# XXIV. *Researches in Spectrum-Analysis in connexion with the Spectrum of the Sun.*—No. IV. *By* J. Norman Lockyer, *F.R.S.*

Received May 11,—Read June 18, 1874.

I beg to lay before the Royal Society a Map of that portion of the spectra of calcium, strontium, and barium comprised between wave-length 3900 and 4500. This Map has been constructed from photographs of the spectra taken by the method described by me in a former communication (the third paper of this series) to the Society, and I am induced to send it in as a specimen of the results to be obtained by the method in the hope that other observers will co-operate; for I am of opinion that it will be necessary to construct similar maps for all the metallic elements before either our knowledge of the composition of the sun's reversing layer can be said to be in any way perfect, or we can be said to have a ready means of determining cyclical changes in its composition. The great labour attending and long time required for the construction of these maps results from the universal presence of impurities, even in the purest specimens of the metals or metallic salts prepared by the ordinary chemical methods; and although the method employed is the only one which enables us to eliminate them eventually, this elimination necessitates a photographic comparison of the spectrum mapped with those of all the substances present as impurities. Hence there are numerous records to be discussed, and the discussion requires special treatment.

## Method of Mapping.

The method of treatment which I have employed in constructing the Maps is as follows:—

1. *Elimination of lines due to impurities.*—The spectrum of the element is first confronted with the spectra of the substances most likely to be present as impurities, and with those of metals which, according to Thalén's measurements, contain in their spectra coincident lines. Lines due to impurities, if any are thus traced, are marked for omission from the Map and their true sources recorded, while any line that is observed to vary in length and thickness in the various photographs is at once suspected to be an impurity line, and if traced to such is likewise marked for omission.

The retention or rejection of lines coincident in two or more spectra is determined by observing in which spectrum the line is thickest; and it is then, as indicated in my last paper, assigned to that element. Where, as in the present case, several elements are mapped at once, all their spectra are confronted on the same Plate, as by this means the presence of one of the substances as an impurity in the others can be at once detected.

Many lines due to impurities have in this manner been traced in the photographed

spectra of calcium, strontium, and barium. For instance, the two longest aluminium lines (3943 and 3961) are invariably present in all three spectra, and the long iron lines (4045, 4063, and 4071) can in most cases be likewise detected. The lines 4076·9 and 4215·4 present in all photographs of calcium, and assigned to this element both by Ångström and Thalén, are, as I showed in my last paper, really due to strontium.

Similarly the two H lines (3933 and 3968), assigned both to iron and calcium by Ångström, are proved to belong to calcium by the following observations:—

*a*. The lines are well represented in the spectrum of commercial wrought iron, but are absolutely coincident with two thick lines in the spectrum of calcium chloride with which the iron spectrum has been confronted.

*b*. The lines are represented by mere traces in the spectrum of a specimen of pure iron prepared by the late Dr. Matthiessen, and obligingly placed at my disposal by Dr. Russell. In this photograph (Plate LXXXV. Spectrum 7) both poles of the lamp were of iron, the lower pole consisting of an ingot of the metal which had been cast in a lime-mould.

*c*. The lines are altogether absent in a photograph of pure iron, where both poles of the lamp were of the pure metal *not* cast in lime, and they are likewise absent in a photograph of the spectrum of the Lenarto meteorite (Plate LXXXV. Spectrum 1)*.

These examples serve to illustrate the manner in which large numbers of the coincidences recorded by former observers have been disposed of in the course of mapping by the photographic method.

In determining the coincidence of very thick lines, such as the H lines just mentioned for example, the centre of the thick line is taken, except in instances where the whole of a spectrum has been slightly displaced to the right or left by the displacement of the apparatus during the act of photographing, in which case a correction has to be made for the position of every line in such displaced spectrum. It not unfrequently happens that a very thick line will reverse itself, a circumstance which greatly facilitates its comparison with confronted lines, since a thin dark line then runs down the centre of the thicker bright one (Plate LXXXV. Spectra 2 & 3)†.

2. *Determination of the positions and lengths of new lines.*—By eliminating lines due to impurities in the manner just described, a spectrum is at length obtained, of which every line is assignable to the particular element photographed.

These lines are then entered in a map, those measured by Ångström or Thalén being placed in the positions assigned by those authors, while the new lines are at first entered approximately. The wave-lengths assigned to the new lines, although probably not far from the truth, must, in the absence of actual measurement, be regarded only as approximate. They have been found in the following manner:—

The admirable photographic print of the solar spectrum, from H to F, obtained some

* In both these photographs, however, the *longest line* of calcium is to be traced.

† The absorption-line does not always occupy the *exact* centre of the bright band. This point is occupying my attention, as it raises a very interesting question connected with molecular vibrations.

time ago by Mr. RUTHERFURD (and which I have not yet been able to equal*), was first divided (from 3900 to 5000) into portions corresponding each to a difference of wave-length of $\frac{1}{100,000}$ millim. by identifying in the print the more prominent of the FRAUNHOFER lines mapped by ÅNGSTRÖM, and attaching the proper numbers to the consecutive divisions. The spaces between these larger divisions were then, by a similar use of ÅNGSTRÖM'S map, divided into tenths, each of these divisions corresponding consequently to a difference of wave-length of $\frac{1}{1,000,000}$ millim. The millimetres of ÅNGSTRÖM'S scale (equal to a difference of wave-length of $\frac{1}{10,000,000}$ millim. each) were found by dividing the $\frac{1}{1,000,000}$ millim. divisions into ten equal parts. From this standard print the position of any new line is found by carefully observing (in a photograph of the spectrum of the metal confronted with the solar spectrum) the precise position of the new line with respect to the solar spectrum, and then finding the corresponding position in the print†. Although absolute accuracy cannot be claimed for the positions of lines determined in this way, I have nevertheless expressed the wave-lengths in the Tables in the usual scale ($1–10^{10}$ metre) in order to distinguish between lines which occur close together, of which there are several instances in the present Map.

The lengths of the new lines are determined from special photographs (Plate LXXXIV.), to obtain which a horizontal arc is employed, as explained in my last paper.

### REVERSAL OF THE NEW LINES IN THE SOLAR SPECTRUM.

With regard to the reversal or non-reversal in the solar spectrum of the new lines revealed by the photographs, I refrain for the present from making any positive statements, as I have not yet been able to obtain sufficiently good photographs of the metallic and solar spectra confronted. I may add, however, that lines are to be found in Mr. RUTHERFURD'S photograph of the solar spectrum in the positions, within the limits of error, of nearly all the new lines; but the close approach to coincidence between lines undoubtedly distinct, which I have observed in many cases in the course of constructing the accompanying Map, convinces me that in future much greater precision will be necessary before assigning any line in the solar spectrum to a particular metal, and I therefore reserve the question of the reversal of the new lines till our knowledge of the solar spectrum is more complete. For a similar reason it is obvious that greater attention will have to be given to the precise *character* as well as to the position of each of the FRAUNHOFER lines, in the thickness of which I have already observed several anomalies. I may refer more particularly at present to the two H lines 3933 and 3968 belonging to calcium, which are much thicker in all photographs of the solar spectrum than the longest calcium line of this region (4226·3), this latter being invariably thicker than the H lines in all photographs of the calcium spectrum, and remaining, moreover, visible in the spectrum of substances containing calcium in such small quantities as not to show any traces of the H lines. How far this and other similar variations between

* Owing, among other causes, to constant vibrations incident to observations in London.

