XIII. THE BAKERIAN LECTURE.—*Researches in Spectrum-Analysis in connexion with the Spectrum of the Sun.*—No. III. *By* J. NORMAN LOCKYER, *F.R.S.*

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Introduction.

THE Researches in Spectrum-Analysis in which I have been engaged are opening out into so many lines of work that I think it desirable to communicate to the Royal Society the present state of the inquiry on its most general aspect, and also to enter somewhat into detail on some of the points to which my attention has specially been directed, the more so as the methods employed are such as can be, and I sincerely trust will be, taken up by other workers.

To commence, then, by a general statement, I may remark that I have in the first place endeavoured to determine whether the new method of spectroscopic observation, which I have before described to the Royal Society, is really as competent as it promised to be in the quantitative direction, what are the conditions essential to its successful employment, and how far it would take us.

As the time I could devote to this inquiry was limited, I confined myself to mixtures of two metals. The results of the experiments which I have to report in the present paper, and in a separate one which will be communicated by Mr. W. C. ROBERTS, Chemist of the Mint, and myself, are in more ways than one satisfactory, the history of science having shown that a great increase in theoretical work may be hoped for as soon as an instrument such as the spectroscope gets into practical use in the arts.

It may be said that while the qualitative spectrum-analysis depends upon the *positions* of the lines, the quantitative analysis depends not upon their position but upon their *length*, *brightness*, *thickness*, and *number*, as compared with the number visible in the spectrum of a pure vapour.

The character of a spectrum when observed by the new method is so entirely different from that which results from following the integrating method, that maps of the various spectra, in which not only the relative lengths of the various lines, but their individuality shall be faithfully recorded once for all, are an absolute necessity before much further progress can be made in the research; while, from what has been stated in my former paper, it is clear that for this purpose volatilization of the vapours of the metals in the electric arc is necessary, as by this means the densest vapour can readily be procured. I have therefore rendered the vapours I have investigated incandescent by a current from a battery of 30 pint GROVE'S cells.

The difficulties of eye-observations were found to be very great, not only in identifying the lines, but in retaining their characteristics in the memory until a record of length, thickness, and brilliancy could be placed on paper. Further, I have determined that when it is a question of mapping the various characteristics of the lines which the new method reveals in the spectrum of the vapour of a metal in the electric arc, and not the position only, on an average ten lines an hour is the progress made. At this rate the work I have proposed to execute would be interminable. I have therefore attempted to bring in the aid of photography.

But there was another reason. I have long had cause to think that many, if not all, of the coincidences which ÅNGSTRÖM, THALÉN, and others have chronicled—coincidences which made the allocation of the FRAUNHOFER lines so difficult and, worse still, doubtful—had no real physical existence, but resulted from impurities; and it seemed to me that this question could be at once settled by confronting photographs of the spectra of those vapours in which the coincidences have been recorded; because if the coincidences were due to impurities, the lines would be longest and thickest in the spectrum to which they really belonged.

The portion of the spectrum on which the attempt has at present been made is that from H to F. I may add that I have grounds for supposing that the least refrangible part of the spectrum thus left unrecorded is, in the case of the metallic elements, the least important one to study, and that I am making arrangements for photographing the part of the spectrum more refrangible than H.

I have been fortunate enough not only to devise a very convenient method of thus confronting spectra, but of applying it under almost the best possible conditions, since, by the kindness of Dr. FRANKLAND, I have been permitted the use of a room in his laboratory, where I have been enabled to photograph the spectra of the vapours of the solar metals, confronting these spectra with the solar spectrum and the spectra of other allied metals on the same plate.

As this branch of the research has necessitated the use of a battery of 30 or 40 cells, it would have been impossible to carry it on in my dwelling-house, where all my previous work has been conducted.

The construction of a Table of all the named FRAUNHOFER lines, showing the length and thickness of the lines of the metallic vapours to the absorption of which they are probably due, has also been taken in hand. This Table enabled me, before the photographic work was commenced, to allocate upwards of 50 lines in the solar spectrum, which had, I presume, been overlooked by ÅNGSTRÖM and THALÉN.

It is, however, incomplete, inasmuch as I was not in a position to record the lengths of all the lines of iron and titanium with the induction-spark; and since the photographic work has been going on such a flood of light has been thrown on the true origin of so many of the unnamed FRAUNHOFER lines, that the Table in question may be said to be already useless for the part of the spectrum from H to F.

This Table was made as a preliminary to the construction, on a much larger scale than ÅNGSTRÖM'S, of a new photographic map of the part of the spectrum from H to F, in which

I proposed to myself to attempt to clear away all difficulties touching coincidences, and to give below it complete maps of all the solar elements with the long and short lines, showing at a glance, therefore, those which are and are not reversed at the present epoch. I am glad to say that the map is making good progress.

I have also commenced a preliminary search for other elements in the sun; and this has necessitated an inquiry into the absorption-spectra of the metalloids by means of photography, which is not yet complete.

Of the above-named branches of the research I propose on the present occasion to refer more particularly to the following:—

I. The experiments made on a possible quantitative spectrum-analysis.
II. The method of photographing spectra.
III. The coincidences of spectral lines.
IV. The preliminary inquiry into the existence of elements in the sun not previously traced.

I. THE EXPERIMENTS MADE ON A POSSIBLE QUANTITATIVE SPECTRUM-ANALYSIS.

Some time ago I gave an account of some experiments with some tin and magnesium amalgams, and I remarked[*]:—"It is possible to begin with an alloy which shall only give us the longest line or lines in the spectrum of the smallest constituent, and by increasing the quantity of this constituent the other lines can be introduced in the order of their length. This reaction is so delicate that I learnt from it a thing I had not before observed, that the least refrangible line of *b*, the triple line of magnesium, is really a little longer than its more refrangible companion; for the spectrum of magnesium was reduced to this one line in an alloy in which special precautions had been taken to introduce the minimum of magnesium.

"It follows from this statement that not only is the spectrum-analysis almost infinitely more delicate than it has hitherto been supposed to be in the case of the elements in which the difference between the longest and the shortest lines is least[†], but that in time it may become quantitative." On a second occasion[‡] I went further and laid before the Society for their inspection maps of the spectra of certain alloys, pointing out that the lines of any constituent of a mechanical mixture disappeared from the spectrum as its percentage was reduced.

After the second paper was sent in to the Royal Society I commenced a series of observations, the object of which was to study not only the disappearance of the lines, but other general changes which might supervene; and for this purpose I mounted a micrometer eyepiece on the observing-telescope of the spectroscope. This enabled me

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[*] Philosophical Transactions, 1873, p. 261.

[†] "The great lengths of the lines of sodium, lithium, &c. at once account for the delicacy of their spectrum reactions."

[‡] Philosophical Transactions, 1873, p. 655.

to notice the following additional phenomena, in which a change in the lines which remained was brought about by a change of composition.

I. The lines varied in their lengths as the percentage of the element to which they were due varied.

II. Some of the lines appreciably varied in their thickness and brightness, or both, in the same way.

III. In cases where the brightness of a line was estimated through a considerable range of percentage composition by comparison with an air-line, the latter was observed to grow faint and then to disappear when the brightness of the line compared with it increased.

IV. In cases where the brightness or thickness of the line of one element was estimated by comparison with the adjacent line of the other constituent of the alloy, the point of equal brightness was observed to ascend or descend (I used this method in order to avoid the uncertainty of micrometric measurements of the tips of the lines in consequence of their variation in length due to the unequal action of the spark).

V. In some cases where the percentage of a constituent was so small that none of its lines were visible, there yet seemed to be an effect produced upon the lines of the other constituent as compared with those of the spectrum of the same vapour of the opposite pole.

These conclusions were derived from observations of the alloys which I had made in the manner indicated in my second paper; and I saw that it would be important to observe series in which the change of percentage composition between the specimens was not so great, and of which actual assays had been made.

I therefore begged Mr. C. FREEMANTLE, the Deputy Master of the Mint, to allow me the use of specimens of the gold-copper and silver-copper alloys prepared for the coinage, as in them I had exactly what the research required—namely, ranges with small variations and of undoubted accuracy. I have here to express my deep obligations to that gentleman, who at once, with the greatest promptitude and courtesy, acceded to a request made to him in the interests of science.

Before, however, I proceed to consider the cases of the Mint alloys, it will be well to briefly notice some experiments with alloys in which the variations in the proportions of constituents were greater.

As an instance of a moderately small difference, an attempt was made with a portion of a half-sovereign to which $\frac{1}{1000}$ of its weight of copper was added. This was compared with another portion of the same coin; but no difference was detected, possibly on account of a failure in making an alloy on so small a scale without some loss of the smaller and more oxidizable constituent.

An alloy of 5·5996 grms. lead and 0·6221 grm. silver was then made, the silver being dissolved in the lead, which was fused in a bent hard-glass tube in a current of hydrogen.

The percentage composition of this alloy was 89 per cent. lead and 11 per cent. silver. The silver lines at w. l. 5470, 5464, 5209 were recognized in its spectrum, and another line at 5401 was uncertain.

The opposite pole was composed of some supposed pure lead, and it was observed that its lines were longer than those of the lead in the alloy. A very faint line was observed in its spectrum opposite to the silver line 5290; but this was most probably the faint lead line 5206, as the longer silver lines did not exhibit themselves in its spectrum.

The opposite pole was now replaced by one of common sheet lead (it had at first been pure assayers' sheet), and the line in question was not stronger than in the pure lead; hence it was almost certainly the line 5206 of lead.

In order to see how much silver was required to render its spectrum visible, and as the common sheet lead was suspected to contain traces of silver, an alloy was made which contained 0·01 per cent. of silver. In this no silver lines were visible; and the same result appeared when ·05 per cent. silver was alloyed with the lead. The same was the case when 0·11 per cent. was added; and even the use of a large jar failed to cause the silver lines to appear.

Finally, an alloy containing 1·0 per cent. was made, and in this the silver lines appeared very distinctly, and three in number; 5464 was the longest, 5209 next, and 5470 the shortest.

Another alloy with 0·5 per cent. was now made, and in this the two lines of silver at w. l. 5464, 5209 were at last discovered, but they were very short and faint. Continued work showed that the line 5464 dies out between ·05 per cent. and 0·2 per cent. of silver (for it was at last discovered in the ·05 per cent. alloy), and also convinced me of the extreme irregularity of the various portions of the alloy, though they had been made with the greatest accuracy which the means at my command permitted.

Experiments were also made with alloys of tin and cadmium, the latter forming 0·154 per cent. of the alloy. The longest cadmium line at w. l. 5085 alone remained permanently visible, exceedingly faint, but unchanged in length; it had a short bright stump. When the line at w. l. 4799 was observed it appeared as a stump only, and neither 4677 nor any other cadmium lines could be found. Another alloy of tin with 1·0 per cent. cadmium showed 5085 distinct and bright, as was 4799; 4677 was likewise distinctly visible, and the tip of the least refrangible winged line 5377 commenced to appear. The other winged cadmium line, 5338, could not be identified, as it is nearly coincident with a tin line. After this, with the increased percentages of 5 per cent. and 10 per cent. of cadmium, the effect was mainly to lengthen and brighten the longest lines.

In order to determine whether these results would be affected by the presence of other metals in the alloy, one was made of 89·11 per cent. lead, 9·90 per cent. zinc, ·09 per cent. cadmium, and 0·85 per cent. tin; and the cadmium line showed no appreciable difference from its appearance in an alloy containing 0·1 per cent. cadmium with 99·9 per cent. of a single other metal.

In the Mint specimens with their small variations I found the same phenomena *en* *petit* which I was already familiar with *en grand*, and the smaller variations in the phenomena enabled me to understand them better.

I found that in the gold-copper standards an increase of a 1000th part in the gold brought the lines down, while a similar increase in the copper carried them up, *i. e.* increased the height of the vapour from the pole.

I found, on the other hand, that in the silver-copper standards an increase of a 1000th part in the silver carried the lines up, while a similar increase in the copper brought them down in the field of view, *i. e.* reduced the height of the vapour from the pole.

After registering these facts, I saw at once that all the phenomena might be explained by assuming a change of volatility; by assuming, in fact, that alloys differing a 1000th part are different physical things, and that the spark acts upon the alloy as a whole as well as upon each vapour separately.

Thus in the cases referred to, in which copper is common to both, we find the melting-points to be as follows:—

Gold . . . 1200° (POUILLET).
Copper between 1200° and 1000°, precise point not determined.
Silver . . . 1000° (POUILLET).

And the intermediate position which copper occupies at once explains the different actions on its lines brought about by the addition of gold and of silver.

