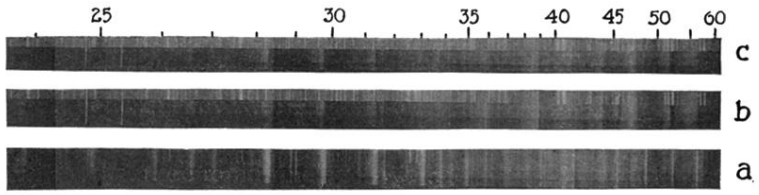

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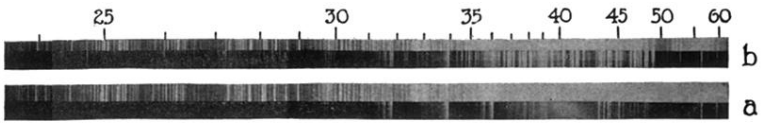

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