† A photograph in which all the metals mapped are confronted on the same plate is a useful guide for checking the positions of the lines when found as above.

photographic records and the solar spectrum are due to causes incident to the photographic record itself, or to variations of the intensities of the various molecular vibrations under solar and terrestrial conditions, are questions which up to the present time I have been unable to discuss.

## Observations on the Maps.

In the accompanying Map I have placed under each spectrum the spectra mapped by Ångström and Thalén for the sake of comparison. In constructing the Map only those lines distinctly referable to the metal have been inserted; minute traces of faint lines and the banded structure visible in most of the photographs, and belonging most probably to the carbon of the lamp-poles, have been omitted.

The lines described in the Index as "nebulous" are of a peculiar and distinct nature, presenting the appearance of being out of focus, and suggesting that they arise from the surface of the arc. Whether these lines are due to the metal itself or to some compound of the metal stable at the temperature of the electric arc, I am at present unable to say. Special experiments will have to be made upon this point. The calcium lines 4091·8, 4093·3, and 4097·5, and the barium lines 4081, 4084, and 4087, are of the nature indicated.

In certain cases lines have been found of equal thickness, and absolutely coincident in two confronted spectra, without being referable to any known impurity common to the two metals. In these instances the lines have been assigned to both metals, but must be considered as subject to correction. The lines 4282·5* (common to calcium and barium) and 4325 (common to barium, strontium, and iron) are instances of coincidences occurring in the present Map.

The scale of lengths given in the Index is that made use of by Thalén† for indicating the intensities of the lines, 1 being the longest and 5 the shortest line. In my former papers, where eye-observations were made use of, the scale of length ranged only from 1 to 4; but in the present case we have photographs to decide from, and these permit a more satisfactory determination.

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The Map and accompanying Tables have been constructed by my assistant, Mr. R. Meldola, to whom I am much indebted for the skill and patience he has brought to bear upon the inquiry.

The photographs which accompany this paper have been taken in the room in Dr. Frankland's private laboratory, to which I made reference in my former communication. In again tendering my thanks to Dr. Frankland for having placed it at my disposal, I cannot refrain from pointing out that without such aid my present researches would have been impossible.

* It has since been found by using a camera of 6 feet focus that this line is not absolutely coincident in both spectra, the calcium line being very slightly more refrangible. The Map and Index have been altered accordingly. —J. N. L., September 26, 1874.

† "Mémoire sur la détermination des longueurs d'onde des raies métalliques," Nova Acta, Upsala, 1868.

# INDEX TO MAP. (Plate LXXXVI.)

## CALCIUM.

Lines marked * are those in the Maps of other observers which have been omitted from the present Map on the photographic evidence.

| Wave-length. | State in Ångström's Maps. | State in Thalén's Maps. | Length in Calcium Photographs. | Remarks. |
|---|---|---|---|---|
| 3932·8 [$H_{II}$] | Present. Assigned also to Fe. | Present. | 1 | One of the longest Ca lines. In all photographs of substances containing the smallest trace of Ca. |
| 3956·0 | Not present. | Not present. | 5 | Short Ca line nearly coincident with an Fe line. In all photographs. |
| 3968·0 [$H_I$] | Present. Assigned also to Fe. | Present. | 1 | Long Ca line in the centre of a complex group of Fe lines. This line is grazed on its right by an Fe line, but is not coincident as in Ångström's Map. |
| 3974·0 | Not present. | Not present. | 4 | Short Ca line in all photographs. |
| *4077·0 | Present. | Present. | 3 | One of the longest Sr lines present in all photographs of Sr and Ca, but invariably thicker in the Sr. |
| *4078·5 | Not present. | ,, | .... | No line in this position in any of the photographs. It is probable that this is identical with the foregoing line. |
| 4091·8 | Present. | ,, | 5 | A nebulous line in all photographs. |
| 4093·3 | Not present. | Not present. | | |
| *4095·5 | Present. | Present. | .... | Not in any photograph. |
| 4097·5 | ,, | ,, | 4 | Nebulous line in all photographs. |
| *4098·0 | Not present. | ,, | .... | This line is probably identical with the foregoing. |
| *4131·5 | Present. Assigned also to Fe. | Present. Assigned also to Fe. | .... | Present as mere traces in some photographs, absent altogether from others. |
| *4143·0 | ,, | ,, | | |
| *4188·5 | Present. | Present. | .... | Not in photographs. |
| *4192·2 | ,, | ,, | | |
| *4192·5 | Not present. | ,, | .... | Not in photographs. ? Identical with foregoing line. |
| *4215·3 | Present. | ,, | 2 | One of the longest Sr lines present in all photographs of Sr and Ca, but invariably thicker in Sr. |
| 4226·3 | ,, | Present. Assigned also to Sr. | 1 | Longest Ca line in this part of the spectrum. In all photographs of substances containing the smallest trace of Ca. |
| *4233·0 | Present. Assigned also to Fe. | Present. Assigned also to Fe. | .... | Not a Ca line. |
| 4237·5 | ,, | Present. | 5 | Nebulous line in all photographs. Not an Fe line. |
| *4247·5 | ,, | Present. Assigned also to Fe. | .... | Not in photographs. |
| *4249·8 | ,, | ,, | .... | |
| *4253·9 | Present. Assigned also to Fe and Cr. | Present. Assigned also to Cr. | .... | |

## CALCIUM (continued).

| Wave-length. | State in Ångström's Maps. | State in Thalén's Maps. | Length in Calcium Photographs. | Remarks. |
|---|---|---|---|---|
| *4271·5 | Present. Assigned also to Fe and Cr. | Present. Assigned also to Cr. | .... | Not in photographs. |
| *4274·5 | Present. Assigned also to Cr. | Present. Assigned also to Cr. | | |
| 4282·4 | Present. | Present. | 3 | Ca line in all photographs. Very nearly coincident with a Ba line, and almost coincident with an Fe line. |
| *4285·5 | ,, | Not present. | .... | Not in photographs. |
| 4289·4 | Present. Assigned also to Cr. | Present. Assigned also to Cr. | 3 | In all photographs. Just to left of a Ba line, and apparently coincident with a line in Al photograph. |
| 4298·5 | Present. Assigned also to Fe. | Present. Assigned also to Fe. | 3 | In all photographs. Almost but not quite identical with Fe line, as in Ångström's and Thalén's Maps. |
| *4300·2 | Present. | Not present. | .... | Not in photographs. |
| 4302·0 | Present. Assigned also to Fe. | ,, | 3 | In all photographs. Not assignable to Fe, as in Ångström's Map. |
| *4302·3 | Not present. | Present. | .... | Probably identical with preceding line. |
| 4306·5 | Present. | ,, | 3 | In all photographs. Nearly coincident with an Fe line. |
| 4318·0 | ,, | ,, | 3 | In all photographs. |
| 4354·0 | Not present. | Not present. | 4 | Nebulous line in all photographs. |
| *4379·1 | Present. Assigned also to Fe. | Present. | .... | Not in photographs. |
| *4384·7 | Present. | ,, | | |
| *4389·4 | ,, | ,, | | |
| *4393·0 | ,, | ,, | | |
| *4405·7 | ,, | ,, | | |
| *4407·0 | ,, | ,, | | |
| *4407·7 | Present. Assigned also to Fe. | ,, | | |
| 4425·0 | Present. | ,, | 3 | In all photographs. |
| 4434·5 | ,, | ,, | 2 | |
| 4435·3 | Not present. | ,, | .... | Not in photographs, unless identical with preceding line. Although both lines are down in Thalén's Tables only one is shown in his Map. |
| 4454·2 | Present. | Present [4454·0] | 2 | In all photographs. |
| *4455·2 | Not present. | Present. | .... | Not in photographs unless identical with preceding line. Here also Thalén has the two lines in the Table, but only one in the Map. |

