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A DETERMINATION OF THE ABSORPTION SPECTRA OF SOME SALMON OILS AND OTHER EXPERIMENTS

by

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ILLUSTRATIONS

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A DETERMINATION OF THE ABSORPTION SPECTRA OF SOME SALMON OILS

INTRODUCTION

In connection with research on the determination of the pigment content of salmon oil being conducted by Mr. Basil E. Bailey of the Fisheries Experimental Station at Prince Rupert, B.C., it was desirable to obtain the absorption spectra of these oils in the visible region, as a check on the biological results. This report outlines the method used in obtaining the absorption spectra of the samples of salmon oil submitted to us for test.

APPARATUS AND METHOD USED

The essential parts of the apparatus used were a Hilger sector photometer and a constant deviation spectrograph for use in the visible region of the spectrum. In Fig. 1 are shown the details of the optical train. Light from the source S (an incandescent 32 C.P. automobile headlight bulb, which is almost a point source) passes by two routes through the sector photometer. Part of the diverging beam from the point source passes through the cell C containing the sample of oil being tested, through the opening in the upper rotating sector R of the photometer, is bent downward by the prism P, and then made slightly converging by the lens L before falling on the biprism B

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Fig. 1 (a) Top View

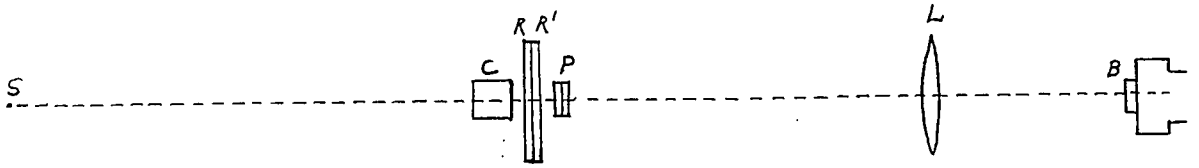


Fig. 1 (b) Side View

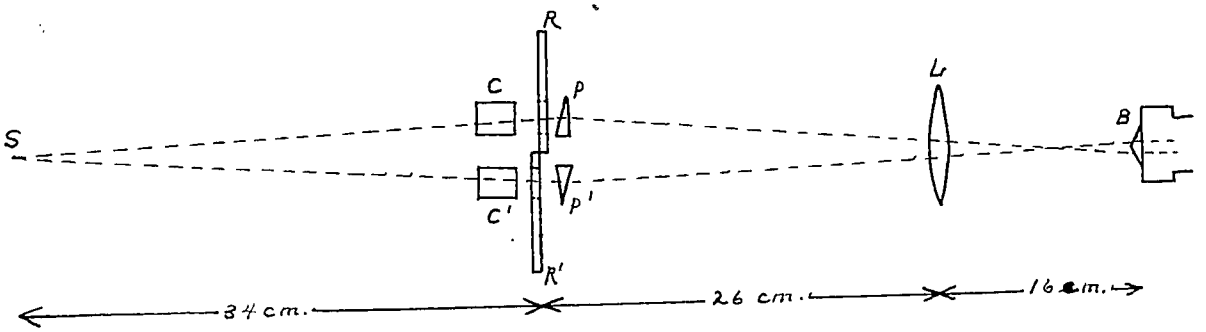


Fig. 1 (c)
Biprism

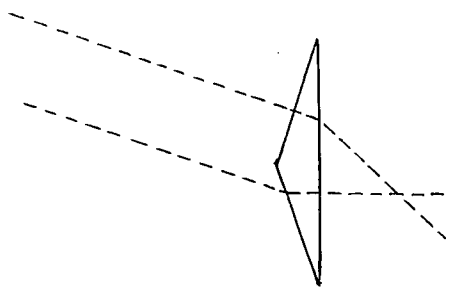
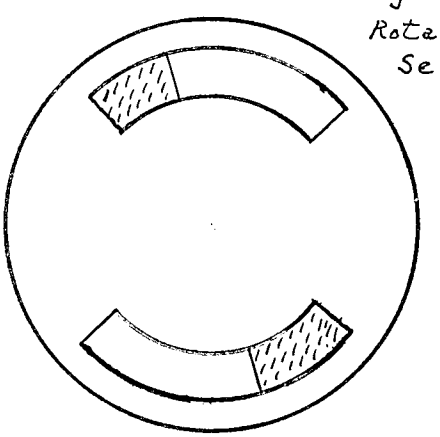