II. THE METHOD OF PHOTOGRAPHING SPECTRA.

The camera employed in the attempts already made is one for the use of which I am indebted to Lord LINDSAY. It is furnished with a 3-inch lens by DALLMEYER, of about 23 inches focal length, and carries a plate 5×5 inches. The camera has replaced the observing-telescope of the spectroscope described in my former paper. Three prisms of 45° and one of 60° have been employed.

With these arrangements the whole spectrum from beyond H to the red falls upon a 5-inch plate. In order to show how abundantly qualified the lens used is for its work, I may state that the solar spectrum from w. l. 3900·0 to 4500·0 has been obtained at once in tolerably fair focus.

In order to obtain photographs of the solar spectrum of the very best kind, it is necessary to limit the beam passing through the prisms to very small dimensions—a method employed with such admirable results by Mr. RUTHERFURD.

In the attempts to photograph the long and short lines of metallic spectra, it was found that this object could not be well obtained with the electric lamp in its usual position (with vertical poles), as the central column of dense vapour, as a rule, extended across the arc, *i. e.* from pole to pole, and gave all the short lines.

In order to obviate this I determined to make use of a horizontal arc. This was accomplished by placing the lamp on its side and firmly securing it in that position. The image of the horizontal arc was then thrown on the vertical slit in the usual manner. This method was found to be perfectly successful. The central portion of the spectrum due to the dense core of the arc is found to consist of all the lines which this part of the arc alone can give, the longer lines given by the outer less dense strata extending beyond the spectrum of the core to the various distances from the centre to which the vapour capable of giving them extends. (See Plate XL.)

The lines thus photographed are pointed at either end, and disappear from the centre in the order of their length, so that a double or duplicate determination exquisitely symmetrical of their lengths is thus obtained.

Although the lengths, thicknesses, and intensities of the lines are thus readily recorded, we have so far no scale by which to fix their positions. In order to obviate this objection, I resolved to photograph the solar spectrum on each plate immediately above or below the metallic spectrum under examination. To accomplish this an extension of the ordinary method of working was introduced, depending upon the following considerations.

It is obvious that when we observe a spectrum its breadth will depend upon the length of the slit. If we could at the same time illuminate different portions of the slit with rays proceeding from different vapours, the spectra of the different light-sources could be seen at once. But we cannot do this. What we can do when we introduce photography is to illuminate *successively* different portions of the slit, the effect being that on different portions of the photographic plate the various spectra will successively record themselves.

Acting on this principle I first covered up the upper half of the slit, allowing the image of the horizontal arc to fall centrally on the slit, so that in this way I got impressed an image of half the thickness of the horizontal arc. After this was accomplished I covered up the half of the slit first used, opening that which was previously closed, and through this newly opened portion I admitted sunlight. But to do this effectively certain precautions were necessary. A description of the method used will show how these have been taken.

The laboratory in which the work has been carried out has two windows, one nearly due (magnetic) south, the other nearly (magnetic) west. Outside each window level slate slabs have been erected as supports for a heliostat. Either window can be used at pleasure. The spectroscope is supported on a platform on rollers, the height of the platform being such that the horizontal beam from the heliostat is coincident with the axis of the collimator. In addition to the lens placed between the lamp and the slit to throw an image of the arc on the latter, another lens is now introduced between the heliostat and the lamp—heliostat, lenses, lamp, and collimator being of course in the same straight line. The action of the newly interpolated lens is to throw an image of the sun between the poles of the lamp, so that when the spectrum of the arc is properly focused by the camera lens on to the photographic plate, the solar spectrum, when subsequently thrown in, is also in focus.

By these means we not only obtain a photographic record of the long and short lines with the individuality of each, but we get the solar spectrum as a scale.

The accompanying diagrams show the arrangements adopted in the cases mentioned.

Fig. 1.—Arrangement for obtaining solar spectrum alone.

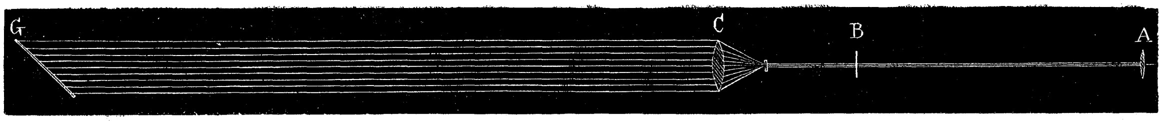


Fig. 2.—Arrangement for obtaining long and short lines.

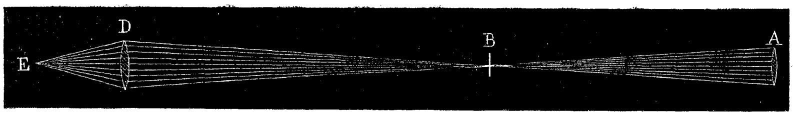
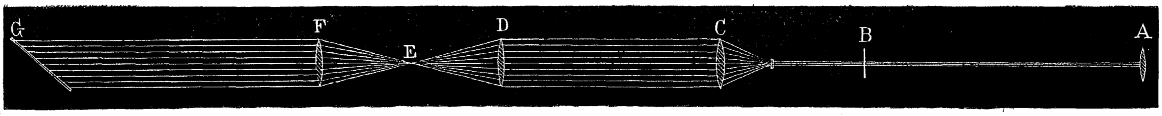


Fig. 3.—Arrangement for obtaining and comparing lines with solar spectrum.



A, collimating lens; B, slit; C, opera-glass; G, heliostat; D, lens; E, poles; F, lens throwing image of sun between poles.

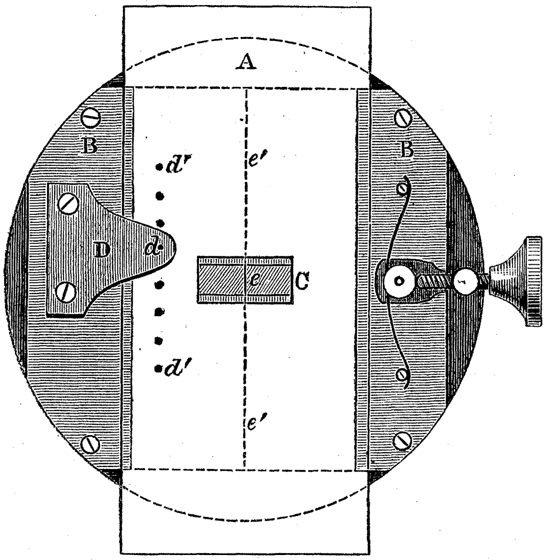
In that branch of the research which deals with the causes of the coincidences of the lines in the various spectra, it is not absolutely essential that we should refer the lines to the solar spectrum each time; thus if we study the cases of aluminium and calcium impurities, it is better to photograph the suspected spectra side by side and confront them.

To do this all that is necessary is to extend the application of the principle already referred to. In fact the only practical limit to the number of spectra we can get on to one plate is the time the plate takes to dry, and instead of uncovering half of the slit at one time we may uncover any smaller portion. (See Plate XXXIX.)

This I have effected by means of a brass shutter with a square opening cut through it, which slides in grooves in front of and up and down the slit. On one side of the shutter holes are bored, the distance between each hole being the same as the height of the opening in the shutter. A short pin fixed to a spring falls into each hole in succession as the shutter is moved up or down, and so ensures that there shall be neither superposition of spectra nor gaps between them. The accompanying diagram (fig. 4) will make the arrangement quite clear.

I find that, by the use of the shutter, four or more spectra showing positions and thicknesses (but not lengths of the lines) can readily be obtained on one plate; and by having the solar spectrum in the middle it serves as a scale (Plate XXXVIII.). Such spectra directly compared are shown in the accompanying Plates (XXXVIII.-XL.).

Fig. 4.—Slit plate with sliding shutter (actual size).



A, shutter; B B, grooves in which it slides; C, opening; D *d*, spring; *d'*, holes to regulate motion of shutter; *e*, slit seen through opening; *e'*, slit behind shutter.

III. ON THE COINCIDENCES OF SPECTRAL LINES.

In former references to this subject I have shown:—

1st. That the lines of metallic spectra do not all extend to the same distance from the pole which is emitting the light. In other words, some lines are short, others are long.

2nd. That in those cases where in the solar spectrum the whole number of lines given by a metal do not appear, those that do thus appear are the longest lines.

3rd. That it was possible to ascertain roughly by the number of lines left in a spectrum when a metal was alloyed, the percentage of it existing in the alloy.

4th. That greater tension of the incandescent vapour giving a spectrum would probably increase the number of lines in a spectrum.

The examination of the various spectra of metals and alloys undertaken in connexion with these researches afforded evidence not only of the great impurity of most of the metals used, but of the fact that many, if not all, of the coincidences observed by THALÉN and others might be explained in the light of former work.

An examination of ÅNGSTRÖM'S map of the solar spectrum shows many cases in which a line has been observed to be common to two or more spectra; and this is especially the case with the lines of iron, titanium, and calcium, nearly every other solar metallic spectrum exhibiting one or more cases of coincidence with the latter.

Now it is first to be remarked that these cases of coincidence can scarcely be accidental.

In those cases which have been examined, it has frequently been found that a line coincident in different spectra is long and bright in only one of them, and that in others it is short, or faint, or both; or it may even, in certain specimens of the substances, be altogether absent from the spectrum.

As an instance of this difference of behaviour, the following cases in the spectra of calcium and strontium may be considered. The numbers are wave-lengths taken from THALÉN'S list.

The longest line in the visible portion of the calcium spectrum, wave-length 4226·3, is found in the strontium spectrum as a line of medium length. 4607·5, one of the longest lines of strontium, appears in the calcium spectrum as a short line.

Another very long line of strontium occurs at 4215·3, in close proximity to the longest calcium line, and, according to THALÉN, occurs also in the spectrum of that metal.

I have, however, never, until lately, succeeded in obtaining any evidence of its presence in the calcium spectrum; but there is evidence to show that the metal I employed was very pure.

We have here, then, two metals with two lines common to their spectra; and it is found that the line which was long and bright in one spectrum, is faint in the other; and with regard to a third line, one observer finds it in both spectra, the other in one only, and after many attempts succeeds in observing it in the second, *but only in a specimen known to be contaminated with the first.*

The simplest explanation of the case, bearing in mind the facts already established in my first paper, is that the calcium used to produce the spectrum was contaminated to a certain extent with strontium, the strontium in turn containing calcium, a state of things which a moment's consideration will show to be not only possible but most probable, the close chemical relation of the two metals, and the extreme difficulty of making even an approximate separation when mixed, being well known.

Even if we knew nothing of the probability of mixture occurring in the cases of the two metals in question, the behaviour of the line at w. l. 4215·3 is sufficient to show what is the true cause of the coincidences.

The longest lines of calcium at wave-lengths 4226, 3968, and 3933 occur also in iron, cobalt, nickel, barium, &c., and assume very considerable proportions, equalling or surpassing in length many undoubted lines of those elements; on the other hand, the iron lines at wave-lengths 4071, 4063, and 4045 occur in calcium, strontium, and barium, and in other metals.

Again, the longest lines of aluminium at wave-lengths 3961 and 3943 occur usually in the spectrum of iron as longish lines, and are to be found in the spectra of cobalt, nickel, calcium, strontium, and barium, and in other metals, where they are even longer than some of the true lines of the metals in which they occur.

As a result of these considerations the following general statements may be hazarded, premising that it is possible that further inquiry may modify them.

1st. If the coincident lines of the metals are considered, those cases are rare in which the lines are of the first order of length in all the spectra to which they are common:

those cases are much more common in which they are long in one spectrum and shorter in the others.

2nd. As a rule, in the instances of those lines of iron, cobalt, nickel, chromium, and manganese which are coincident with lines of calcium, the calcium lines are long, while the lines as they appear in the spectra of the other metals are shorter than the longest lines of those metals. Hence we are justified in assuming that short lines of iron, cobalt, nickel, chromium, and manganese, coincident with long and strong lines of calcium, are really due to traces of the latter metal occurring in the former as an impurity.

3rd. In cases of coincidences of lines found between the lines of various spectra the line may be fairly assumed to belong to that one in which it is longest and brightest.

In order to show what a fair promise there is that all these questions will in time be set at rest by photography, and set at rest in the direction I have indicated, I beg permission to refer to one of the very earliest photographs taken by the method which has been described in a former part of this paper. It is a confronting of the spectra of the metals calcium and strontium.