## STRONTIUM.

| Wave-length. | State in Ångström's Maps. | State in Thalén's Maps. | Length in Strontium Photographs. | Remarks. |
|---|---|---|---|---|
| 3940·0 | Not present. | Not present. | 5 | Short line in all photographs. Nearly coincident with a faint line in Fe spectrum. |
| 4029·4 | Present. Assigned to Mn. | Present. Assigned to Mn. | 2 | In all photographs. Nearly coincident with a long Mn line. |
| 4031·5 | Present. Assigned to Fe. | Not present. | 4 | In all photographs of Sr; faint in some. Apparently coincident with lines in Mn and Fe spectra. Another line occurs in photographs of Sr about W. L. 4033, but is very faint, and is moreover common to Fe and Mn, and has not therefore been inserted in Map. The spectrum is much confused at this region. |
| 4031·7 | Present. Assigned to Mn. | Present. Assigned to Mn. | | |
| 4077·0 | Present. Assigned to Ca. | Present. Assigned to Ca. | 1 | The longest Sr line in this portion of the spectrum; generally present also in Ca photographs. |
| *4078·5 | Not present. | Present. | .... | No line in this position in any of the photographs unless identical with preceding. |
| 4161·0 | A line at 4160·8. Not assigned to any thing. | „ | 3 | In all photographs. |
| 4215·3 | Present. Assigned to Ca. | Present. Assigned to Ca and Sr. | 1 | One of the longest Sr lines in this portion of the spectrum; generally present also in Ca photographs. |
| *4226·3 | Present. Assigned to Ca. | „ | 2 | Longest Ca line. Present in all photographs of Ca and Sr, but invariably thicker in Ca. |
| 4305·3 | Not present. | Present. | 2 | In all photographs. |
| 4235·0 | Present. Assigned to Fe. | A line of W. L. 4325·2. Assigned to Fe. | 3 | In all photographs. Coincident with a thick Fe line and with a Ba line. |
| 4336·0 | Not present. | Not present. | 3 | In all photographs. Just to right of a line in Fe spectrum. |
| 4365·0 | „ | „ | 4 | In all photographs. |
| 4437·0 | „ | „ | 5 | |

## BARIUM.

| Wave-length. | State in Ångström's Maps. | State in Thalén's Maps. | Length in Barium Photographs. | Remarks. |
|---|---|---|---|---|
| 3934·0 | Not present. | Not present. | 3 | In all photographs. Apparently coincident with a very faint line in Fe spectrum. |
| 3937·0 | ,, | ,, | 4 | In all photographs. |
| 3994·5 | ,, | ,, | 2 | In all photographs. A double line. |
| 3996·2 | ,, | ,, | 3 | In all photographs. Almost coincident with a short Fe line. |
| 4081·0 | ,, | ,, | 5 | Very nebulous line in all photographs. Just to right of a line in Fe spectrum. |
| 4084·0 | ,, | ,, | 5 | Broad and very nebulous line in all photographs. Coincident with a thick Fe line. |
| 4087·0 | ,, | ,, | 5 | Very nebulous line in all photographs. Just to right of a faint double line in Fe spectrum. |
| 4130·5 | ,, | Present. | 1 | Longest Ba line in this portion of the spectrum. |
| 4131·5 | ,, | Present. Assigned to Fe. | 3 | In all photographs. Almost coincident with a thick Fe line. |
| 4165·5 | Not present. | Present. | 2 | In all photographs. |
| 4224·0 | ,, | Not present. | 3 | In all photographs. Just to left of a thin line in Fe spectrum. |
| 4239·0 | ,, | ,, | 4 | In all photographs. Almost coincident with a thin line in Fe spectrum. |
| 4241·5 | A line at 4241·6. Not assigned to any thing. | ,, | 4 | In all photographs. |
| 4264·0 | A line at 4264·1. Assigned to Fe. | ,, | 3 | In all photographs. Between two thick Fe lines. Slightly nebulous. |
| 4282·5 | Present. Assigned to Ca. | Present. Assigned to Ca. | 1 | In all photographs. Very nearly coincident with a Ca line. |
| 4290·6 | Not present. | Not present. | 3 | In all photographs. Just to right of a Ca line. |
| 4323·0 | ,, | ,, | 3 | In all photographs. A nebulous line. |
| 4325·0 | Present. Assigned to Fe. | A line of W. L. 4325·2. Assigned to Fe. | 3 | In all photographs. Coincident with a Sr and thick Fe line. |
| 4332·0 | Not present. | Not present. | 4 | In all photographs. |
| 4351·0 | ,, | ,, | 2 | In all photographs. To left of a Ca line, and nearly coincident with a thin line in Fe spectrum. |
| 4401·5 | ,, | ,, | 4 | In all photographs. To left of a thick Fe line. |
| 4433·0 | ,, | ,, | 5 | In all photographs. Between two Ca lines. |
| 4488·0 | ,, | ,, | 5 | In all photographs. A nebulous line. |
| 4493·0 | ,, | ,, | 5 | In all photographs. A nebulous line. Apparently coincident with a thin line in Fe spectrum. |

## Description of the Photographs.

### PLATE LXXXIV.

Spectrum 1. Long and short lines of calcium.
Spectrum 2. Long and short lines of strontium.
Spectrum 3. Long and short lines of barium.

*Note.*—In these photographs the impurity lines which have been eliminated from the map by the process described in the paper are present.

The photographs illustrate the use of the horizontal arc.

### PLATE LXXXV.

Spectrum 1. Comparison of the spectra of the Lenarto meteorite, calcium, and aluminium.

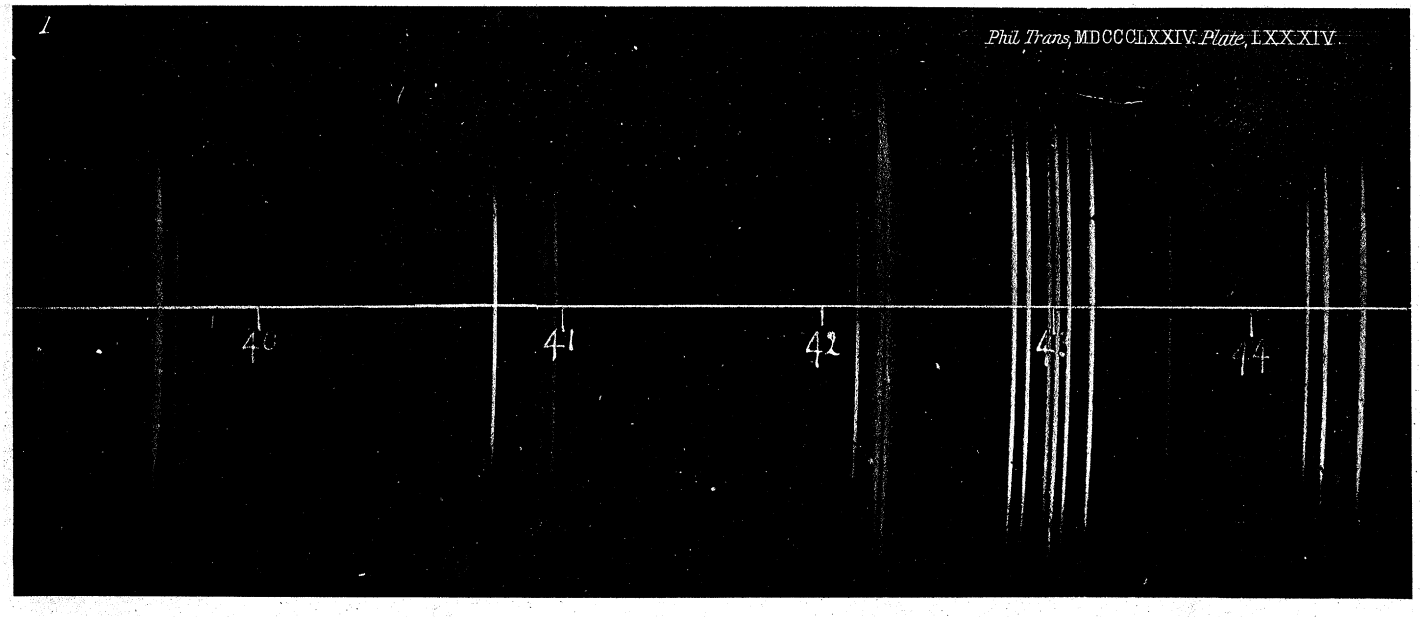
1, spectrum of the meteorite.
2, „ calcium.
3, „ aluminium.

