*ON DIFFRACTION SPECTRUM PHOTOGRAPHY, AND THE DETERMINATION OF THE WAVE-LENGTHS OF THE ULTRA-VIOLET RAYS**

Illustrated by an Albert-type Plate.

THERE are, as is well known, two methods by which spectra may be obtained: (1) by the action of a prism; (2) by a system of closely-ruled lines. In the latter case it is convenient to speak of the contrivance employed as a grating, and of the spectrum as an interference or diffraction spectrum. A casual inspection shows that there is a great difference between the spectra produced by these two methods, and close investigation proves that the diffraction spectrum is by far the more suitable for accurate scientific work. For this reason it has seemed desirable to make a trustworthy map of those parts of the solar diffraction spectrum which can be photographed on collodion, and to attach to it a scale for reading the wave-lengths of the rays.

The plate accompanying this memoir is from collodion photographs made by myself, transferred to a thick piece of glass, the latter process being known as the Albert-type. For the entire success of this transfer I am indebted to my friend Mr. E. Bierstadt, the owner of the patent in America. The glass is then used in a printing press in the same manner as a lithographic stone. The spectrum is absolutely unretouched. It represents therefore the work of the sun itself, and is not a drawing either made or corrected by hand.

The picture consists of two portions: first, the upper, which gives all the lines of the spectrum from near G to O, or from wave-length 4350 ten-millionths of a millimetre to 3440. Above that is placed a scale, which is a copy of Angström's from just below G to H_2, with the same-sized divisions carried out from H_2 to O. The second, or lower, is a magnified portion of the same negative, having H_1 and H_2 about its middle, and extending from wave-length 4205 to 3736.

It follows therefore that the lines in the solar spectrum are correctly represented in their relative positions. The only errors are those which may have arisen from maladjustment of the scale. The precautions that were taken to avoid such errors will be described. With a certain correction, to be mentioned hereafter, it may also be stated that the relative shadings and intensities are preserved.

The value of such a map depends on the fact that it not only represents parts of the spectrum which are with difficulty perceived by the eye (though they may be seen by the method of Stokes and Sekulic), but also that even in the visible regions there is obtained a far more correct delineation in those portions which can be photographed. In the finest maps drawn by hand, such as those in the celebrated "Spectre Normal du Soleil" of Angström, the relative intensity and shading of the lines can be but partially represented by the artist, and a most laborious and painstaking series of observations and calculations on the part of the physicist is necessary to secure approximately correct positions of the multitude of Fraunhofer lines. Between wave-lengths 3925 and 4205, Angström shows 118 lines, while my original negative has at least 293.

For such reasons many attempts have been made to procure good photographs of the diffraction spectrum. The earliest were by my father, J. W. Draper; his results were printed in 1843-44 in a work entitled "On the Forces which produce the Organisation of Plants." This memoir was accompanied by plates drawn from his daguerreotypes, and the wave-lengths, which he first suggested as the proper indices for designating the Fraunhofer lines, were used as a scale.

Since that time the most important experiments in this direction have been by Mascart and Cornu. These eminent physicists have, however, resorted to the plan of taking portions of the spectrum on a small scale and subsequently making enlarged drawings therefrom. This course introduces the defects of handwork, and the artistic difficulties of copying intensity and shading, as well as the omission of fine lines.

In the photographs of the spectrum which I have taken I have tried to get as large a portion as I could at once, and on as large a scale as possible. I have usually obtained images from below G (wave-length 4307) to above O (wave-length 3440) of about 12 inches (·305 metre) long. I have succeeded, however, in photographing from near *b* (wave-length 5167) to T (wave-length 3032) by resorting to a ruled speculum plane and a concave speculum mirror, but the photographic and optical difficulties in securing an enlarged spectrum of that length are great.*

Of course, in such a research as this an essential is a finely and evenly ruled plane of glass or other material. Those which I have used were made by a machine devised and constructed by Mr. L. M. Rutherfurd, whose beautiful lunar and prismatic spectrum photographs are so well known to the scientific world. The plate generally employed is of glass ruled with 6481 lines to the inch; the ruled part is $1\frac{8}{100}$ inch (·027 metre) long, and $\frac{64}{100}$ inch (·016 metre) wide. It is unquestionably much more nearly perfect than similar gratings made by Nobert and others, for the character of the photographs and the uniformity of the orders on either side of the normal, together with its behaviour under a searching examination, show that it leaves little to be desired. As it is on glass, and gives a bright transmitted spectrum, I have constructed the remainder of the optical apparatus of glass achromatised, according to the plan used by J. W. Draper in 1843, except that I have not silvered the ruling, and therefore have used the refracted, and not the reflected beam. The slit is $\frac{8}{10}$ of an inch (0·2 metre) long, and $\frac{1}{110}$ of an inch (·00023 metre) wide; the jaws are of steel, and there is not only a micrometer screw for separating them, but also one for setting them at an angle. Occasionally I have taken photographs with the jaws $\frac{1}{90}$ of an inch (·00028 metre) apart at the top, and $\frac{1}{130}$ (·00019 metre) at the bottom, so as to obtain different intensity in the two edges of the spectrum.