A simple comparison of the two spectra shows that there are three strong and thick lines common to the two at w. l. 3968, 3943, the two H lines, and 4226·3, the large calcium line near G. The spectrum of strontium shows three lines which are very much thicker than the corresponding lines in the (calcium) spectrum; they are situated near wave-lengths 4029 and 4077 and at 4215·3. The latter line has been ascribed by THALÉN to calcium, and is coincident with a strong solar line. An inspection of the photograph, however, at once showed me that this line is really a strontium line, since it is thickest in the spectrum of that metal; so that this single plate was at once sufficient, in the light of these researches, to establish the presence of strontium in the reversing layer of the sun.

It is seen, then, that a comparison of a photograph of any spectrum with the photographs of the other spectra in which coincident lines occur, will be sufficient to show to which spectrum a disputed line belongs. It will be also noticed that the three calcium lines first mentioned are nearly as thick in the lower (strontium) spectrum as in that of calcium itself, while the difference between the thick lines of strontium and the corresponding lines also visible in the calcium spectrum is very great. All these facts are easily explained on the supposition that the calcium was very much less impregnated with strontium than the strontium with calcium. In fact I had such faith in the efficacy of the method, and in the opinion that coincidences are merely due to impurities, that I did not even consider it necessary to change the poles, but proceeded at once to place the strontium salt on that which had just before served for the ignition of the calcium. This at once accounts for the greater impurity of the former. In nearly pure strontium the same lines are seen, but they are then thinner and shorter.

I may remark that the lines at 4045, 4063, and 4071 are due to an iron impurity; these are the longest lines of iron in that portion of the spectrum photographed.

I may conclude this statement by remarking that the above facts have been given as instances of the results to be obtained by the confronting of the spectrum of each solar metal with every other, a task which it will be necessary to accomplish before the Table and Maps referred to can be presented to the Royal Society.

IV. PRELIMINARY INQUIRY INTO THE EXISTENCE OF ELEMENTS IN THE SUN NOT PREVIOUSLY TRACED.

In a paper communicated to the Royal Society on December 12, 1872 (Phil. Trans. 1873, p. 253), I have shown that the test formerly relied on to decide the presence or absence of a metal in the sun (namely, the presence or absence of the brightest and strongest lines of the metal in question in the average solar spectrum) was not a final one, and that the true test was the presence or absence of the longest lines of the metal, this longest line being that which remains longest in the spectrum when the pressure of the vapour is reduced.

Of the test in question I have said, in the paper already mentioned, "It is one, doubtless, which will shortly enable us to determine the presence of new materials in the solar atmosphere, and it is seen at once that to the last published table of solar elements (that of THALÉN) must be added zinc, aluminium, and possibly strontium as a result of the new method."

In order to pursue the inquiry under the best conditions, complete maps of the long and short lines of all the elements are necessary. It was, however, not absolutely necessary for the purposes of a preliminary inquiry to wait for such a complete set of maps, for the lists of lines given by the various observers may be made to serve as a means of differentiating between the longest and shortest lines, because I have also shown that the lines given at a low temperature, by a feeble percentage composition, or by a chemical combination of the vapour to be observed are precisely those lines which appear longest when the complete spectrum of the pure dense vapour is studied.

Now with regard to the various lists and maps published by various observers, it is known (1) that very different temperatures were employed to produce the spectra, some investigators using the electric arc with great battery-power, others the induction-spark with and without the jar; (2) that some observers employed in certain cases the chlorides of the metals the spectra of which they were investigating, others used specimens of the metals themselves.

It is obvious, then, that these differences of method could not fail to produce differences of result; and accordingly, in referring to various maps and tables of spectra, we find that some include large numbers of lines omitted by others. A reference to these tables, in connexion with the methods employed, shows at once that the large lists are those of observers using great battery-power or metallic electrodes, the small ones those of observers using small battery-power or the chlorides. If the lists of the latter class of observers be taken, we shall have only the longest lines, while those omitted by them and given by the former class will be the shortest lines.

In cases, therefore, in which I had not mapped the spectrum by the new method of observation referred to in my paper, I have taken the longest lines as thus approximately determined; for it seemed desirable, in view of the very large number of unnamed lines, to search at once for the longest elemental lines in the solar spectrum without waiting for a complete set of maps.

A preliminary search having been determined on, I endeavoured to get some guidance by seeing if there was any quality which differentiated the elements already traced in the sun from those not traced; and to this end I requested my assistant, Mr. R. J. FRISWELL, to prepare two lists showing broadly the chief chemical characteristics of the elements traced and not traced. This was done by taking a number of the best known compounds of each element (such, for instance, as those formed with oxygen, sulphur, chlorine, bromine, or hydrogen), stating after each whether the compounds in question were unstable or stable. Where any compound was known not to exist, that fact was indicated.

Two Tables were thus prepared, one containing the solar, the other the more important non-solar elements (according to our knowledge at the time).

These Tables gave me, as the differentiation sought, the fact that in the main the known solar elements formed stable oxygen-compounds.

I have said in the main, because the differentiation was not absolute; but it was sufficiently strong to make me commence operations by searching for the outstanding strong oxide-forming elements in the sun.

The result up to the present time has been that *strontium*, *cadmium*, *lead*, *copper*, *cerium*, and *uranium**, in addition to those elements in THALÉN'S last list, would seem with considerable probability to exist in the solar reversing layer. Should the presence of *cerium* and *uranium* be subsequently confirmed, most of the iron group of metals will thus have been found in the sun.

As another test, certain of those elements which form unstable compounds with oxygen were also sought for, gold, silver, mercury being examples. None of these were found.

The same result occurred when the lines due to the jar-spark taken in chlorine, bromine, iodine, and those of some of the other non-metals were sought, these being distinguishable as a group by formation of compounds with hydrogen.

Now other researches, not yet completely ready for publication, have led me to the following conclusions:—

I. The absorption of some elementary and compound gases is limited to the most refrangible part of the spectrum when the gases are rare, and creeps gradually into the visible violet part, and finally to the red end of the spectrum, as the pressure is increased.

II. Both the general and selective absorption of the photospheric light are greater (and therefore the temperature of the photosphere of the sun is higher) than has been supposed.

III. The lines of compounds of a metal and iodine, bromine, &c. are observed generally in the red end of the spectrum, and this holds good for absorption in the case of aqueous vapour.

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* Potassium has since been added.

Such spectra, like those of the metalloids, are separated spectroscopically from those of the metallic elements by their columnar or banded structure.

IV. There are, in all probability, no compounds ordinarily present in the sun's reversing layer.

V. When a metallic compound vapour, such as is referred to in III., is dissociated by the spark, the band spectrum dies out, and the elemental lines come in, according to the degree of temperature employed.

Again, although our knowledge of the spectra of stars is lamentably incomplete, I gather the following facts from the work already accomplished with marvellous skill and industry by SECCHI of Rome.

VI. The sun, so far as the spectrum goes, may be regarded as a representative of class (β) intermediate between stars (α) with much simpler spectra of the same kind and stars (γ) with much more complex spectra of a different kind.

VII. Sirius, as a type of α, is (1) the brightest (and therefore hottest?) star in our northern sky; (2) the blue end of its spectrum is open; it is only certainly known to contain hydrogen, the other metallic lines being exceedingly thin, thus indicating a small proportion of metallic vapours; while (3) *the hydrogen lines in this star are enormously distended*, showing that the chromosphere is largely composed of that element.

There are other bright stars of this class.

VIII. As types of γ the red stars may be quoted, the spectra of which are composed of channelled spaces and bands, and in which naturally the blue end is closed. Hence the reversing layers of these stars probably contain metalloids, or compounds, or both, in great quantity; and in their spectra not only is hydrogen absent, but the metallic lines are reduced in thickness and intensity, which in the light of V., *antè*, may indicate that the metallic vapours are being *associated.* It is fair to assume that these stars are of a lower temperature than our sun.

I have asked myself whether all the above facts cannot be grouped together in a working hypothesis which assumes that in the reversing layers of the sun and stars various degrees of "celestial dissociation" are at work, which dissociation prevents the coming together of the atoms which, at the temperature of the earth and at all artificial temperatures yet attained here, compose the metals, the metalloids, and compounds.

On this working hypothesis, the so-called elements not present in the reversing layer of a star will be in course of formation in the coronal atmosphere and in course of destruction as their vapour-densities carry them down; and their absorption will not only be small in consequence of the reduced pressure of that region, but what absorption there is will probably be limited wholly or in great part to the invisible violet end of the spectrum in the case of such bodies as the pure gases and their combinations and chlorine (see I. *antè*).

The spectroscopic evidence as to what may be called the plasticity of the molecules of the metalloids, including of course oxygen and nitrogen, but excluding hydrogen, is so overwhelming, that even the absorption of iodine, although generally it is transparent to violet light, may (as I have found in a repetition of Dr. ANDREWS's experiments on the dichroism of iodine, in which I observed the spectrum) in part be driven into the violet end of the spectrum, for iodine in a solution in water or alcohol at once gives up its ordinary absorption properties and stops violet light[*].

A preliminary comparison of the ordinary absorption-spectrum of a stratum of 6 feet of chlorine renders it not improbable that chlorine at a low temperature is the cause of some of the FRAUNHOFER lines in the violet, although, as said before, I have not yet obtained certain evidence as to the reversal of the bright lines of chlorine seen in the jar-spark.

There is also an apparent coincidence between some of the faint FRAUNHOFER lines and some of the lines of the low temperature absorption-spectrum of iodine.

Should subsequent researches strengthen the probability of this working hypothesis, it seems possible that iron meteorites will be associated with the metallic stars and stony meteorites with metalloidal and compound stars. Of the iron group of metals in the sun, iron and nickel are those which exist in greatest quantity, as I have determined from the number of lines reversed. Other striking facts, such as the presence of hydrogen in meteorites, might also be referred to.

An interesting physical speculation connected with this working hypothesis is the effect on the period of duration of a star's heat which would be brought about by assuming that the original atoms of which a star is composed are possessed with the increased potential energy of combination which this hypothesis endows them with. From the earliest phase of a star's life the dissipation of energy would, as it were, bring into play a new supply of heat, and so prolong the star's light.

May it not also be that if chemists take up this question which has arisen from the spectroscopic evidence of what I have before termed the plasticity of the molecules of the metalloids taken as a whole, much of the power of variation which is at present accorded to metals may be traced home to the metalloids? I need only refer to the fact that, so far as I can learn, all so-called changes of atomicity take place when metalloids are involved, and not when metals alone are in question.

As instances of these, I may refer to the triatomic combinations formed with chlorine, oxygen, sulphur, &c. in the case of tetrad or hexad metals.

May we not from these ideas be justified in defining a metal, provisionally, as a substance, the absorption-spectrum of which is *generally* the same as the radiation-spectrum, while the metalloids are substances the absorption-spectrum of which, generally, is not the same? In other words, in passing from a cold to a comparatively hot state, the plasticity of these latter comes into play, and we get a new molecular arrangement. Hence are we not justified in asking whether the change from oxygen to ozone is but a type of what takes place in all metalloids?

My best thanks are due to Mr. R. J. FRISWELL for the valuable aid he has afforded me in these investigations.

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[*] I have since obtained the same result by observing the absorption of I vapour in a white-hot tube.

Explanation of the Plates.

PLATE XXXVIII.

Illustrating use of slit plate.

Comparison of the spectra of Calcium and Barium with the solar spectrum.

Upper spectrum	Barium,	H to beyond G.
Middle ,, ...	Solar	,, ,, ,,
Lower ,, ...	Calcium	,, ,, ,,

Note.—The Calcium contains Aluminium, Strontium, and Iron as impurities. The barium contains the same impurities in addition to calcium.

PLATE XXXIX.

Illustrating use of slit plate.

Confronting of spectra of Manganese, Nickel, Lenarto meteorite, and Iron containing calcium and other impurities.