Fig. 1 (d)
Rotating Sector



immediately in front of the slit of the spectrograph. This is for the purpose of increasing the intensity at the slit. In a similar manner that portion of the beam which passes through the lower cell C' and rotating sector R' is bent upward by the prism P' and also made slightly converging by the lens before striking the biprism. Fig. 1(c) represents a side view of the biprism.From an examination of it, and a consideration of the properties of refraction of glass, it is seen that that portion of the upper beam, striking the prism at a downward angle, which falls on the upper half of the prism is refracted off to the side and absorbed by the blackened walls of the inside of the collimator, but that portion which falls on the lower half is refracted so as to emerge horizontally. The angle of incidence of the beam on the prism is arranged so that this is so. In a similar manner, since the lower beam strikes the biprism at an upward angle, only that part of it which falls on the upper half of the biprism passes along the collimator. Thus the spectrum observed is divided horizontally into two sections, one due to light coming from the lower half of the slit, which has all passed through the cell C containing the absorbing solution, and the other due to light coming from the upper half of the slit, which has all passed through the cell C' containing no solution. The purpose of passing this beam through a cell at all is to counterbalance the loss of intensity in the upper beam due to reflection from

the glass walls at the ends of the cell, so that after emerging from the cells the difference in intensity of the beams is due only to the absorbing solution. The relative intensity of the two beams is, of course, independent of fluctuations in the intensity of the light source, since both beams are from the same source and will always change in the same proportion.

After passing through the cells, the beams must pass through the openings in the rotating sectors shown in Fig. 1(d). The method is to cut down the average intensity of the unabsorbed beam until it matches the absorbed beam in its effect on the photographic plate of the spectroscope. This is done by decreasing the amount of opening of the rotating sector through which the unabsorbed beam must pass, thus decreasing the total exposure time for this beam until the blackening on the plate is the same as for the absorbed beam, which has less intensity but longer exposure. The blackening is proportional to the product of the intensity and the time of exposure[1], so that if this product is the same for both beams, the ratios of the two intensities after passing through the cells is inversely proportional to the ratio of the times of exposure, i.e. inversely proportional to the ratio of the sector openings, since both sectors are rotated at the same speed by an electric motor. The purpose

1. See "Instructions for the use if the sector photometer", Adam Hilger, Ltd., for a discussion of this.

of allowing the absorbed beam to pass through a rotating sector of the same frequency of intermittence as the unabsorbed beam is to compensate for any error in the blackening effect on the plate due th intermittent exposure. This sector is kept at full width, while the other is altered in the ratio required.

The ratio of the intensities of the absorbed and unabsorbed beams will depend, of course, upon the wavelength. Therefore the blackening effect on the plate must be equalized at as many different points of the spectrum as are necessary to obtain an absorption curve in the range of wave-lengths desired. In practice, a series of pairs of photographs is taken on one plate, with different openings for the variable sector. The developed plate is then examined with an ocular, and on each pair of spectra, the points marked where the two densities are the same.These points can be located visually with sufficient accuracy for most purposes.

The samples submitted to us were dissolved in cyclohexane. More cyclohexane was added if necessary to dilute the solution to make it come within the accurate range of measurement of the photometer. As far as possible, each sample was diluted until the maximum absorption in the range of the spectrum being examined was about nine-tenths of the incident light. If the solution was much stronger

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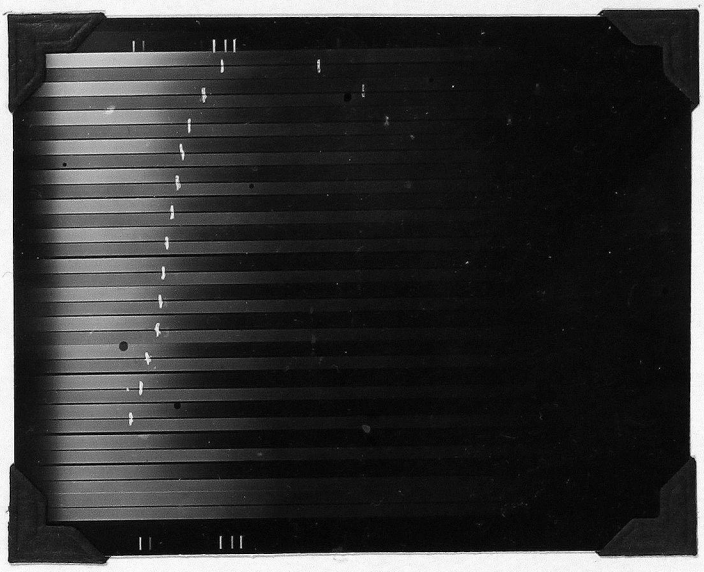