Most of the photographs have been of the spectrum of the third order, which has certain conspicuous advantages. In the first place it is dilated to such an extent as to give a long image, and yet one not too faint to be copied by a reasonable exposure of the sensitive plate; and in the second place, the spectrum of the second order overlaps it in such a way that D falls nearly upon H, and *b* upon O. These coincidences are serviceable in determining the true wave-lengths of all the rays.

The only point of special interest in connection with the photographic part of the operation, is the device for avoiding the unequal action on the sensitive plate of different rays of the spectrum. It has been commonly supposed, until the recent memoirs of J. W. Draper, that there are in the spectrum three different types of force in three different but overlapping regions. Heat was supposed to be principally found at the less refrangible end, light in the middle, and actinism at the more refrangible. But he showed that this error has partly arisen from using prismatic spectra, which condense the red end and dilate the violet, and do not present the rays in the

* From the *American Journal of Science and Art*, Dec. 1873. Communicated by the author.

* Since writing the above I have succeeded in photographing the lines of the visible spectrum from *b* downward, and the picture comprises not only the regions including E, D, C, B, *a* and A, but also the ultra-red rays. The great groups, *α*, *β*, *γ*, below A, discovered by my father in 1843, are distinctly reproduced.

true order of their wave-lengths, and partly from the nature of our ordinary photographic substances. He proved that actinism, or the power of chemical decomposition, does not particularly belong to the violet end of the spectrum, but is found throughout its whole length. But bromide and iodide of silver, as used in collodion photography, are more readily decomposed by vibrations of certain lengths and periods than by others, and hence the excess of action seen at the violet end is a function of certain silver compounds, and not of the spectrum. Other substances, as carbonic acid, show maxima elsewhere, as in the yellow region. The solar beam is therefore not compounded of three forces, light, heat and actinism, but it is a series of ethereal vibrations, which give rise to one or other of these manifestations of force, depending on the surface upon which it falls.

In order to provide against this excess of action in certain parts of the spectrum, I introduced a system of diaphragms placed in the vicinity of the sensitive plate, and removed at suitable times during the exposure. The region from wave-length 4000 to 4350 only requires about one-tenth of the time demanded by that from 3440 in 3510. In the negative which produced the accompanying plate, the line O had 15 minutes and G $2\frac{1}{2}$ minutes, and the former is under-exposed. These exposures seem at first sight unusually long for a wet collodion surface, but it must be remembered that the slit used was only $\frac{1}{1110}$ of an inch wide, and that the diffraction grating gives an almost complete circle of spectra round itself, amongst which this thin band of light is divided. A beam $\frac{1}{1110}$ of an inch (·00023 metre) wide is spread out in this case into a streak about 78 ft. (23·77 metres) long.

After the production of spectra that were in focus from end to end, it was next necessary to attach a scale to them by which the wave-lengths might be read. At first I tried, by reducing Angström's maps to the proper dimensions, to accomplish this object, but the undertaking proved to be difficult, and was unsuccessful, because, though the original drawing on the stone was undoubtedly correct, the paper proof of it which I had, had stretched unequally in printing, and on applying a photographic reduction to my spectra, coincidence could not be obtained. As, however, the subject of dividing a scale for these diffraction spectra is of prime importance in giving value and precision to the wave-lengths presented in this memoir, I propose to describe fully the method eventually employed in fitting a scale to the photograph.

The wave-lengths of the ultra-violet rays have never as far as I know, been either determined or published except by J. W. Draper in 1844, Mascart in 1866, and Cornu in 1872. J. W. Draper's memoir has a steel engraving of some of the principal lines, from which the wave-lengths may be approximately read.

The large plate which accompanies Mascart's long and valuable memoir is of the prismatic spectrum, but he furnishes in addition the following table of wave-lengths :—

L	3819·0
M	3728·8
N	3580·2
O	3440·1
P	3360·2
Q	3285·6
R	3177·5

These numbers do not entirely coincide in all cases with my photograph, as I will show farther on.

The detailed results of M. Cornu have not appeared in any publication that has reached me.