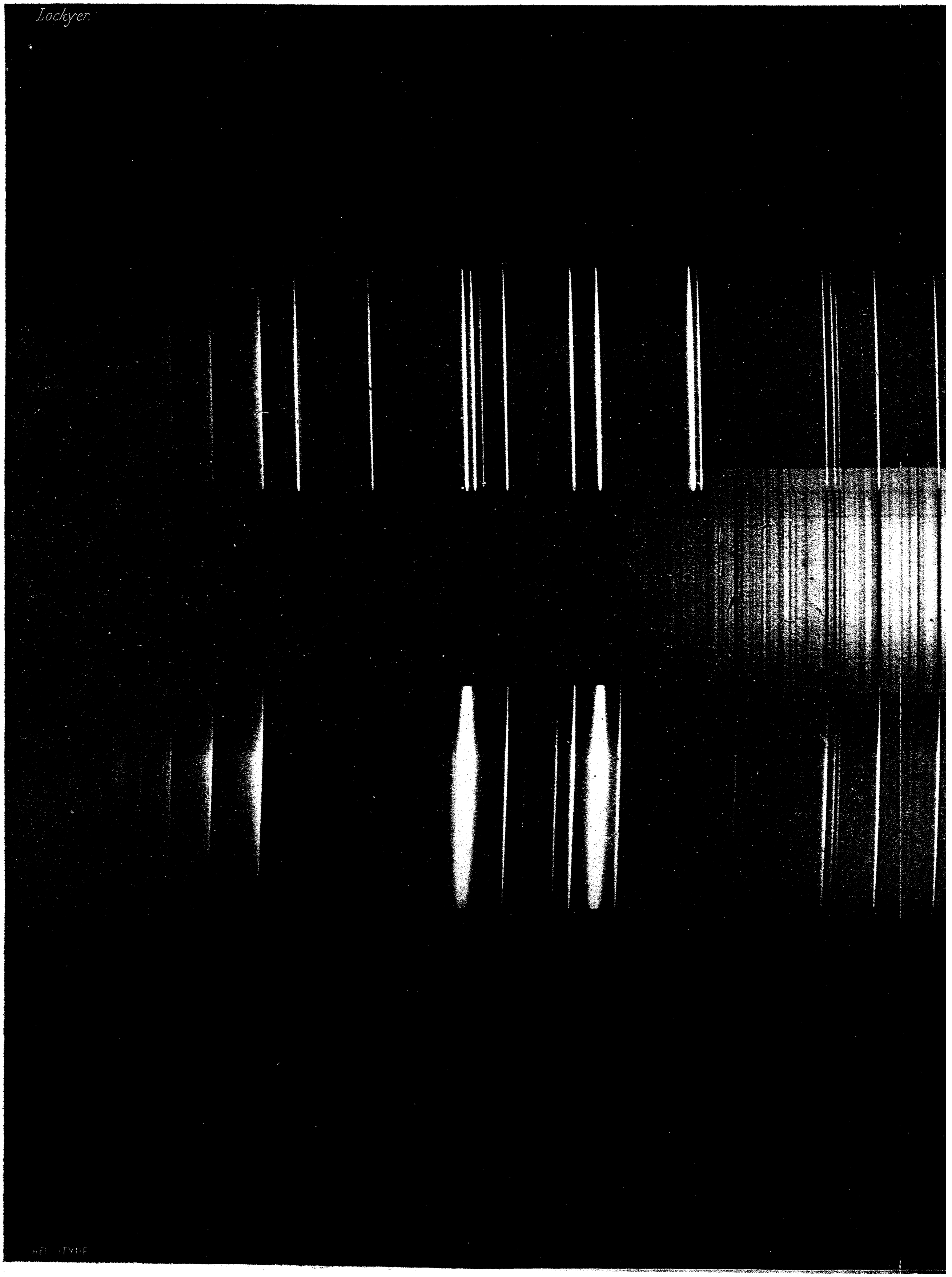
Upper spectrum	Manganese . .	H to beyond G.
	Nickel . . .	,, ,, ,,
	Lenarto meteorite	,, ,, ,,
Lower ,, ...	Impure iron .	,, ,, ,,

Note.—The Manganese spectrum includes the longest lines of Calcium, Aluminium, and Iron. Nickel shows the same impurities in addition to manganese, while the longest nickel lines are to be traced in the spectrum of the Lenarto meteorite.

PLATE XL.

Illustrating use of horizontal arc.

Long and short lines near F of impure iron. The lower part gives the spectrum of the core of the arc; the upper part the spectrum of the extreme limits of the vapour.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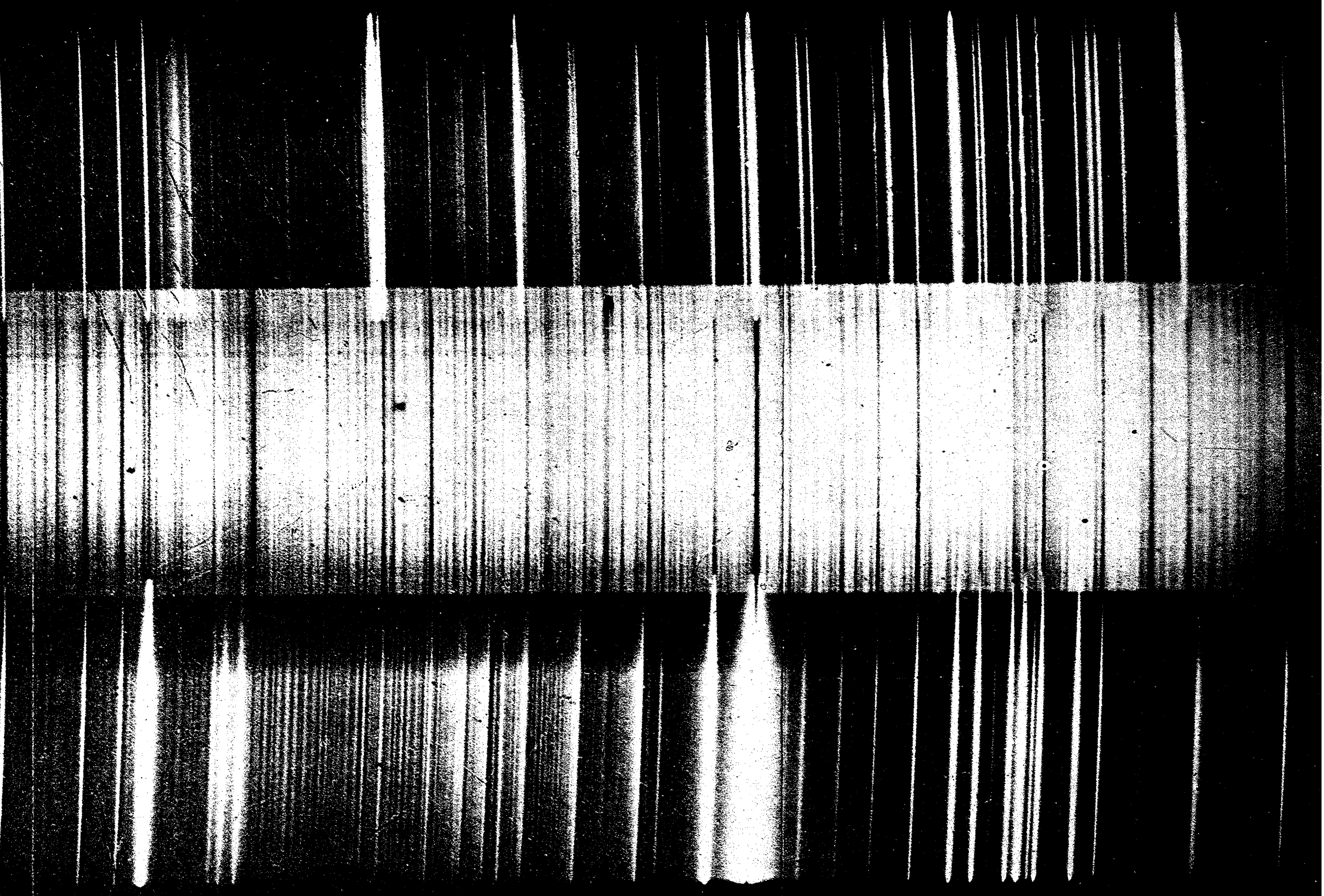
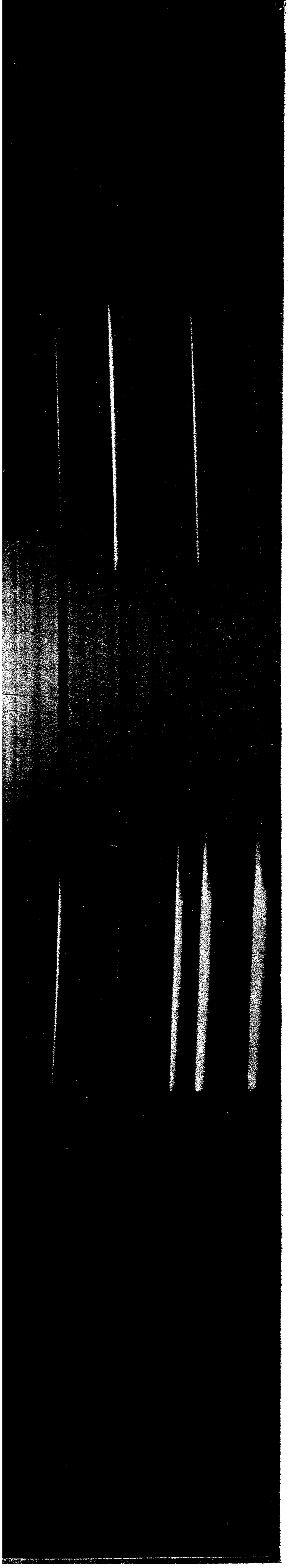
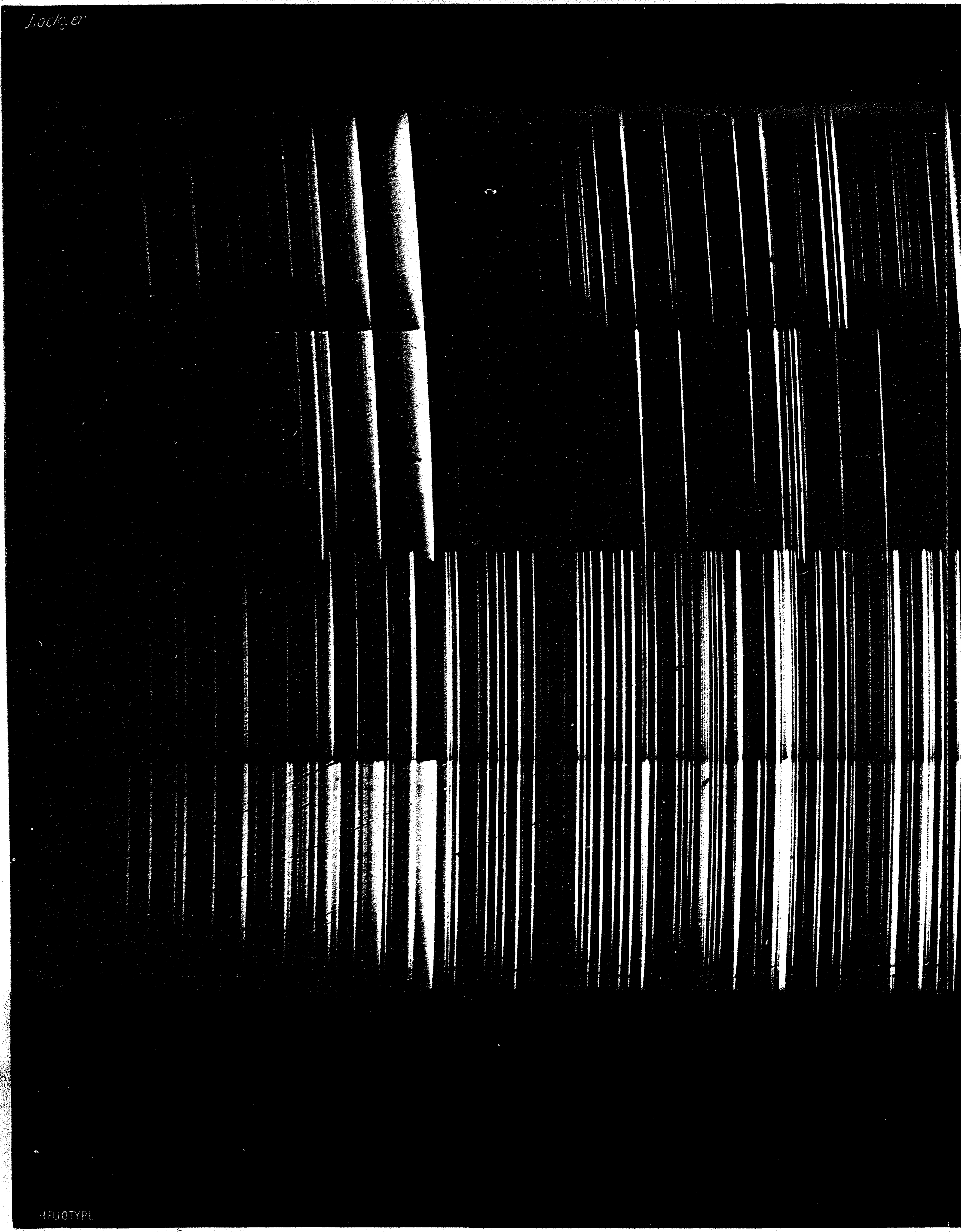