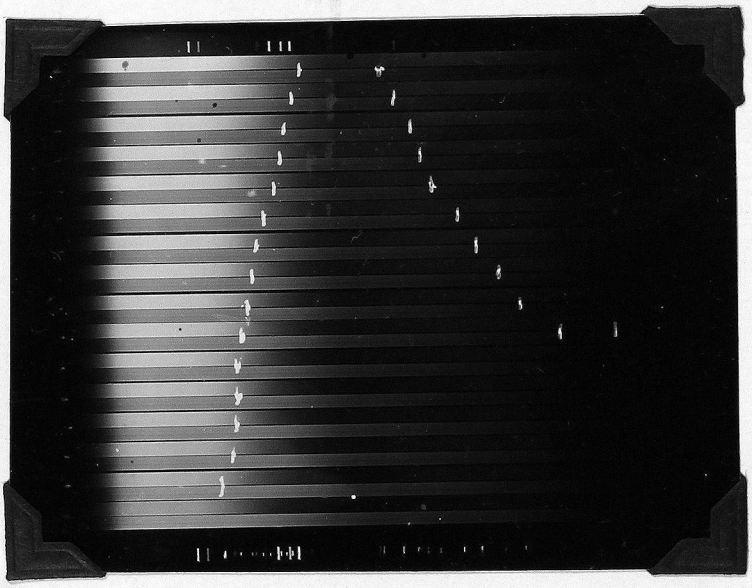

Fig. 2
Absorption Spectra

than this, too long exposures were necessary for matching the spectra at the point of greatest absorption. By observing the spectra visually using different sector openings, it is possible, with a little practice, to gauge this fairly well.

Before making the tests, the light source, photometer, lens, and collimator of the spectrograph were carefully lined up so that when the cells were removed the intensities of the two beams was exactly the same when viewed with an ocular through the slot in the plate-holder of the camera. By placing an old plate in position in the plate-holder, the camera was focused on a distant object for parallel light, and attached to the spectroscope. The collimator was then adjusted until the spectra were sharply focused on the emulsion. The exposure times were lengthened as the variable sector opening was decreased, so that the total time during which light from the beam passing through this sector fell on the plate remained the same. This was necessary to obtain sufficient blackening on the plate for accurate comparison in the case of the spectra taken with small variable-sector opening. The spectrum of a copper arc was taken at the top and bottom of each plate as a standard for identifying wave-lengths. Fig. 2 shows samples of the plates taken, with points of equal intensity marked.

A calibration curve for the spectroscope was drawn by plotting the wave-lengths of several lines throughout the copper spectrum against their distance from an arbitrary zero

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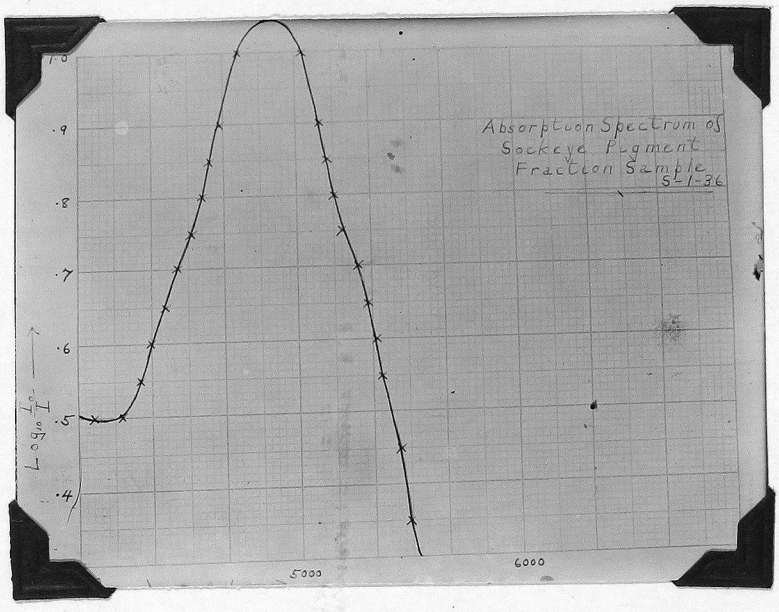