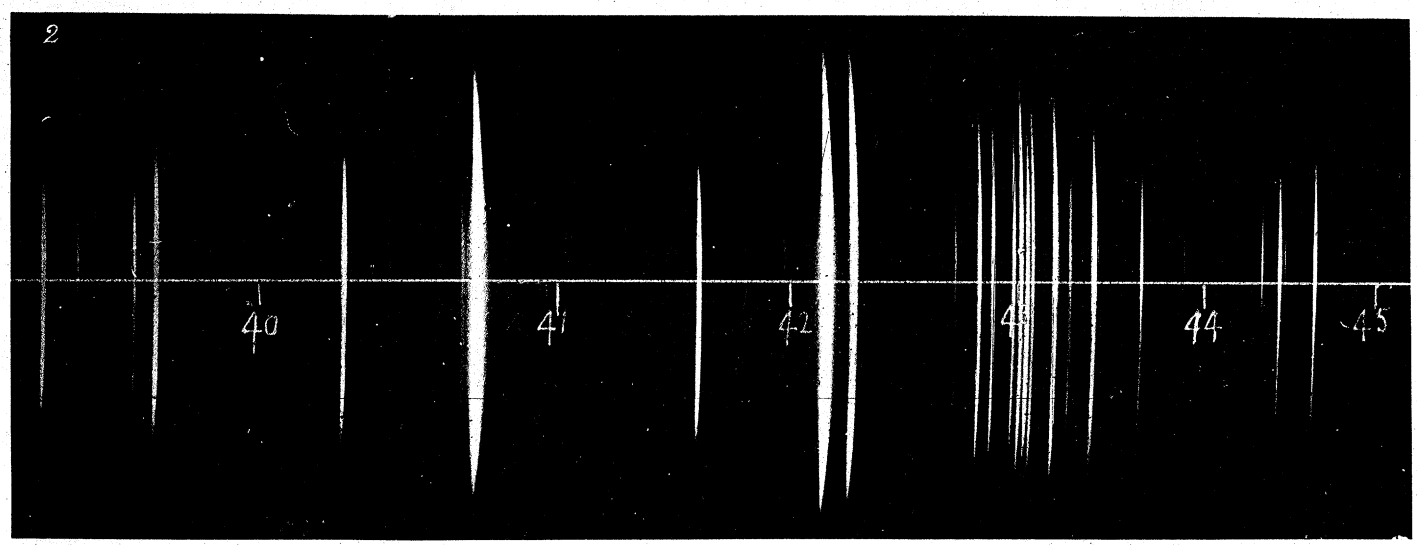
Spectrum 2. Comparison of the spectra of nearly pure iron and strontium.

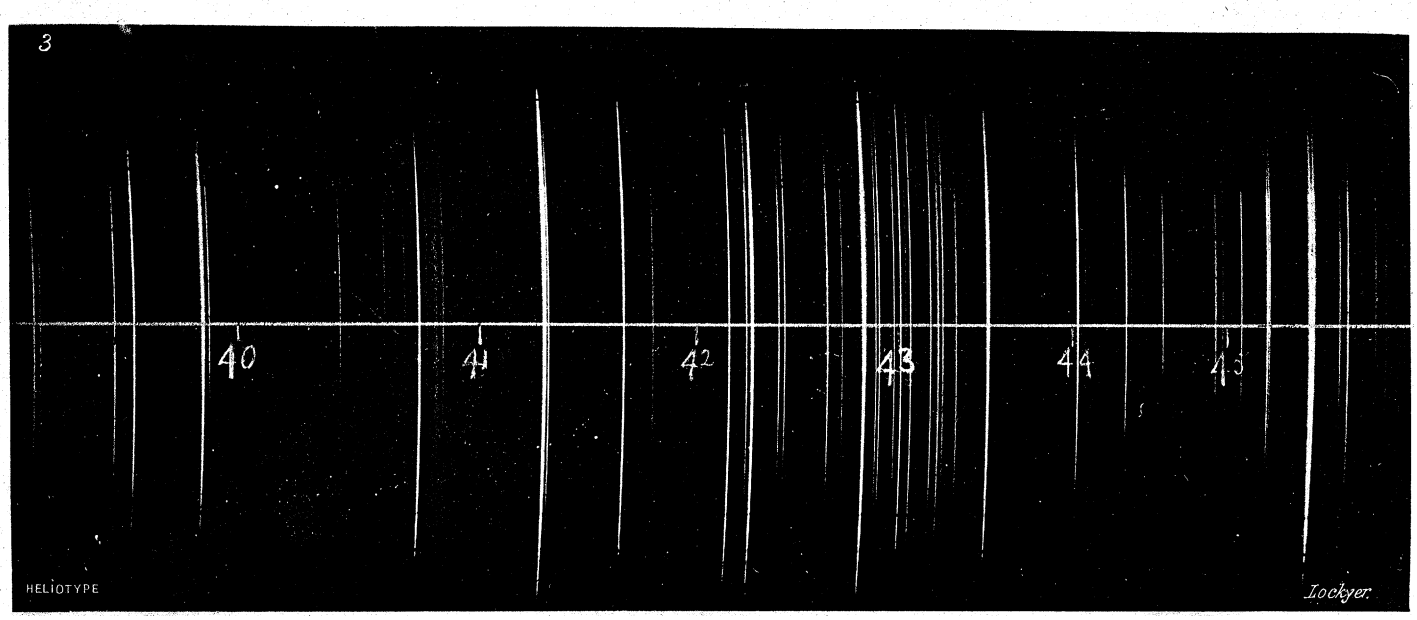
4, spectrum of iron.
5, „ strontium.

Spectrum 3. Comparison of the spectra of Matthiessen's iron and calcium.

6, spectrum of calcium.
7, „ iron when cast into ingot.
8, „ „ before casting.