CLXXIV. *Plate* XXXIV.

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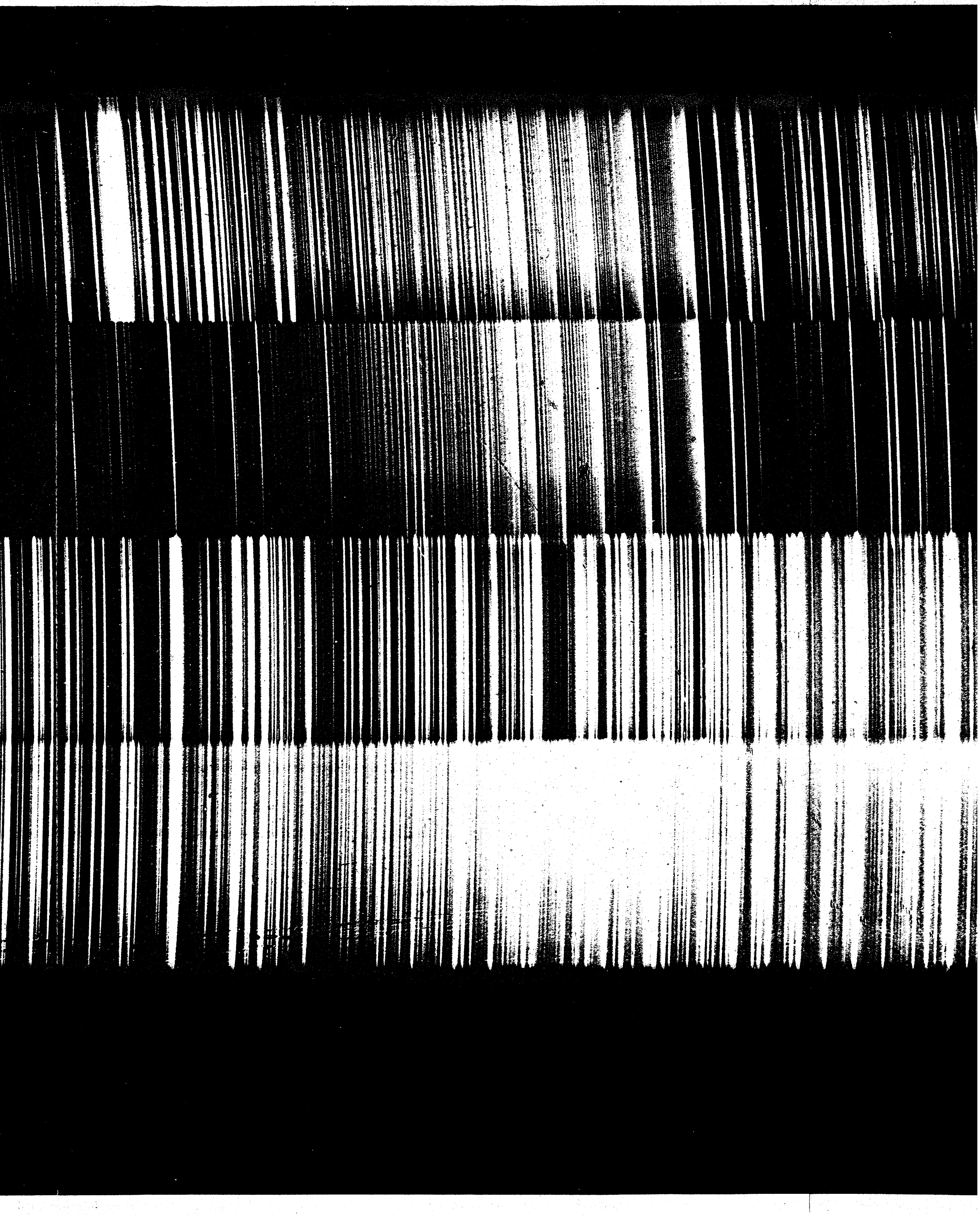

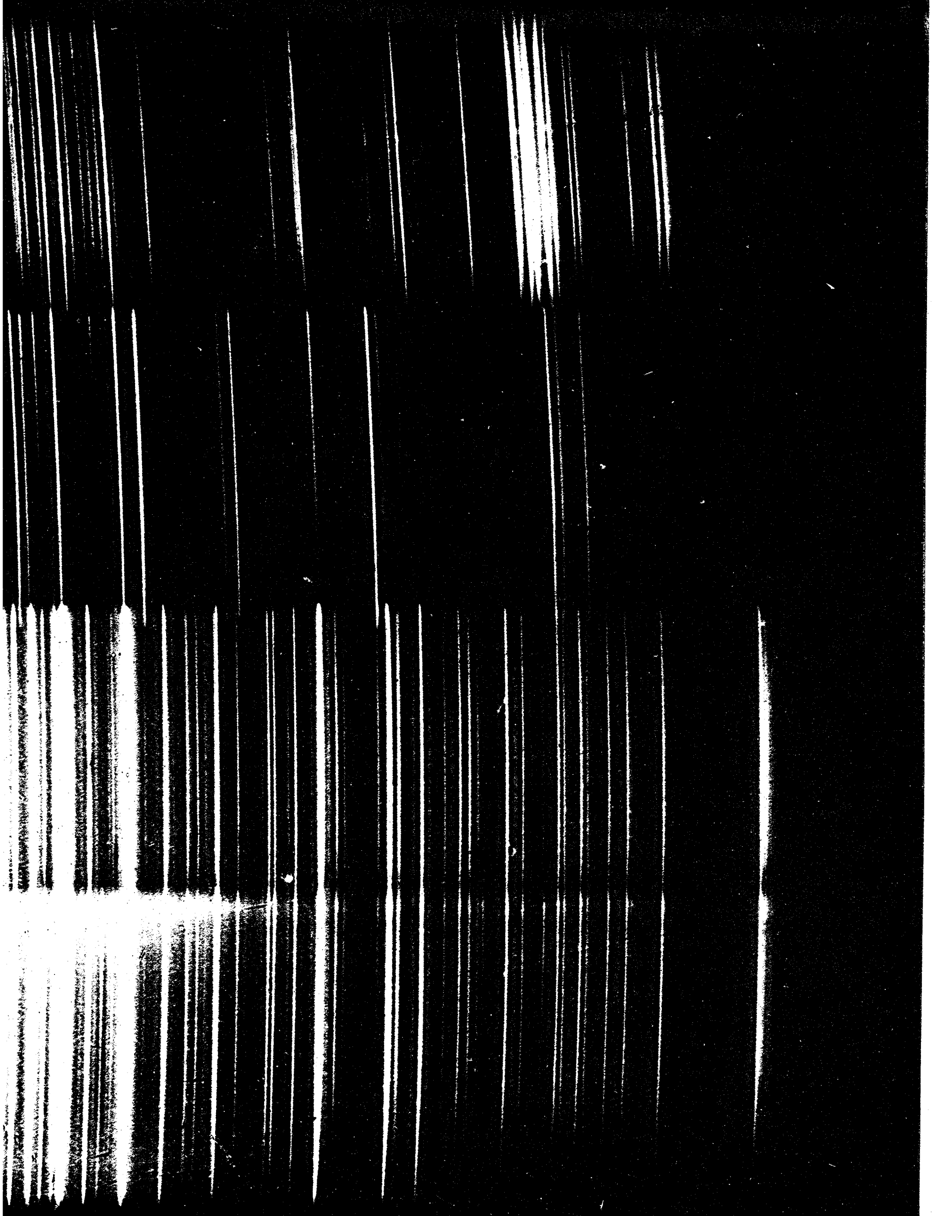

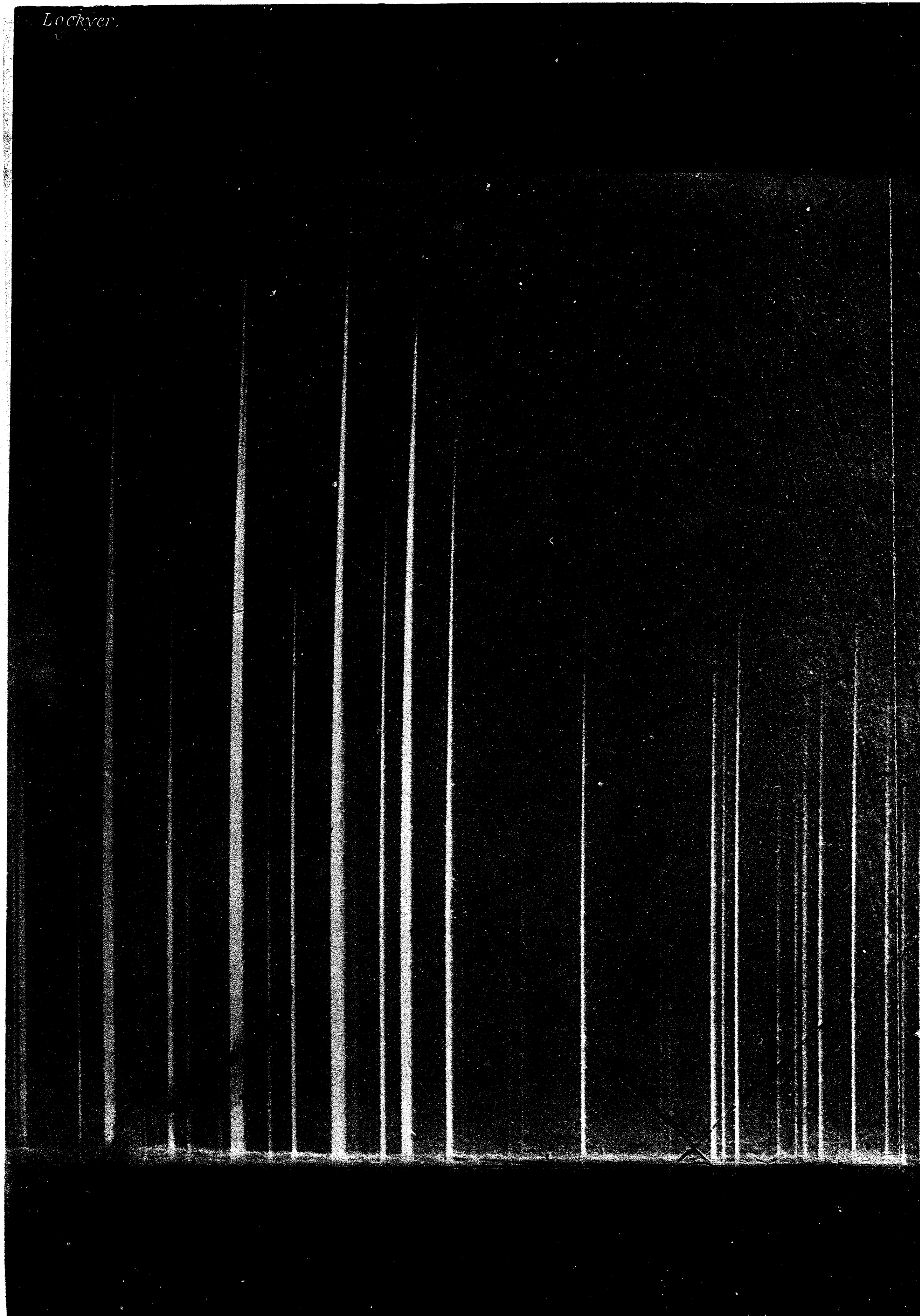
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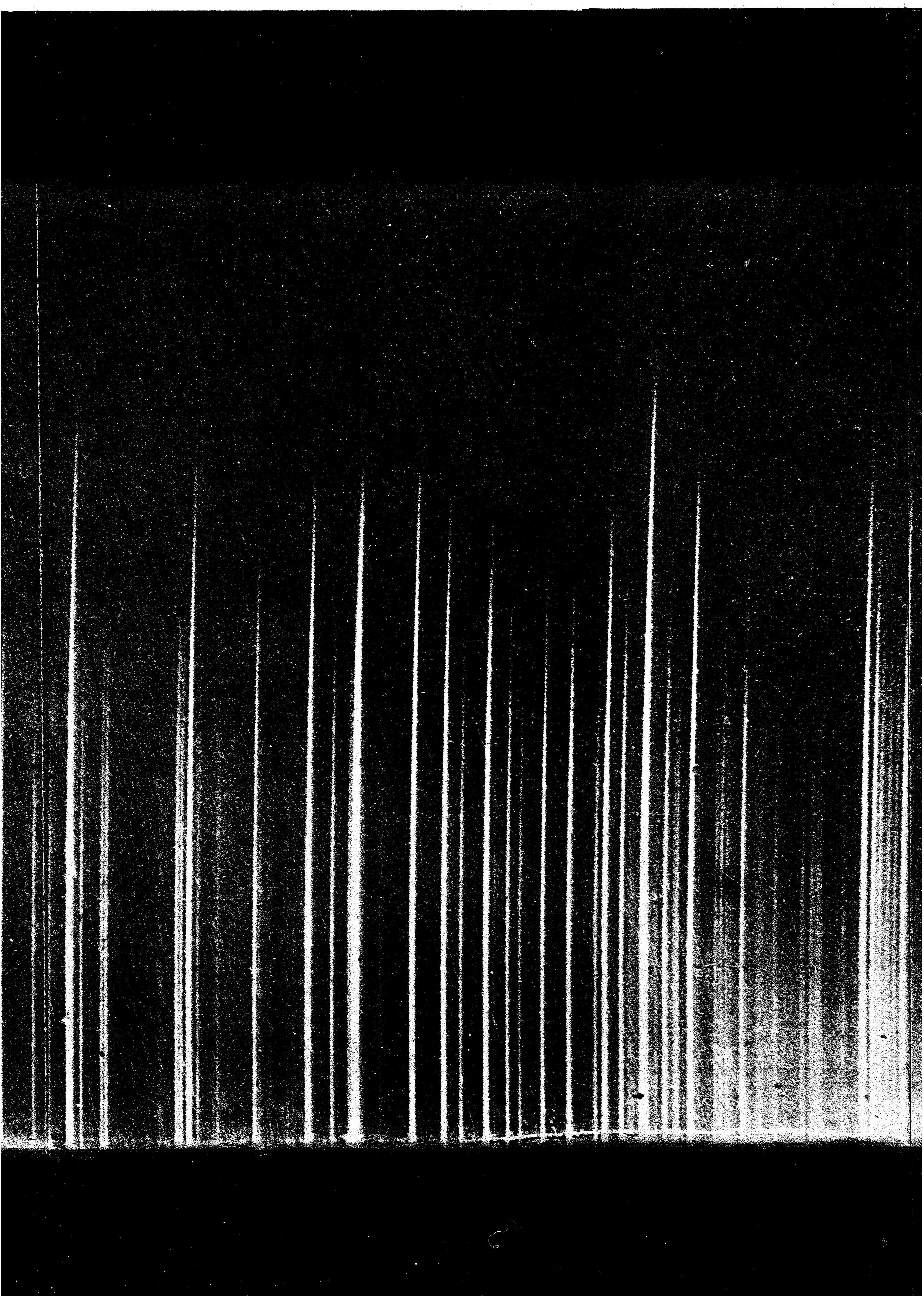