Fig. 3
Absorption Curve

position at the red end of the spectrum, and joining the plotted points with a smooth curve. Then by joining the zero positions of the two copper spectra on the plate with a straight line and from it measuring the distances of the points of equal density, their wave-lengths can be identified from the calibration curve and plotted against the corresponding sector openings to obtain the absorption curve. The variable sector opening is calibrated to read directly, for points in the spectrum of equal density, the quantity $\log_{10}\frac{I_o}{I}$, where I_o is the intensity of the light of the wave-length being matched that falls on the absorbing solution, and I that of the beam leaving the solution; i.e. it reads the logarithm of the ratio of the sector openings. The amount of emergent light due to a thickness x of absorbing solution is given by $I = I_o e^{-ux}$, where u is the extinction coefficient of the solution, which is proportional to the concentration of the absorbing substance, and I_o is the amount of incident light of the same wave-length. In terms of the common logarithmic base this formula becomes $I = I_o(10^{-ux})$. Thus $ux = \log_{10}\frac{I_o}{I}$, and since the thickness of the cell is constant in this experiment, by plotting $\log_{10}\frac{I_o}{I}$ against the wave-length, a curve is obtained such that the relative values of the ordinates depend only upon the nature of the substance and not upon its concentration. Fig. 3 shows the absorption curve for one of the samples of oil tested.

It is worth while observing that in locating the

position of an absorption maximum, it is immaterial whether or not the two beams, when there is no absorbing solution present, are of equal intensity. If they weren't, the amount of absorption read would, of course, be wrong, but the position of the absorption peak would not thereby be shifted.

RESULTS

Some nineteen samples of sockeye and spring salmon pigment were tested, and their absorption curves plotted. Those which showed an absorption band had the peak of the band in the neighborhood of 5000 A.U. On information from Mr. Bailey, this seemed to bear out the conclusion, obtained from biological experiments, that the chief pigment present in the oil was astacene, since previous spectroscopic work on this pigment has shown that it has an absorption band with maximum near 5000 A.U. Other samples showed a continual rise in absorption from the red to the violet, with a flattening around 5000 A.U. The rise in the curve shown by all the samples on approaching the ultra-violet is probably just the beginning of the ultra-violet absorption of the glass parts of the optical train.

ACKNOWLEDGMENT

The writer wishes to thank the Fisheries Experimental Station of the Biological Board of Canada, at Prince Rupert, B.C., and especially Mr. Basil E. Bailey, for supplying the samples of salmon oil used in this investigation.

AN ACCURATE METHOD OF TESTING LIGHT TRANSMITTING PROPERTIES OF GLASS

INTRODUCTION

This report outlines the method used in testing several samples of glare-reducing goggles submitted to us to ascertain percentage total transmission of light, and percentage difference in the transmission of the right and left lenses of a pair; also to obtain the absorption spectrum throughout the visible region.

EXPERIMENTAL

The absorption spectra were obtained in exactly the same way as were the spectra of the salmon oils, described in the previous paper, with the lens being tested mounted in front of the upper rotating sector of the photometer in place of the two cells. This time, of course, there was no compensating clear glass placed in front of the lower sector, since the total absorption of the lens was required, due to both colouring material and any reflection from the surfaces.

In testing total transmission a Lummer-Brodhun photometer was used. Fig. 1 shows the arrangement of the apparatus. S and S' are two 32 C.P. automobile headlight bulbs connected in series, so that the two beams of light falling on the screen P of the photometer have the same relative intensity even though the current through the

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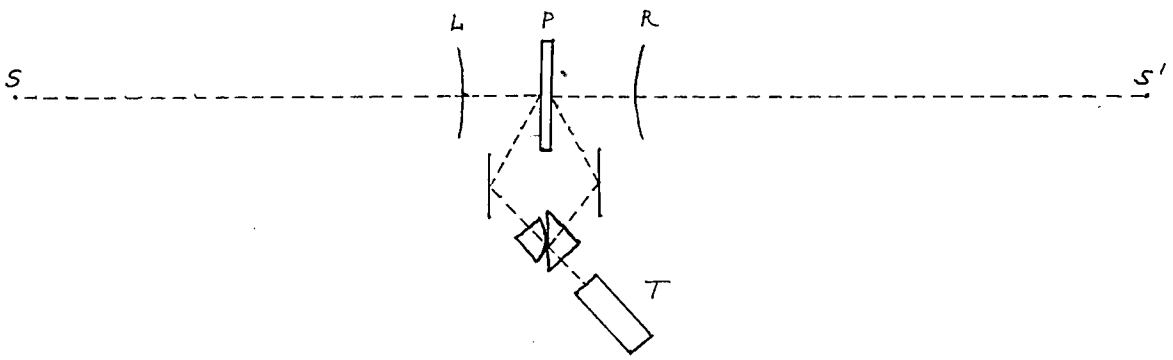