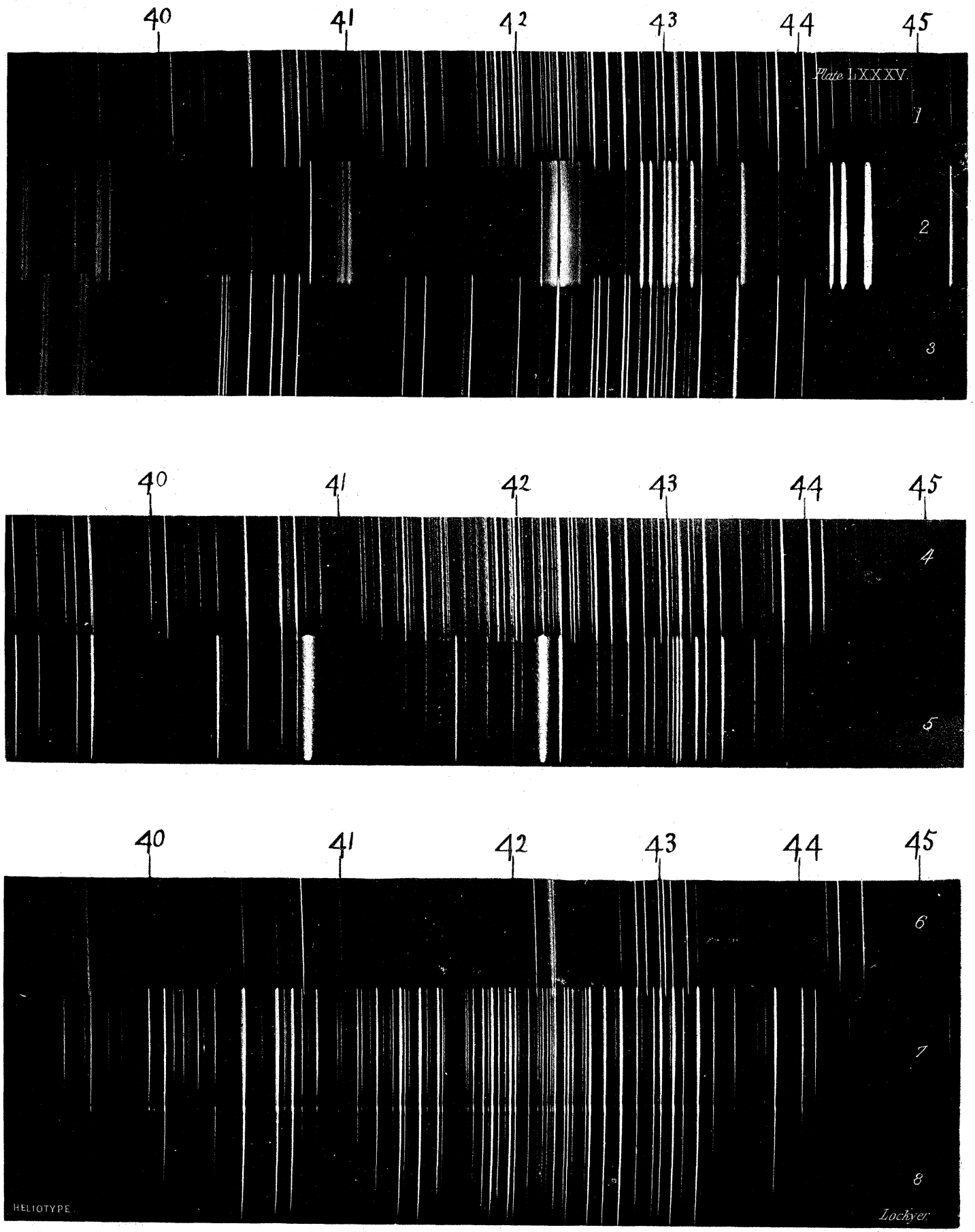



HELIOTYPE

Lockyer.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