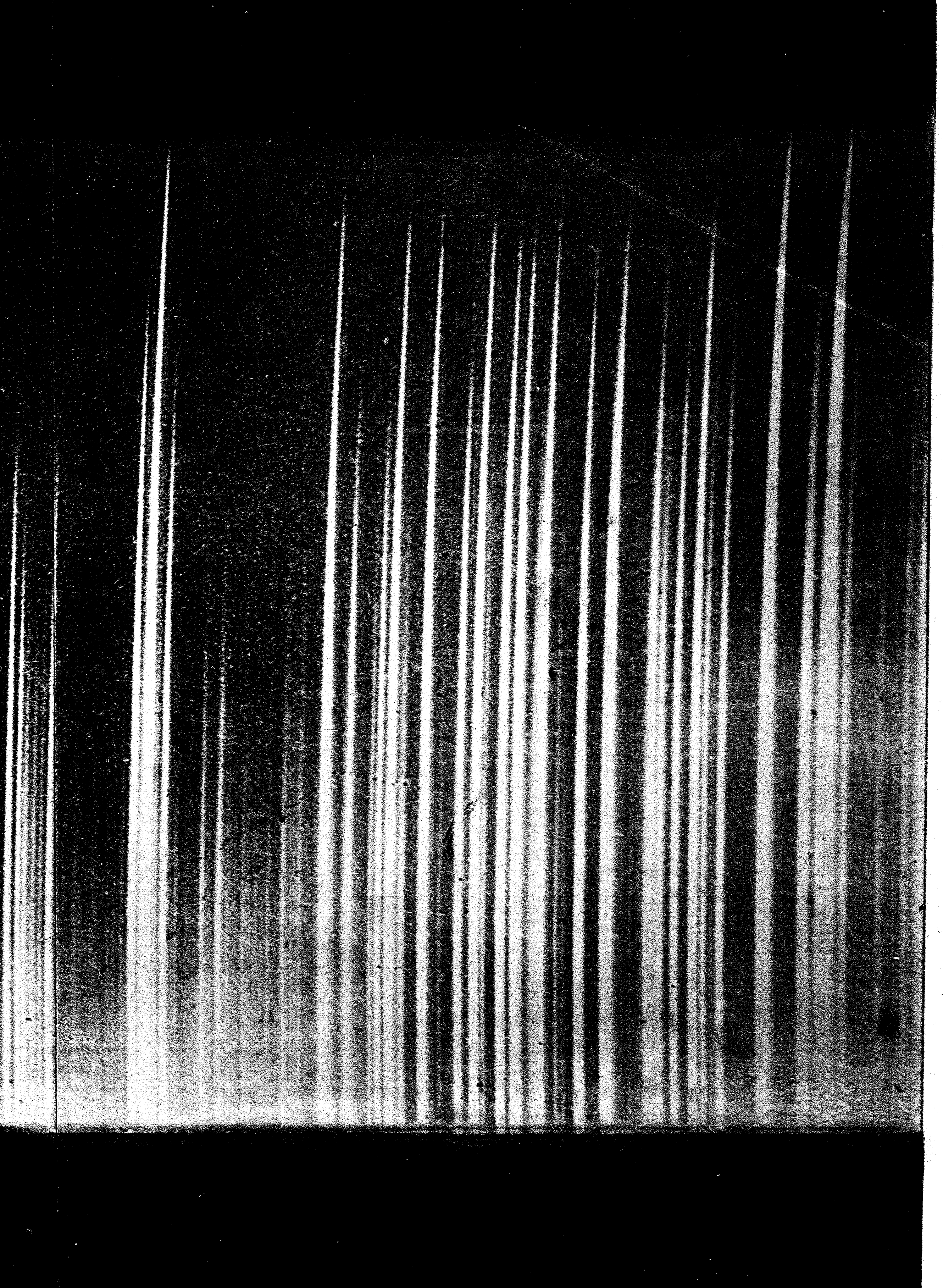


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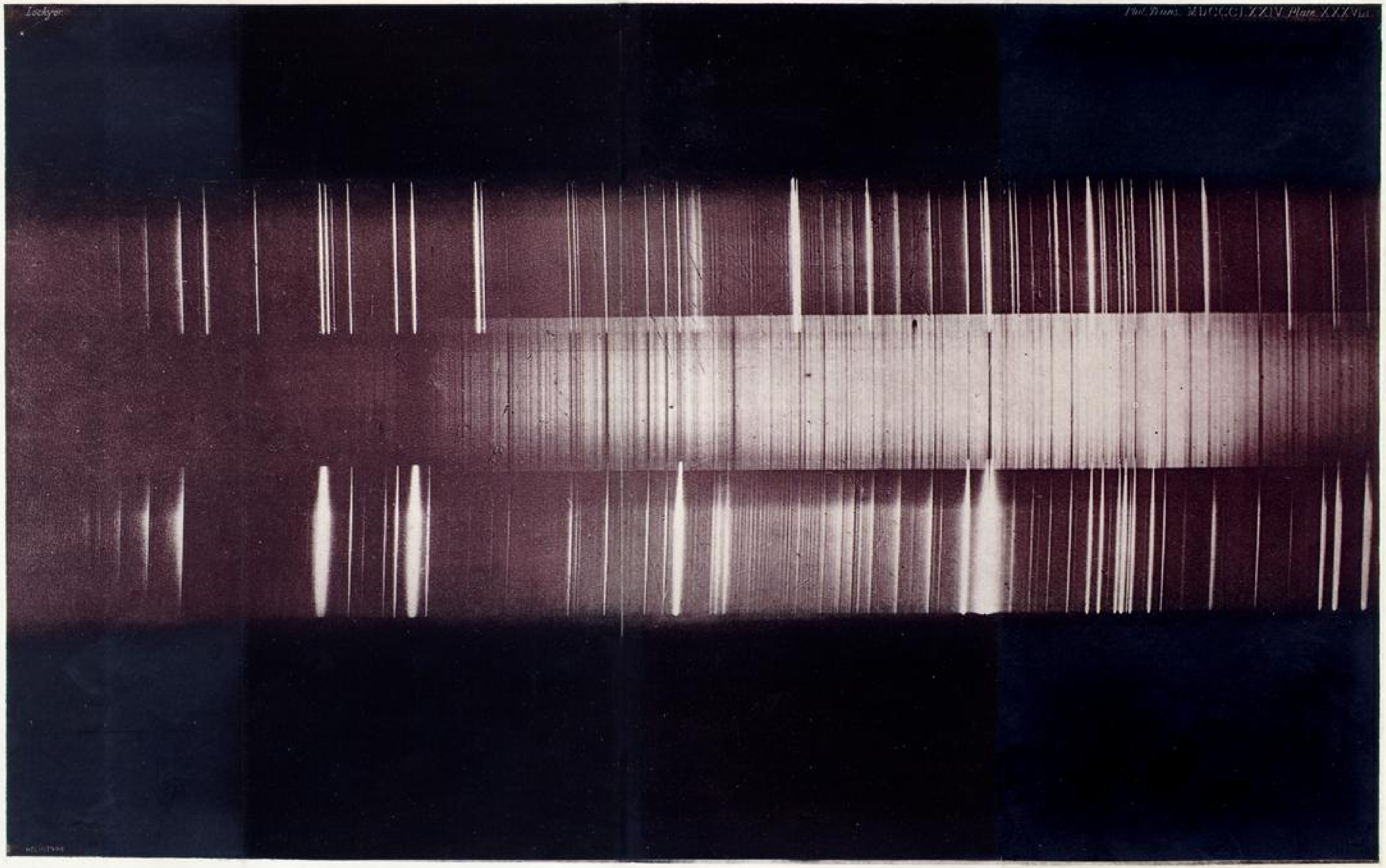

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Phil. Trans. MDCCCLXXIV. Plate XXXVII.