Fig. 1 Top View

lamps fluctuates. By a system of prisms, light from the two sides of the screen is made to enter the telescope T as adjacent fields. When the intensities on the two sides of the screen are equal, the two fields appear of equal brightness, and the line of demarcation between them disappears.

S was placed at a fixed distance of about 1m. from the screen. S' was mounted on an optical bench so that its distance from the screen could be measured to within 1 mm. S' was then moved until the two fields were matched, and its distance d_o from the screen recorded. The left and right lenses of a pair of goggles were then placed in the positions L and R respectively, and S' moved until the two fields again matched. If this new distance is d_1, then by applying the inverse square law of light intensities, $\left(\frac{d_1}{d_o}\right)^2$ gives the fraction of the light transmitted by L that is transmitted by R. The result was checked by interchanging L and R. These fields could be matched very accurately, since both were of the same tint, having both passed through an absorbing lens. With no lens in the path of S, each lens was then placed in the path of S' and the distance of S' altered until the two fields again matched. If this new distance is d_2, then $\left(\frac{d_2}{d_o}\right)^2$ gives the fractional transmission of the lens. This setting could not be made with such great accuracy, since the light transmitted through the lens was not quite of neutral tint, making it more difficult to obtain the balancing point.

Each value of d_1 and d_2 was obtained as the mean of ten settings. The greatest deviation from the mean for any single setting was $\frac{1}{2}\%$, so that the possible error in the calculation of d_1 was about 1%. The probable error would be considerably less than this. The possible error in the settings for d_2 was about twice as great, giving a possible error of about 2% in the percentage transmission of the lenses.

ACKNOWLEDGMENT

The writer wishes to thank the Forestry Department of the Government of the Province of British Columbia for supplying the goggles used in this investigation.

THE VELOCITY OF ATOMS IN A COPPER ARC

INTRODUCTION

In an experiment with a curved copper arc discharge in a vacuum, Tanberg[1] measured the force of reaction on the horizontal cathode, and from this force and the rate of disappearance of the cathode, calculated the velocity which the atoms must have had when they left the cathode, to the momentum of which he attributed the force of reaction against the cathode. He checked the results by measuring the force on a vane suspended in front of the cathode and the rate of deposit of copper on the vane. He obtained velocities of the order of $16(10)^5$ cm. per sec. If this quantity is substituted for v in the formula $1/2\ mv^2 = 3/2\ kT$, where m is the mass of the copper atom and k the Boltzmann constant, an absolute temperature T of 500,000 degrees is obtained for the temperature existing at the cathode spot, if there is justification in assuming, as did Tanberg, that the high speeds of the atoms are due to their temperature motions. Later, K.T. Compton[2] showed that the observed pressures could be accounted for by assuming that about half of the current in the arc was carried by positive copper ions, and that after striking the cathode they did not give up all their energy but rebounded with about 2% of their original kinetic energy. R. Risch and F. Ludi[3] accounted for the stream of atoms by multiple ionization and subsequent collisions of the second kind. Tonks[4] pointed out that the electrons in a

