

placed on its homogeneity. The paper is accompanied by a series of four curves, which show the results of experiments, and in which the coördinates are given by the ordinary method of assay, and by the spectroscopic readings.

The chief practical advantage which appeared to flow from this inquiry was that, if it were possible to replace the parting assay by the spectroscopical method, a great saving of time in ascertaining the value of gold bullion would be effected.

III. "Researches in Spectrum-Analysis in connexion with the Spectrum of the Sun."—Part III. By J. NORMAN LOCKYER.
Received November 20, 1873.

(Abstract.)

The paper commences with an introduction, in which the general line of work since the last paper is indicated. Roughly speaking, this has been to ascertain the capabilities of the new method in a quantitative direction. It is stated that while qualitative spectrum-analysis depends upon the *positions* of the lines, quantitative spectrum-analysis on the other hand depends not on position but on the *length*, *brightness*, and *thickness* of the lines.

The necessity of maps carefully executed and showing the individuality of each line is shown; and it is stated that the execution of these maps required the use of the electric arc to render the vapours of the metals incandescent. A battery of 30 Grove's cells of one pint capacity was accordingly employed in the researches about to be described.

The difficulties of eye-observations of the characters of the lines compelled the application of photography, another reason for the use of which existed in the facility it afforded for confronting spectra with each other, and so eliminating coincident lines, since the lines, if due to impurities, would be longest and thickest in the spectrum to which they really belonged.

The portion of the spectrum at present worked upon is that from H to F.

Another branch of the research has been the construction of a Table of all the named Fraunhofer lines, showing the lengths and thicknesses of the metallic lines to the absorption of which they were due; this Table enabled the author to allocate upwards of 50 lines in the solar spectrum, presumably overlooked by Ångström and Thalén. The Table was intended as a preliminary to a new photographic map of the spectrum from H to F, on a larger scale than Ångström's, which was intended to clear away all the difficulties touching coincidences—and to have below it complete maps of all the solar elements with their long and short lines. This map is incomplete at present, but is making rapid progress.

A preliminary search for elements supposed not to be in the sun has also been commenced.

Of the above-named researches the subsequent parts of the paper refer to:—

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

I. The experiments made on a possible quantitative Spectrum-Analysis.

After the two former papers were sent in to the Royal Society, an investigation of the general changes undergone by spectra given by alloys was commenced.

A micrometer eyepiece was mounted on the observing-telescope of the spectroscope. With this the following phenomena were observed:—

I. The lines which remained varied their length as the percentage of the elements to which they were due varied.

II. Some of the lines appreciably varied their thickness or 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 air-line was observed to grow faint and then disappear as the brightness of the metallic lines increased.

IV. In cases where the brightness or thickness of the line of one element was estimated by comparison with the line adjacent of the other constituent of the alloy, the point of equal brightness was observed to ascend or descend; this method was used 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 on the vapour of the opposite pole.

As these conclusions were derived from coarse alloys, and it was desirable to observe the effect of very fine gradation, Mr. C. Fremantle, the Deputy Master of the Mint, was begged to allow observations to be made on the gold-copper and silver-copper coinage alloys; and he immediately responded most courteously to the request.

Examples of the behaviour of some coarse alloys of silver and lead are given; they were irregular in their action; but it was observed that silver lines remained in the alloy as long as from $\cdot 05$ to $\cdot 02$ per cent. of silver was present. The alloys, however, were very unequal. Experiments on cadmium and tin alloys are described, the cadmium forming 10, 5, 1.0, 0.15 per cent. In the last but one cadmium line was permanent; in the first at least five were seen. In an alloy of 0.099 per cent. of cadmium

with a mixture of lead, tin, and zinc constituting the rest of the alloy, the behaviour of the cadmium lines was sensibly the same as in a mixture of 0.1 per cent of cadmium and 99.9 of tin.

In the Mint specimens the same phenomena were observed *en petit* as the coarser alloys showed *en grand*. In a gold-copper alloy $\frac{1}{1000}$ increase in the gold made the lines shorter, and a similar increase in the copper made them longer.

In the silver-copper alloy an increase of $\frac{1}{1000}$ in the silver lengthened the lines, a similar increase in the copper shortened them.

These phenomena can be explained by assuming such alloys to be different physical things, and that the spark acts upon the alloy as a whole as well as upon each vapour separately.

Thus, in these Mint alloys, copper is common to both, and their melting-points are :—

Gold . . . 1200° (Pouillet).

Copper . . 1200° to 1000°, the precise point not determined.

Silver . . 1000° (Pouillet).

The intermediate position of copper explains the different action on its lines of gold and silver.

II. *The Method of photographing Spectra adopted.*

A camera carrying a 5 × 5-inch plate and a 3-inch lens of 23 inches focus, replaced the observing-telescope of the spectroscope. The lens focused from 3900 to 4500 very fairly upon the plate. The beam passing through collimator and prisms was, as in Mr. Rutherford's researches, very small. As the electric arc in its usual vertical position gave all the lines from pole to pole, the lamp was placed on its side, and the arc used in a horizontal position, the slit being vertical. The dense core of the arc then gave all the short lines in the centre of the field, the longer ones extending beyond them on either side. In order to obtain a scale, it was resolved to photograph the solar spectrum immediately adjacent to the metallic spectrum under examination.

To effect this a portion of the slit was covered up while the solar spectrum passed through the free part, and then the part used for the solar spectrum was covered, while the formerly covered part was opened for the metallic spectrum. This was effected by a shutter, with an opening sliding in front of the slit; a diagram of its action and form is given.