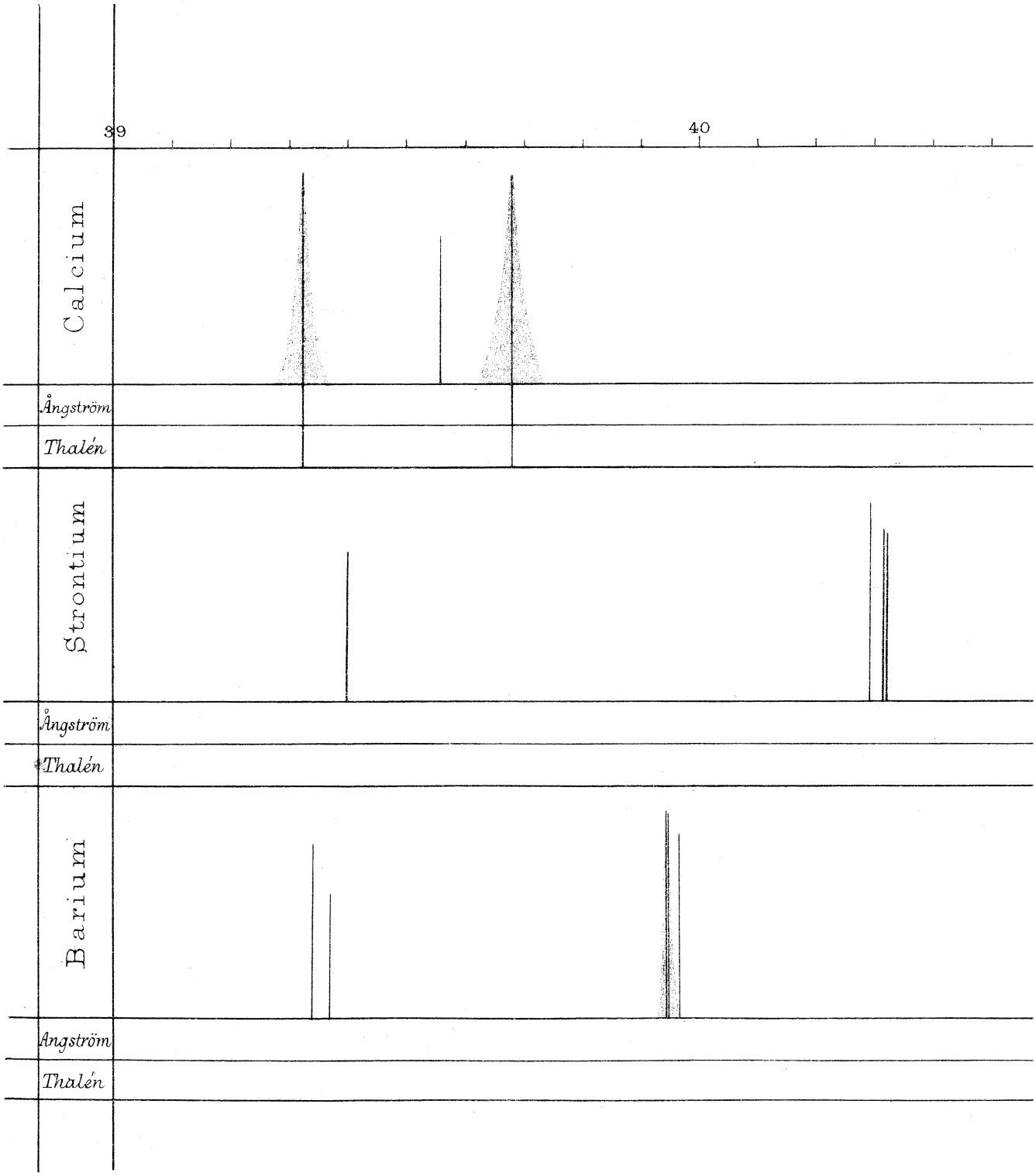
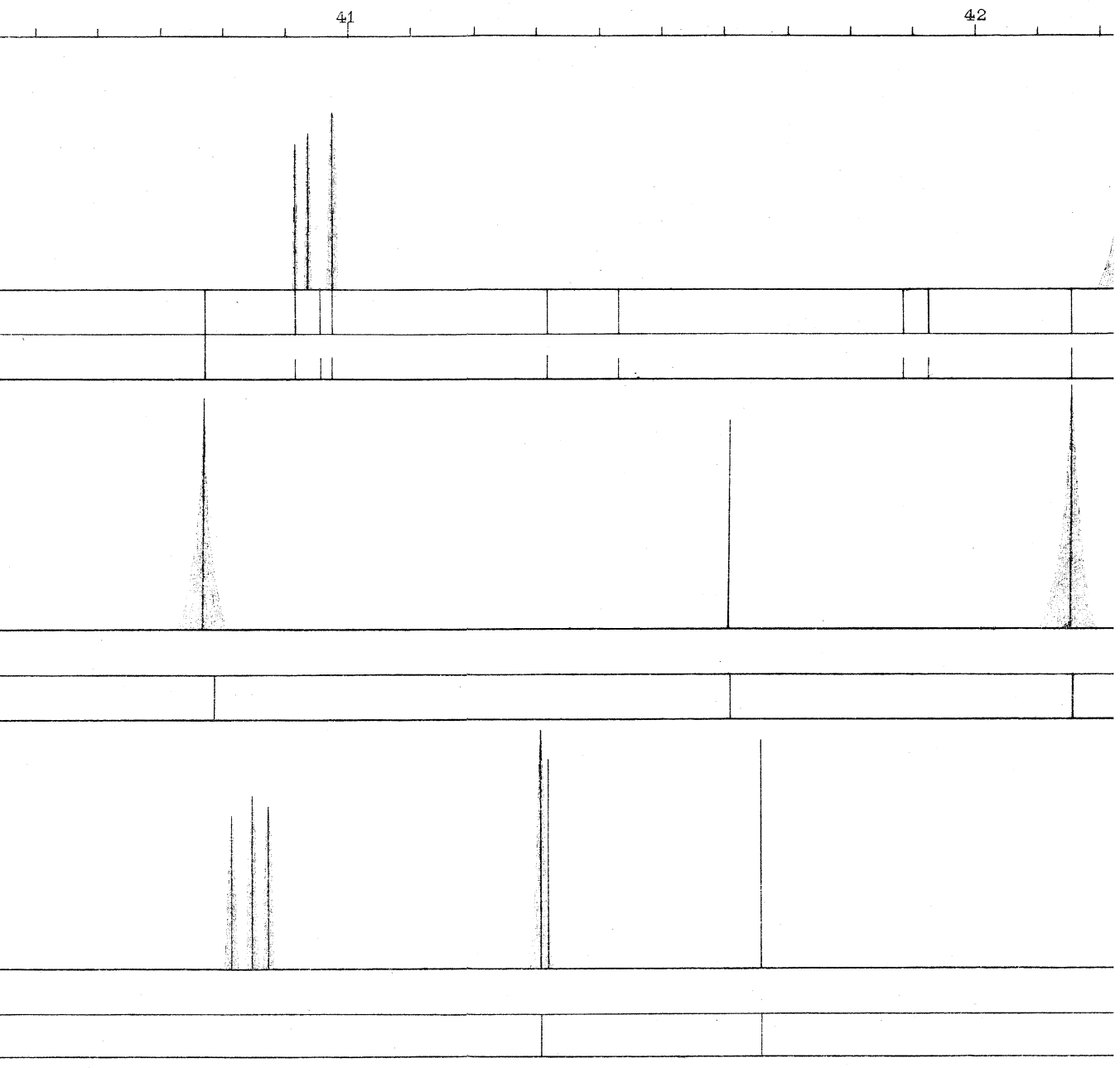
HELIOTYPE
Lockyer

Lockyer.