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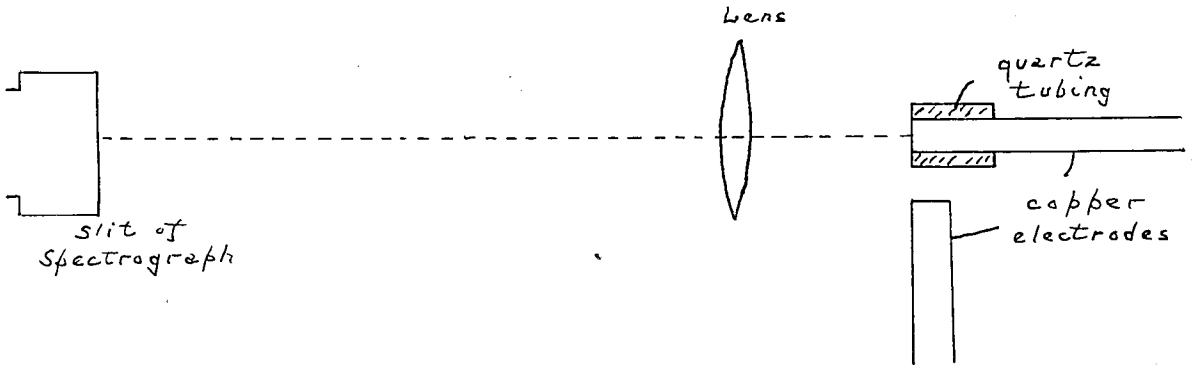

Fig. 1 Side View

plasma, especially those at the cathode, would exert a pressure kT which would account for the major portion of the reaction force, but later Lüdi[5] showed that this would lead to incorrect values for the electron density.

The object of this experiment was to see if information on the problem could not be obtained by making use of the Doppler effect. If atoms of copper are streaming out from the cathode, and are emitting light, the spectral lines , if viewed along the line of sight, should show a Doppler shift $\Delta\lambda$ given by $\Delta\lambda = \frac{v}{c}\lambda$. For λ = 3000 A.U. and v = 16 km. per sec., this would give a shift of 0.16 A.U.

EXPERIMENTAL

As shown in Fig. 1, the copper electrodes are held in an arc holder so that one is vertical and the other horizontal, an arrangement similar to that of Tanberg. The arc was run on 220 volts, with a current of about 4 amperes. In the circuit was a double throw switch so that the current in the arc could be reversed easily when desired.

A Hilger E.1. quartz spectrograph was used to examine the spectrum of the arc. It was focused very finely by a method suggested by Dr. Beals of the Dominion Astrophysical Observatory at Victoria, B.C. The method can be understood by a glance at Fig. 2. A sliding shutter is fixed onto the lens holder of the spectrograph, so that spectrograms can be taken using only part of the beam of light. With light coming from one section of the slit by means of

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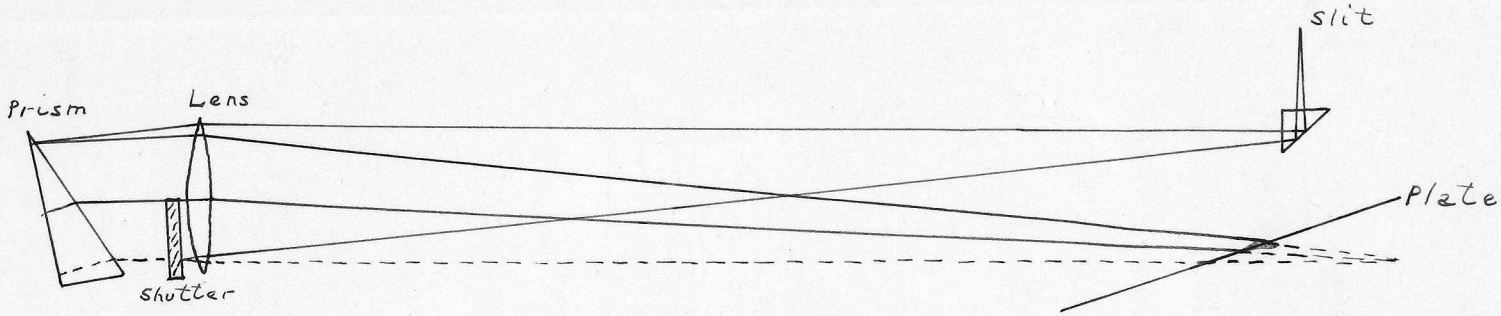