I have used as a basis the numbers given by Angström for the rays D_2, b_4 and G, and if there should be any small error in his determination, my scale will require a proportionate correction, which can easily be effected. At first sight it seemed better to take G and H as fixed points, but the line H is so broad, and has so many component lines, that its position is uncertain, and moreover, being almost at the limit of visibility in Angström's apparatus, it was more open to errors of measurement. These reasons led me to take advantage of the fact that the second spectrum overlaps the third, the ray D of the second being near H of the third, and *b* of the second near O of the third. It is obvious that we have thus the means of ascertaining the wave-lengths of three points, one at each end, and one in the middle of my photograph. As the rays D and *b* cannot impress themselves on collodion by any length of exposure that it is convenient to give, and as in my method of working the ultra-violet rays could not be seen simultaneously with them, it was necessary to resort to the following device :—I placed in front of the sensitive plate and close to it two fine steel points, one of which was carefully adjusted to the position of D_2 of the second order, and the other to b_4 of the second order. When, therefore, after a suitable exposure to the ultra-violet spectrum of the third order, the collodion picture was developed, there were two sharply-defined images of the steel points superposed on the spectrum. The point which had been coincident with D_2 of the second order was then found to have cast its shadow on H_2 of the third order, and the point at b_4 of the second order had impressed itself near O of the third order.

By a simple calculation it was thus rendered evident that a given ray in the compound line H_2 was of the wave-length 3930·1 ten millionths of a millimetre, and that another line near O had the wave-length 3444·6. By looking at the photograph, the reader will see that 3930 falls upon a fine division in H_2, which is beautifully shown in both the spectrum with the scale and the enlarged proof below. Of course, the ray G of the third order, the wave-length of which is known, had impressed itself photographically on the collodion.

Having thus ascertained the wave-lengths of three fixed points in the photograph, the next step was to apply a scale reading to a single ten-millionth of a millimetre, and, if possible, fractions thereof. After many abortive attempts to use that part of Angström's map which lies between G and H, and to attach thereto an additional length of scale sufficient to extend to the end of the ultra-violet region, I was compelled to resort to a linear dividing engine, and rule a scale which was about twice the length of the photographic reduction shown in the accompanying plate. Of course this necessitated drawing in by hand the same systems of lines and lettering as are shown on Angström's chart, and this I did as carefully and faithfully as I could.

It only remained to reduce this divided scale to the proper size to fit the spectrum photograph ; after many trials it was accomplished.

It is proper in this place to make a criticism on my scale, and to point out a small error, which may be due, however, to an incorrect determination of the wave-lengths that I have used as fixed points. Taking the distance from G (wave-length 4307) in the photograph to the fixed line 3930 in H_2, and dividing it into 377 parts, and then prolonging these divisions toward O, it was found that the third fixed point was not attained, but that there was an error of about two divisions. But if the position of D_2 in Angström's determinations should be incorrect to the extent of one ten-millionth of a millimetre, or if this small error should be partly attributed to D_2, and partly to G, my scale would be correct. Future measures of the wave-lengths of these rays, and of b_4, can alone settle this delicate point, for the determinations of Mascart and Angström and Thalen differ nearly to the extent mentioned above. The same remark is true of Angström compared with Ditscheiner, while the difference between Angström and van der Willigen is more than three times the amount necessary to remove my discrepancy. In any case the photograph is correct, as it is the work of the sun, and is only open to errors arising from imperfect flatness in the field of a fine lens, and that field only subtending an angle of about 4°. The angular aperture of the lens, viewed from the sensitive plate, is 20 minutes. I trust, therefore, that the photograph may be of permanent value to physicists, for any one can affix another scale if this be slightly erroneous.

An examination of the photographed spectrum shows many points of interest, some of which are best seen in the spectrum with the scale above, and some in the portion enlarged below. The latter is magnified about twice, and comprises the region from wave-length 3736 to 4205. I have also made photographs on the same scale as Angström's map, but have not as yet printed them. The capital letters which are attached to the region above H are according to the nomenclature of Mascart, although the wave-lengths assigned by him to those letters do not coincide exactly in all cases with the lines in my photograph; for instance, the line L, which he regards as single, is in reality triple, and does not correspond to 3819, but to 3821; M is correctly designated by 3728, but it is double; N is really at 3583, and not 3580. It has been suggested that it would be proper to return to the old nomenclature of Becquerel and J. W. Draper, who simultaneously discovered these lines in 1842-43, but the designation of position by wave-length in reality renders the letters unnecessary.