The arrangement of the spectroscope, heliostat, &c. for obtaining the sun's light is described. The image of the sun was brought to a focus between the poles of the lamp by an extra lens interposed between the lamp and the heliostat.

The use of the shutter enables us to compare either two or more spectra upon a single plate; or the solar spectrum may be compared with

two metallic spectra, being made to occupy the position between the two.

III. *On the Lines coincident in different Spectra.*

The bearing of the former papers on the lengths of the lines of the elements is briefly recapitulated.

The examination of the various spectra of metals and alloys indicated the great impurity of most of the metals used, and suggested the possibility of the coincidences observed by Thalén and others being explained in the light of former work.

It is observed that coincidences are particularly numerous in the spectra of iron, titanium, and calcium, and that nearly every other solar metallic spectrum has one or more lines coincident with lines of the last element. These coincident lines are, as a rule, very variable in length and intensity in various specimens of the metals in which they occur, and are sometimes altogether absent.

One of the longest calcium lines, that at wave-length 4226·3, is also seen in the strontium spectrum as a line of medium length; and 4607·5, a very long line in strontium, appears in calcium as a short line. Another very long strontium line, 4215·3, is asserted by Thalén to be seen in calcium; but the author has never seen it till lately, and *then only in a specimen of calcium known to contain strontium*.

We have here, then, a case of coincident lines, in which the one that is long and bright in one spectrum is short and faint in the other, and a case of a line said to be coincident in two spectra being, though always visible in one, sometimes absent in the other of them, and only appearing in it when the two substances were mixed. The hypothesis of impurity at once explains the whole case, even without the third line, which renders the fact of mixture certain.

The longest lines of calcium occur in iron, cobalt, nickel, barium, strontium, &c.; and the longest lines of iron occur in calcium, strontium, barium, and other metals.

Other cases are adduced; and the following general statements are hazarded, with a premise that further inquiry may modify them.

1. If the coincident lines of the metals be 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 frequent in which they are long in one spectrum and shorter in the others.

2. 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.

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

A description of some photographs of spectra is then given, a photograph of the coincident lines of calcium and strontium being amongst them, and proving that strontium occurs in the sun; and the section concludes with a brief description of the method employed in making the new map, showing lengths and thicknesses, and enumerating coincident lines. This is done thus: papers are pasted on to photographs of the solar spectrum on glass; the lengths of the lines of the metallic spectrum under examination (*e.g.* that of iron) are marked on this paper in prolongation of the solar lines to which they correspond. They are then copied upon a map; and another piece of paper being fixed down, another spectrum is proceeded with in the same way.

IV. *The preliminary inquiry into the existence of elements in the Sun not previously traced.*

The previous researches having shown that the former test for the presence or absence of a metal in the sun, namely the presence or absence of its brightest or strongest lines in the average solar spectrum, was not conclusive, a preliminary search for other metals was determined on; and as a guide, Mr. R. J. Friswell was requested to prepare two lists, showing broadly the chief chemical characteristics of the elements traced and not traced in the sun.

The Tables showed that, in the main, those metals which had been traced formed stable compounds with oxygen.

The author therefore determined to search for the metals which formed strong oxides, but which had not yet been traced.

The result up to the present time has been that *strontium*, *cadmium*, *lead*, *cerium*, and *uranium* would seem with considerable probability to exist in the solar reversing layer. Should the presence of *cerium* and *uranium* be subsequently confirmed, the whole of the iron group of metals will thus have been found in the sun.

Certain metals forming unstable oxides, such as gold, silver, mercury, &c. were sought for and not found. The same was the case when chlorine, bromine, iodine, &c. were sought by means of their lines produced in tubes by the jar-spark. These elements are distinguishable as a group by forming compounds with hydrogen.

It is observed that certain elementary and compound gases effect their principal absorption on the most refrangible part of the spectrum when they are rare, and that as they become dense the absorption approaches the less-refrangible end—that the spectra of compounds are banded or columnar, the bands or columns lying at the red end of the spectrum—that the absorption spectra of chlorine, iodine, bromine, &c. are columnar, and that these are broken up by the spark just as the band

spectra of compounds are broken up—and that it is probable that no compounds exist in the sun. The following facts, gathered from the work already accomplished by Rutherford and Secchi, are stated.

There are three classes of stars :—

1. Those like Sirius, the brightest (and therefore hottest?) star in the northern sky, their spectra showing only hydrogen lines very thick, and metallic lines exceedingly thin.

2. A class of stars with a spectrum differing only in degree from those of the class of Sirius; and to this our sun belongs.

3. A class of stars with columnar or banded spectra indicating the formation of compounds.

The question is asked 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 prevents the coming together of the atoms which, at the temperature of the earth, and at all artificial temperatures yet attained here, form the metals, the metalloids, and compounds.

In other words, the metalloids are regarded as *quasi* compound bodies when in the state in which we know them; and it is supposed that in the sun the temperature is too great to permit them to exist in that state in the reversing layer, though they may be found at the outer portions of the chromosphere or in the corona.

It is suggested that, if this hypothesis should gain strength from subsequent work, stony meteorites will represent the third class of metalloid or compound stars, and iron meteorites the other or metallic stars.

The paper concludes as follows :—

“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 of 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 life.

“May it not also be, 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, that 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 the 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 not this be explained by the plasticity of the metalloids in question?

“May we not from these ideas be justified in defining a metal, provi-

sionally, 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 hot to a comparatively cold 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?"

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