Fig. 2 Method of focusing Spectrograph

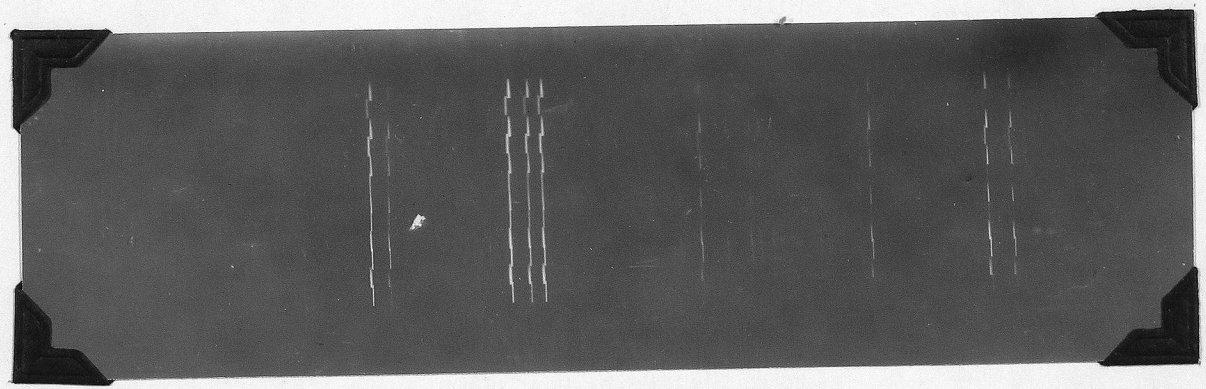

Fig. 3 Test spectrogram used in focusing

a Hartmann diaphragm, a spectrogram is taken using only one-half of the beam as shown. Then another picture is taken using an adjacent part of the slit and the other half of the beam instead. By reference to the figure it is seen that if the plate is not at the focus of the lens, the lines on the adjacent spectra will be displaced relative to one another. A series of pairs of spectra is taken in this way, altering the position of the rack carrying the lens and prism by two divisions of the drumhead each time. Thus the position at which the two lines are directly under one another can be ascertained and this will be the position for which the plate is exactly at the focus of the lens. If the lines are not directly under one another for the whole length of the spectrum, the tilt of the plate-holder is wrongly adjusted. An examination of a series of photographs taken in this way enables one, after a little practice, to obtain quickly the correct position of the lens and the correct tilt of the plate-holder.

If the spectrograph is improperly focused, the position of a line, even when using the whole width of the beam, will be influenced by the angle at which the light from the source strikes the slit, for if the source is moved from side to side the intensity of the beam leaving the slit to traverse the optical path through the spectrograph will be shifted first to one side and then to the other, causing the greatest intensity to be recorded at different

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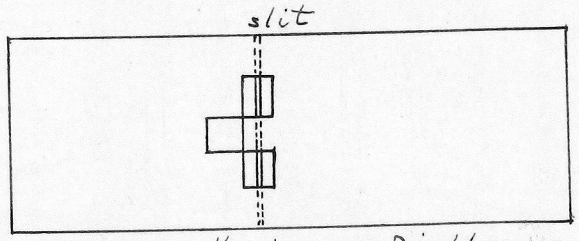

Fig. 4 Hartmann Diaphragm

Fig. 5 Spectrogram showing greatest shift

positions on the plate if it is in the shown in Fig. 2. If the plate is exactly at the focus, however, the light will fall on the same spot no matter where the maximum intensity occurs in the beam, since all the light converges to this point.

One of the plates taken in focusing the spectrograph by this method is shown in Fig. 3.

Great difficulty was experienced in getting the cathode spot to stay on the end of the electrode. Several photographs were taken using different sizes of electrodes and different relative positions of the anode and cathode. Using a Hartmann diaphragm as shown in Fig. 4, an exposure was taken using the two outside portions of the slit and with the upper horizontal electrode as cathode. Then, using the central portion of the slit, and with the electrodes reversed, another exposure was taken of as nearly as possible the same intensity, but on account of the constant fluctuation of the arc, it was difficult to time this accurately. Any shift then observed could be checked for mechanical error of the spectrograph by reversing the exposures, this time using the central part of the slit when the upper electrode is the cathode.

No results of any definite magnitude were obtained until a copper wire surrounded by a piece of quartz tubing was used as the upper electrode. The tubing helped to keep the cathode spot on the end of the electrode. A shift was then observed towards the red end of the spectrum when the

upper electrode facing the spectrograph was the cathode. The shift as measured under a measuring micrometer was about .1 A.U., in the region around 3200 A.U., which would correspond to a velocity in the line of sight of about 10 km. per sec., which is of the same order of magnitude as the velocities that Tanberg calculated. If most of the light were coming from the region around the cathode, the shift toward the red would indicate that the particles were going towards the cathode instead of being emitted from it. The absorption lines of the two strong ultra violet lines 3247 and 3273 were also shifted the same amount. In taking this photograph no lens was used between the source and the slit.