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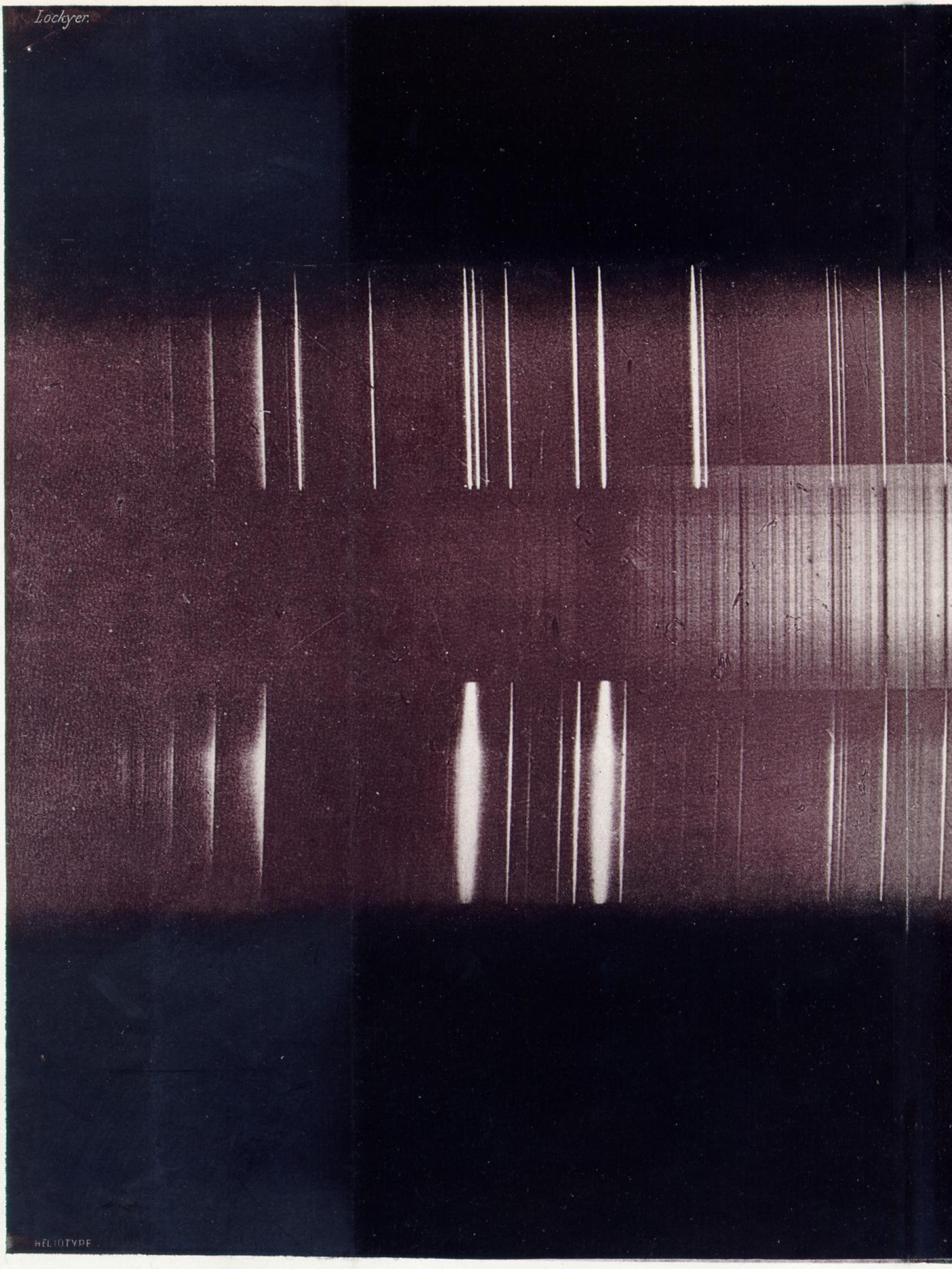
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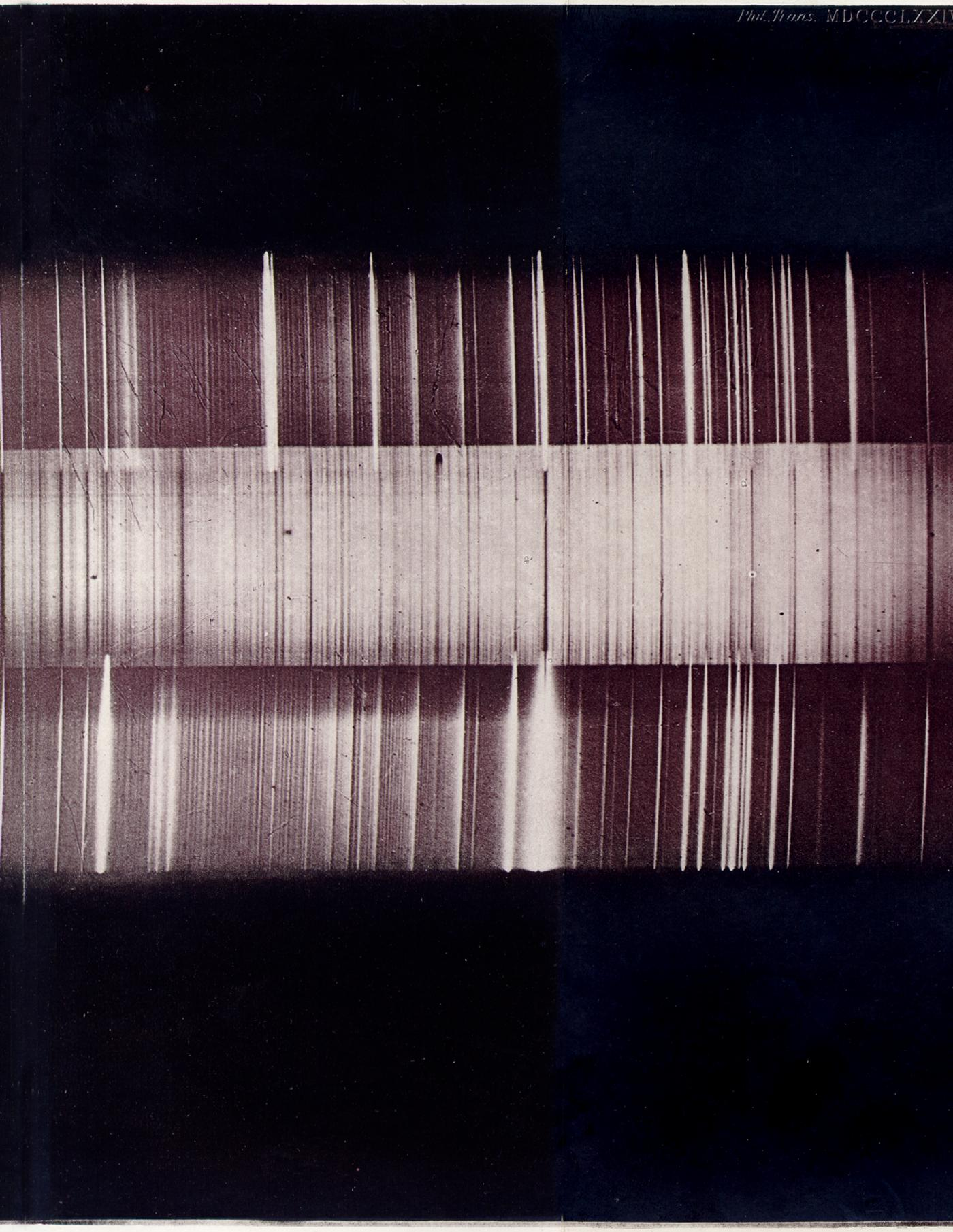

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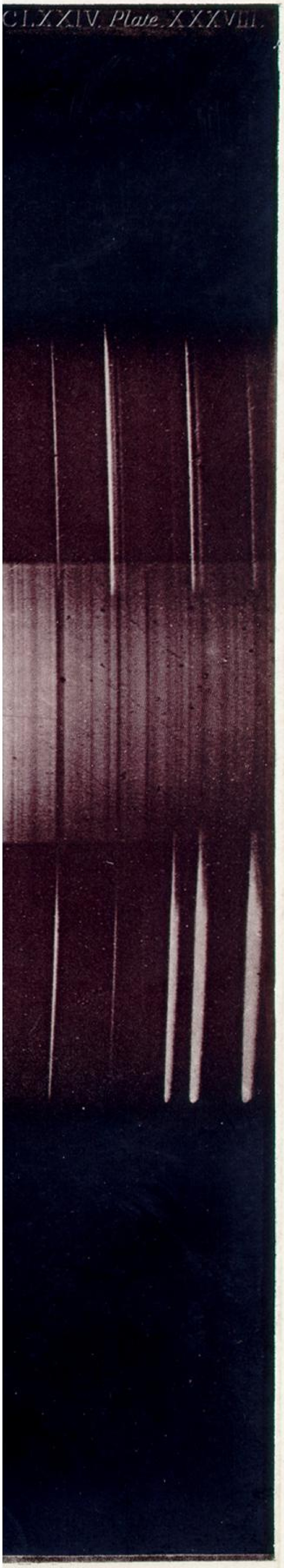

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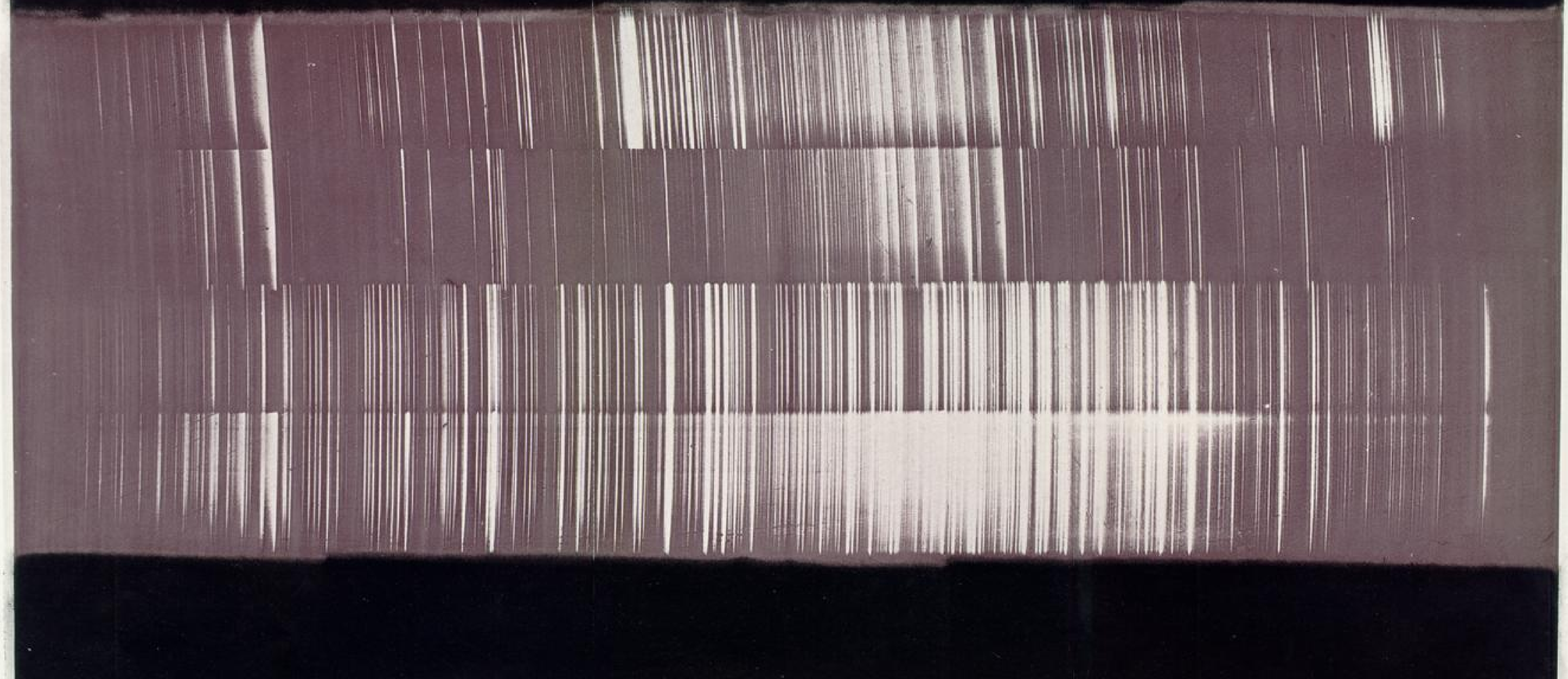