W. H. Wesley lith.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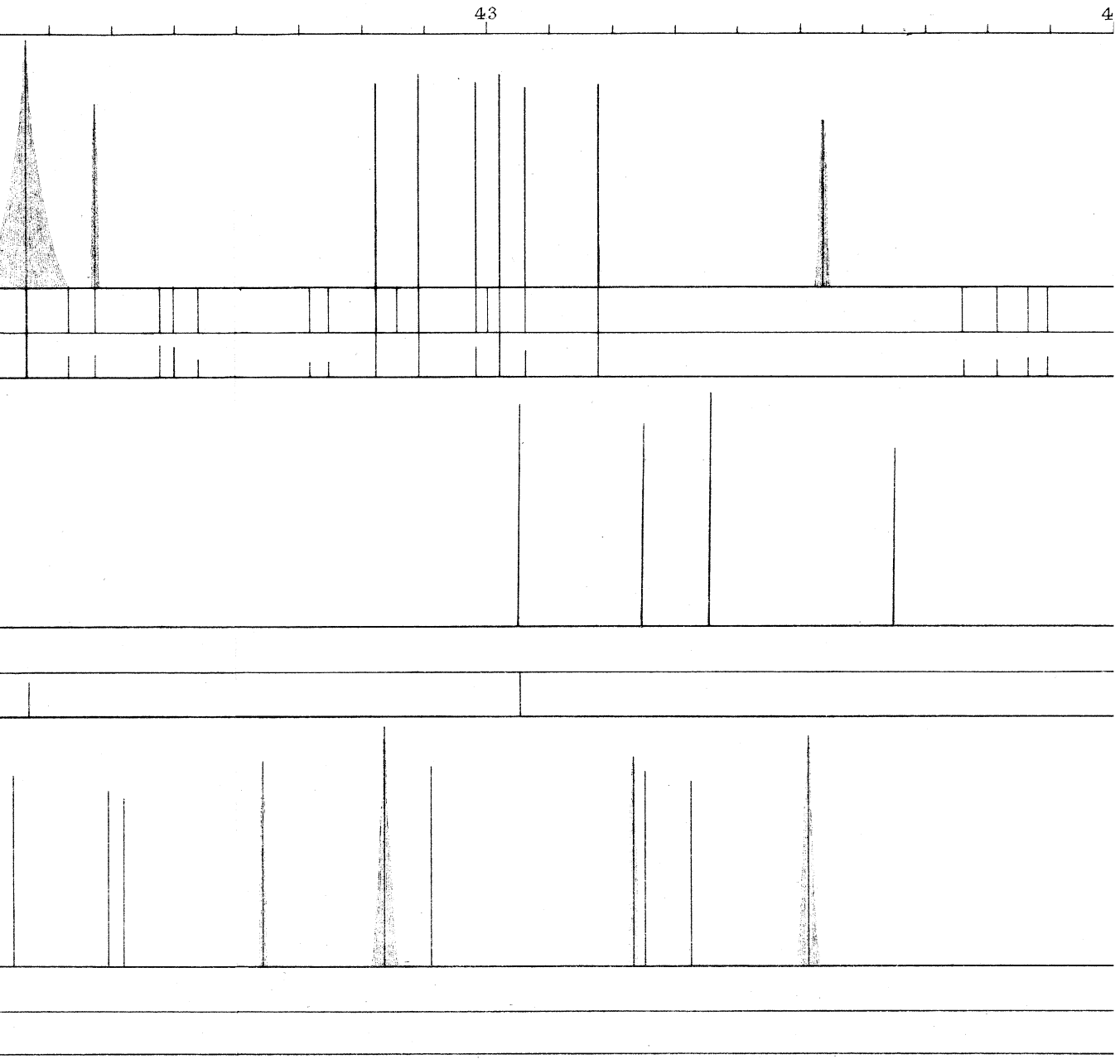
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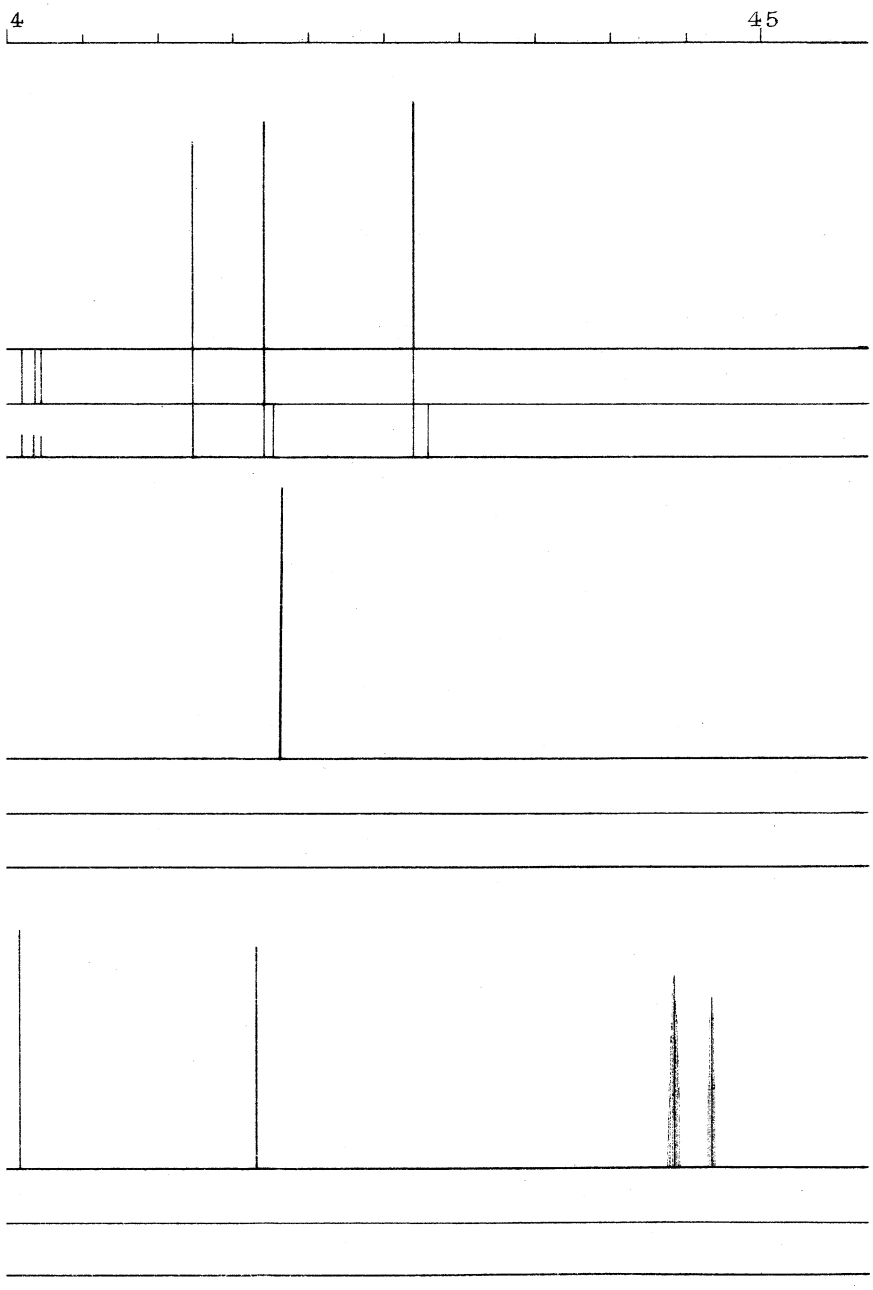
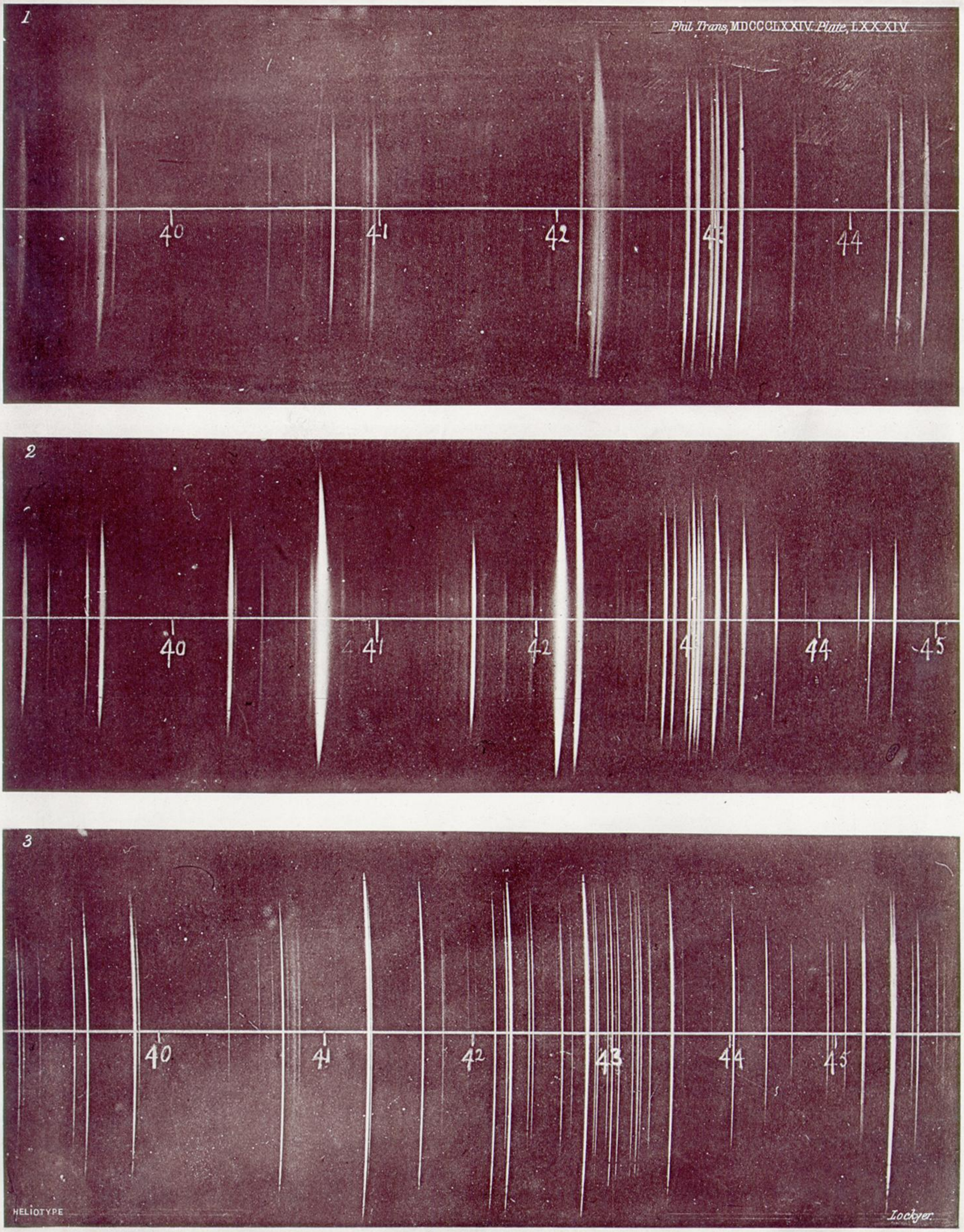