Using a quartz lens, an enlarged image of the arc was projected onto the slit. The end of the upper electrode was focused on the slit, and exposures taken when it was first the cathode and then the anode. Various parts of the arc were photographed in conjunction with other parts and with different arrangements of the electrodes. This time the only definite shift was shown by a plate taken when the upper electrode facing the spectrograph was the anode, and and the spectrum taken from that part of the arc showed a shift toward the red, which would indicate that the light emitting particles were going towards the anode, or that particles were streaming out from the cathode. Most of the plates taken showed either no shift, or so slight as to be hardly detectable.

DISCUSSION OF RESULTS

Theories regarding what is taking place in the arc discharge are very uncertain.[6,7] It has been necessary to assume that there are positive ions in the discharge, since if there were only electrons carrying the current, the resulting space-charge would require more potential than is present in a low-voltage arc, in order to drive it across the gap. One theory is that the positive ions hitting the cathode keep up its temperature so that by thermionic emission it keeps up the supply of electrons for the current, while these electrons hitting the anode keep up the supply of positive ions. The objection to this in the case of the copper arc, however, is that copper boils before it reaches the temperature required for enough thermionic emission to account for the current observed. Just how much of the current is carried by the positive ions is also uncertain.

If the shift stated is really of the order of 0.1 A.U., it could not be due to the pole shift observed first by St. John and Babcock[8], who observed a shift of the order of 0.02 A.U. between the poles and center of the arc, by merely observing the arc laterally. The fact that the cathode disappears, as was observed by Tanberg, would indicate that if ions are striking the cathode and being neutralized, atoms are also leaving. A shift in one direction could be explained as being due to one of these streams of particles, and a shift in the other direction as due to the other stream,

the shift observed depending upon whether the portion of the arc photographed contained one or the other of the streams in greater proportion. A possible explanation of the shifting of the absorption lines of the two strong ultra-violet lines would be that the stream of atoms has this translational velocity imposed upon it in addition to the different random velocities of the different parts of the stream, corresponding to the hot emitting and cooler absorbing parts of the arc.

The shift observed in the two cases is fairly definite, although more work will have to be done before the anomalies in the shift observed in the different plates, the fact that two of the plates showed a decided shift while the majority showed little or none, can be connected up with the theory. The fact that a shift has been observed, however, shows that there must be some velocity effect, unless further investigation indicates another explanation apart from the Doppler effect, or some experimental error.

In any case, the use of the Doppler effect should furnish a powerful method of investigating conditions in the arc. It is worth while observing that the velocities obtained by Tanberg for the stream of atoms leaving the cathode is about the same as a singly-ionized copper atom would have if it fell across a 50-volt arc without collision, and about the velocity corresponding to the spectral shift observed. If there are streams of atoms and ions going in opposite directions, it should be possible to separate them

by means of an imposed magnetic field, and take pictures of each one separately. The main difficulty in the work is to hold the cathode spot steady, as it tends to wander around continuously and never stay in one place for more than a fraction of a second. This being the case, probably the best results can be obtained for the copper arc by using the two strong ultra-violet lines, since they will show up with a very short exposure. Any longer exposures will almost invariably come from different parts of the arc due to the wandering of the cathode spot.

ACKNOWLEDGMENTS

The writer wishes to express his thanks to Dr. G.M. Shrum for suggesting the above research and for helpful suggestions during the course of the work, and to Mr. W. Fraser for assistance with the mechanical details of the experiments.

BIBLIOGRAPHY

1) R. Tanberg, Phys. Rev., 35, 1080 (1930)

2) K.T. Compton, Phys, Rev., 36, 706 (1930)

3) R. Risch & F. Lüdi, Zeits. fur Physik, 75, 812, (1932)

4) L. Tonks, Phys. Rev., 46, 278 (1934)

5) F. Lüdi, Helv. Phys. Acta, 8.3. 272 (1935)

6) J.J. Thomson & G.P. Thomson,"Conduction of Electricity through Gases", 3rd ed.(Cambridge, 1933), vol. 2, chapt. 10.

7) K.K. Darrow, "Electrical Phenomena in Gases" (Williams & Wilkins Co., Baltimore, 1932), chapts. 10 & 13.

8) C.E. St. John & H.D. Babcock, Astro. Jrnl.,42, 231 (1915)