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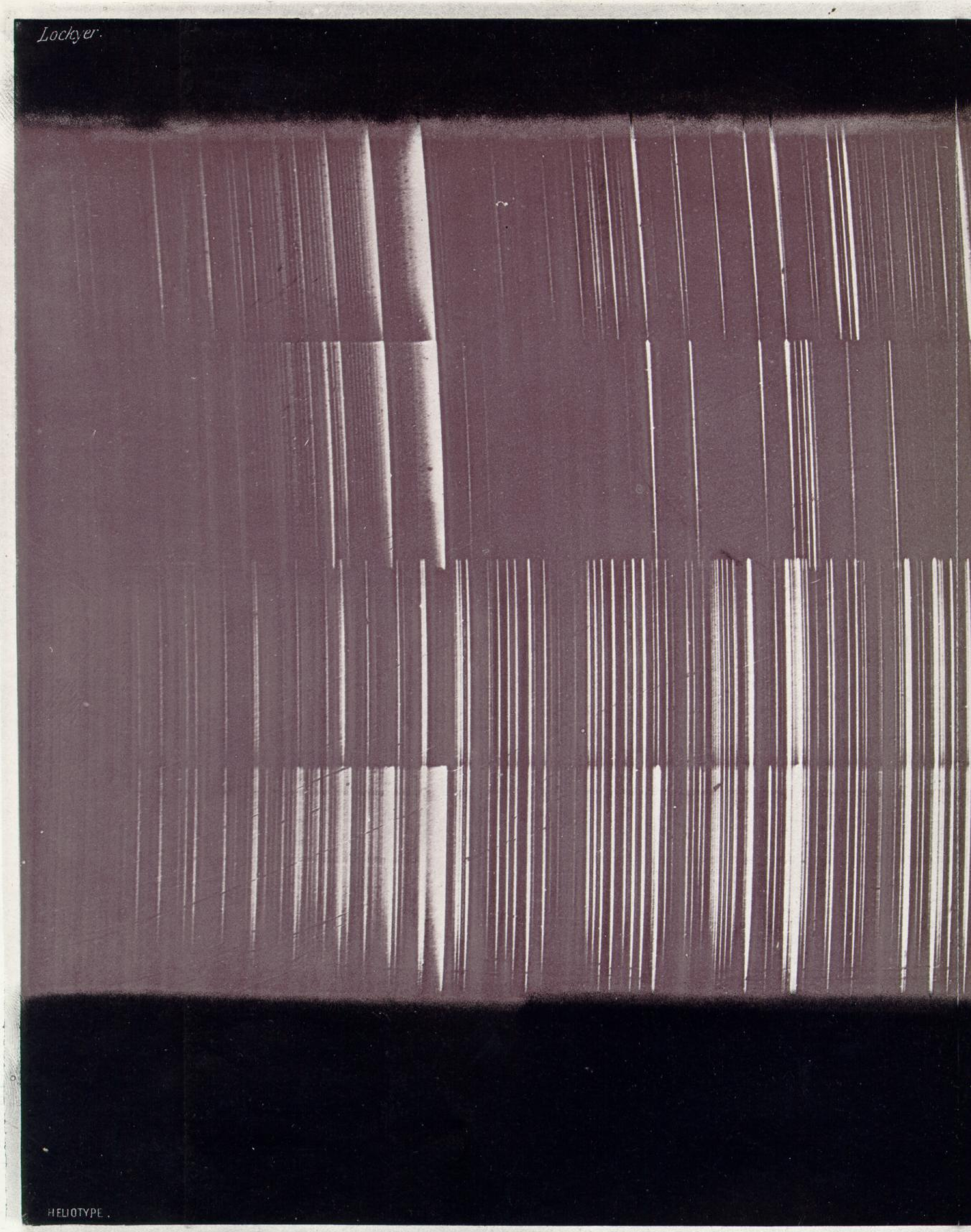
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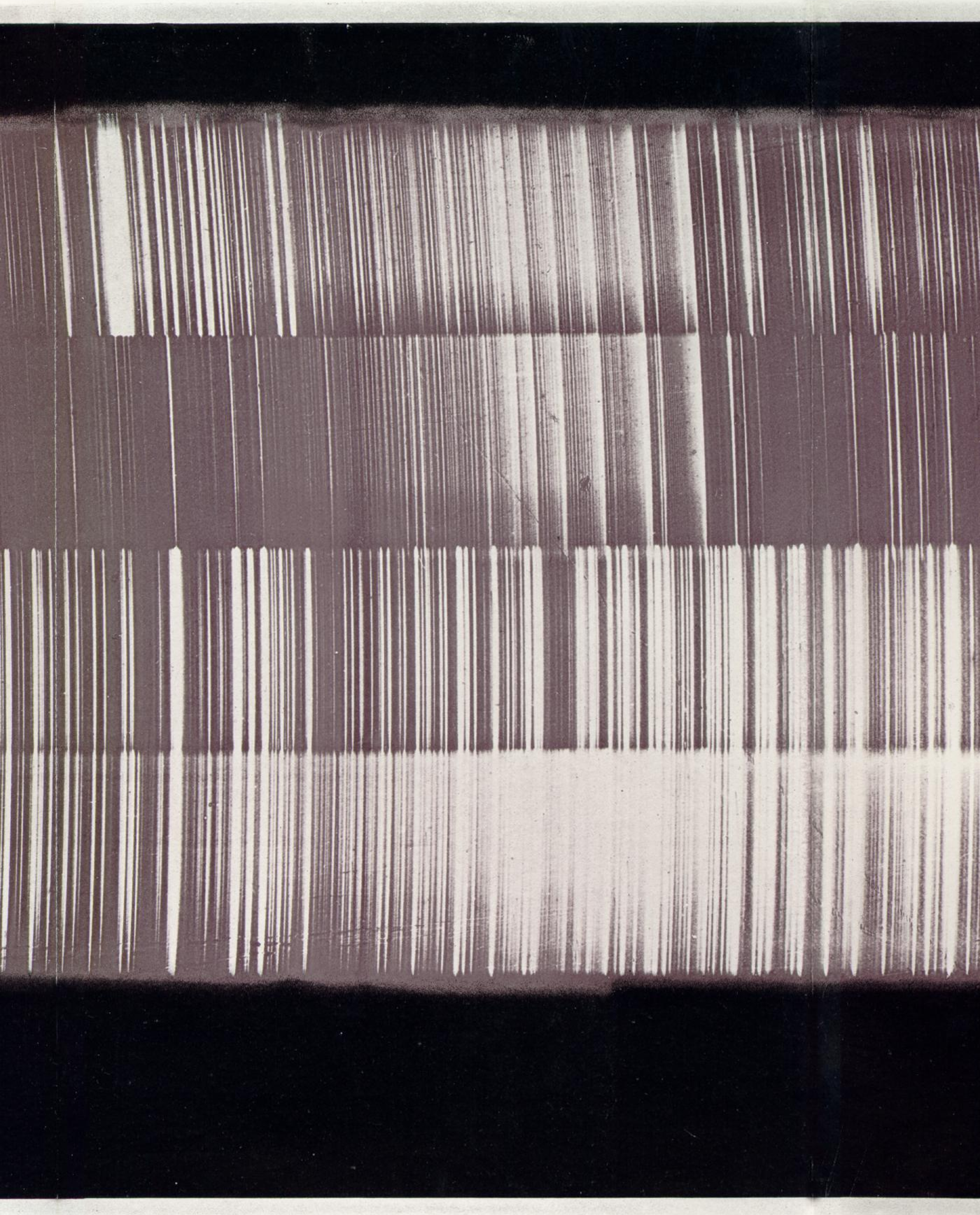

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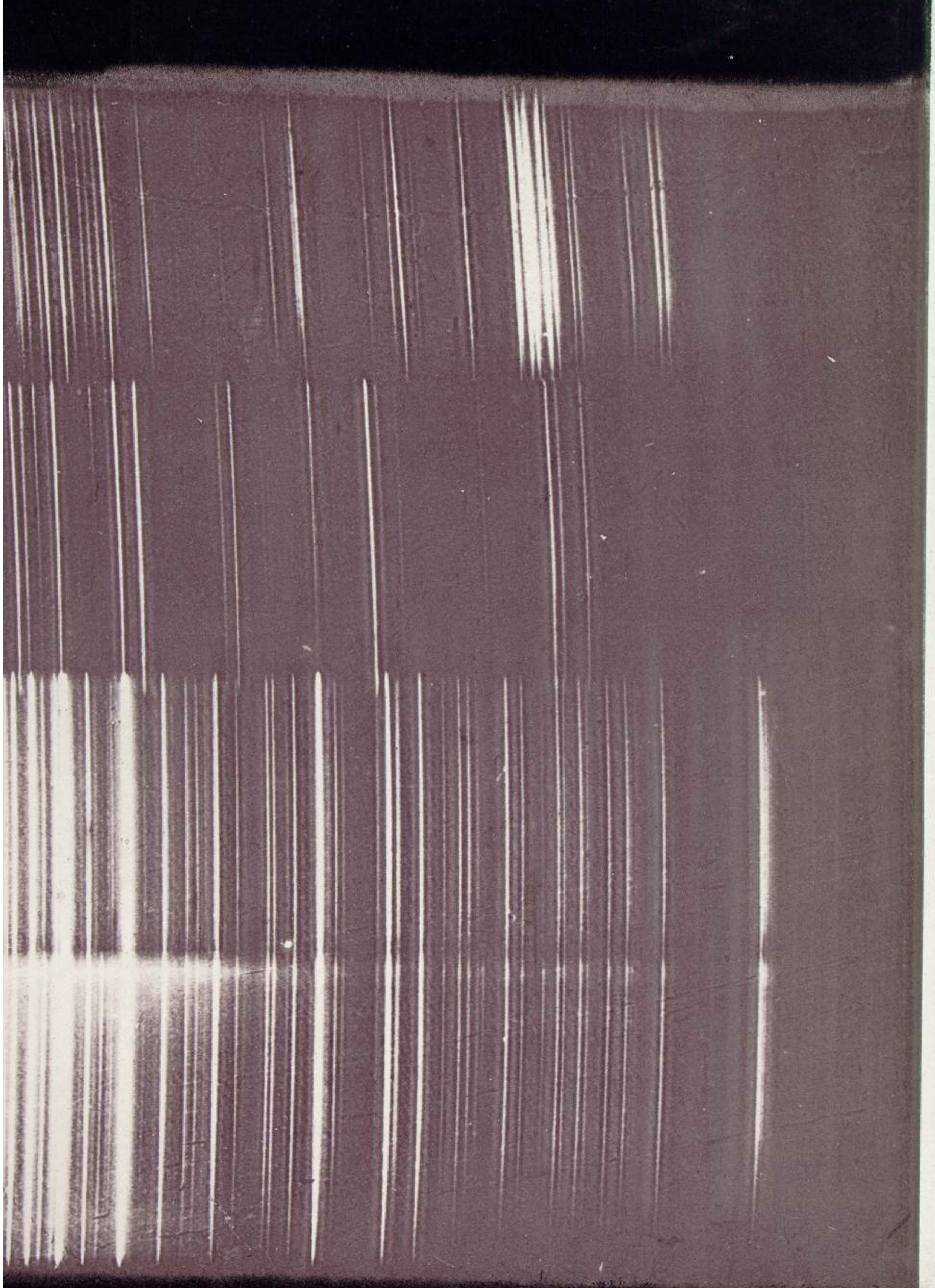

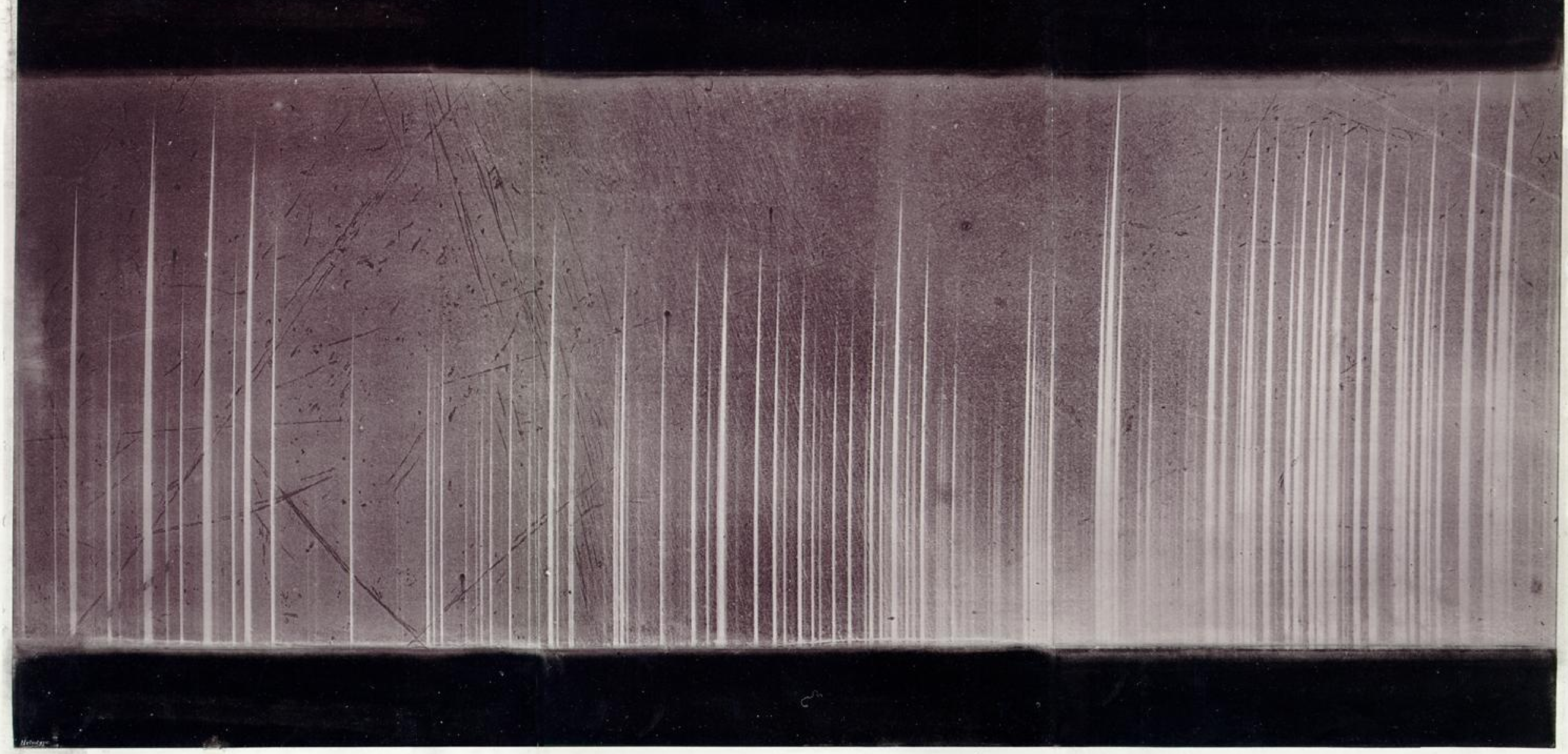


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