W. West & Co. imp.

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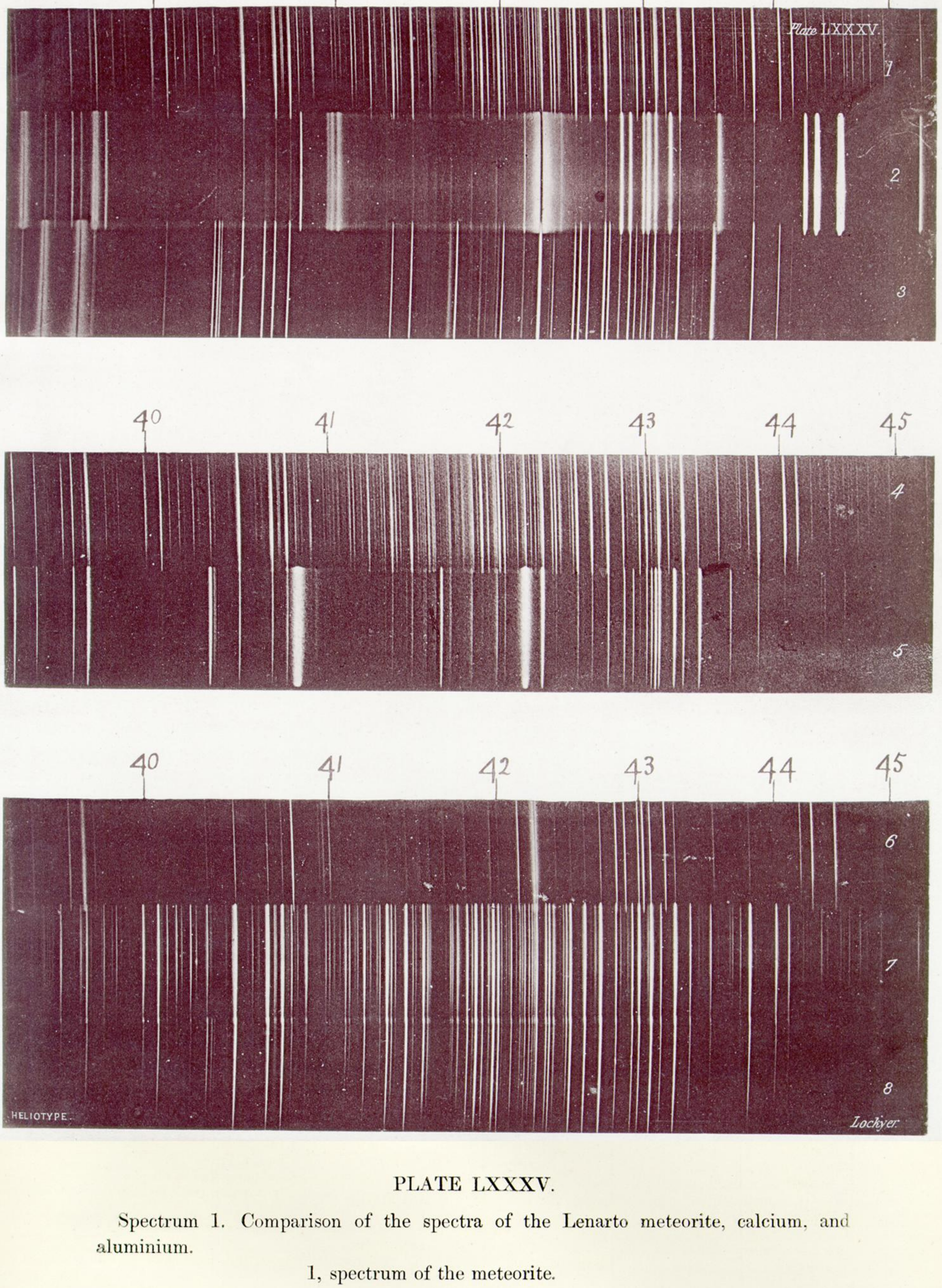
Spectrum 2. Long and short lines of strontium.
Spectrum 3. Long and short lines of barium.

*Note.*—In these photographs the impurity lines which have been eliminated from the map by the process described in the paper are present.

The photographs illustrate the use of the horizontal arc.

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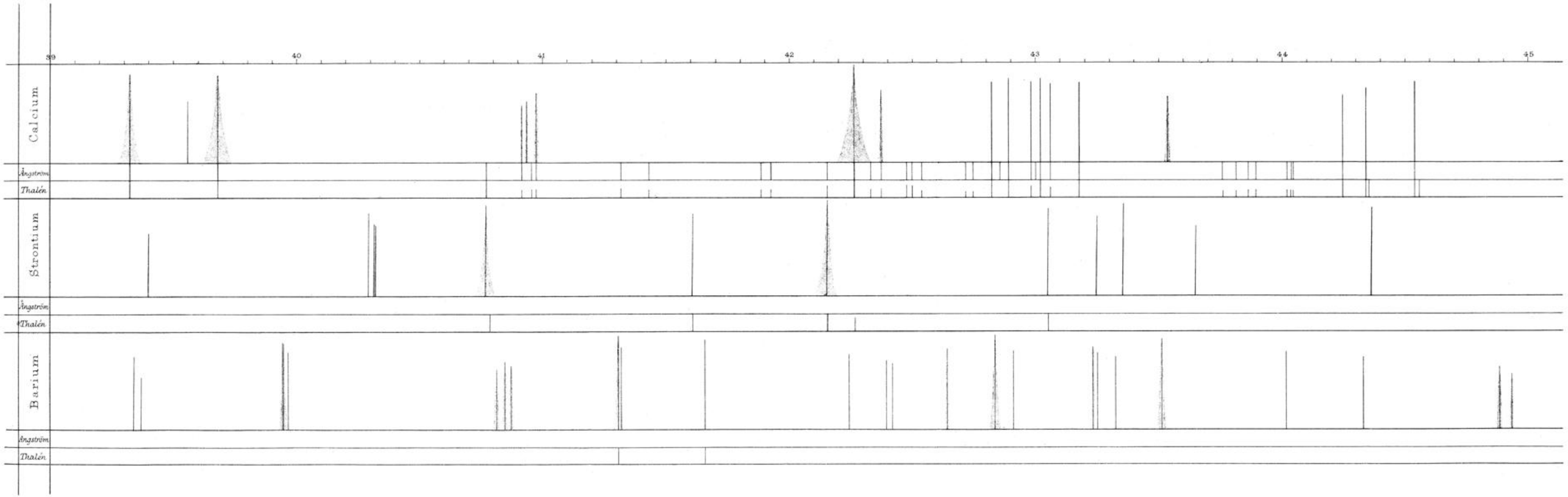
6, spectrum of calcium.
7, „ iron when cast into ingot.
8, „ „ before casting.




W. H. Wesley lith.

W. West & Co. imp.