The spectrum above H, when compared with the region from G to H, is marked by the presence of bolder groups of lines, and most conspicuous are those between 3820-3860, 3705-3760, 3620-3650, 3568-3590, 3490-3530. The first of these groups is strikingly shown in the enlarged photograph. I am not as yet able to offer an opinion as to the chemical elements producing these groups, for almost all the photographs of the ultra-violet spectra of metalline vapours that I have thus far made were produced by a quartz train, and have not yet been reduced to wave-lengths. Indeed, that is a separate field of inquiry, and could not be comprised in a memoir of this length. I have also tried to utilise the photographic spectra of the late Prof. W. A. Miller, published in the "Transactions" of the Royal Society for 1862, but for some reason, probably insufficient intensity of the condensed induction spark, his pictures do not bring out the peculiarities of the various metals in the striking manner that is both necessary and attainable. The diffraction spectra of metalline vapours that I have made are not yet ready for use.

The probabilities are that each of these groups will be found to be due to several elements, as is plainly seen in the group H. This compound line, which is commonly spoken of as being caused by calcium, iron, and aluminum, is in reality much more complex, for there can readily be counted in it more than fifty lines in the original negative, and a careful inspection of the accompanying paper picture shows a large proportion of them. This observation leads us to a more general statement. *The exact composition of even a part of the spectrum of a metal will not be known until we have obtained photographs of it on a large scale.* The coincidences which were so thoroughly examined by Mr. Huggins (Trans. Royal Society, Dec. 1863) will only disappear when we can, in addition to the position of a line, have a clear idea of its size, strength, and degree of sharpness or nebulosity. The eye is not able to see all the fine lines, or even if it does, the observer cannot map them with precision, nor in their relative strength and breadth. For example, in Angström's justly celebrated chart, of which the G-H portion is copied in this plate, and in the construction of which the greatest pains were taken by him, many regions are defective to a certain extent. The region from 4101 to 4118 is without lines, yet the photograph shows in the enlarged copy seventeen that can easily be counted, and the original negative shows more yet. The reader of course understands that a paper print of a collodion picture is never as good as the original; the coarseness of grain in the paper, want of contact in transferring, &c., effect such a result. Moreover, the Albert-type process depends on a certain fine granulation which is given to the bichromated gelatine, and this forbids the use of a magnifier upon these paper proofs. It is only just, however, to Mr. Bierstadt to state, that without his personal supervision, such sharp and fine-grained proofs could not have been obtained, and that no other printing-press process that I know of could have accomplished this work at all.* As an illustration of the difficulty of depicting the relative intensity of lines, we may examine 3998, which in Angström's chart is shown of equal intensity with 4004, while in reality it is much fainter, and instead of being single, is triple, as is well seen in the enlarged spectrum.

When, however, we compare Angström's chart with the photograph, it requires, as the above remarks show, a critical examination to detect defects, and we have a striking confirmation of the surprising accuracy of the Swedish philosopher.

So also in comparing Mascart's excellent map of the prismatic spectrum with the photograph, the difficulty of depicting all the fine lines is seen. In the group L he shows twelve lines, while even in the Albert-type copy of my photograph twenty-five can be counted, and in the original negative many more. From H to L he exhibits seventy lines; in my plate 138 can be observed, besides many unresolved bands.

In the earlier part of this memoir it was stated that the relative intensities of the lines in the spectrum were correctly represented if a certain allowance was made. If an unshielded collodion plate were presented to the image of the spectrum, there would be produced a stain very dense from G to H, fainter above H, and still fainter below G. But this stain would not represent the actinic force of the sun; it would merely be the index of the decomposability of a mixture of iodide and bromide of silver. I have for this reason adopted the idea of J. W. Draper, that force is equally distributed through the spectrum, and have tried to produce a photograph of equal intensity throughout. This has been accomplished, as I have before stated, by suitable diaphragms. But whether this view be correct or not, lines which are not far distant from one another are presented virtually without any interference by diaphragms, and must therefore be correct both as to shading and intensity.

Besides the points above mentioned, there are many theoretical considerations suggested by the photograph which it does not seem expedient to enter upon fully at present. Among such is the possibility of arriving at an estimate of the sun's temperature, by interpreting the apparent bands, such as those near G and H, by the aid of Lockyer's researches on the temperature of dissociation of compounds. No one has yet ascertained whether there are or are not unresolvable bands in the solar spectrum. If they do exist, the compounds to which they belong, and the necessary temperature for dissociation, remain to be determined.

It would seem also to be possible to find out whether, as asserted by Zöllner, there is a liquid envelope around the sun, by a search for more diffused bands in its photographed spectrum.

In the hope that this photograph may prove to be of value to scientific men for further investigations upon the sun and the elements, I have caused a number of extra copies to be printed, and shall be glad to present them to anyone who can make use of them.

HENRY DRAPER

* From the original negative of the spectrum 12,000 copies have up to the present been printed, and it is not in the slightest degree injured as yet.