IV. *Researches on Spectrum Photography in relation to New Methods of Quantitative Chemical Analysis.*—Part I.

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[Plate 3.]

Contents.

Introduction.

In the year 1878 I submitted to the Council of the Chemical Society a series of photographs executed with roughly constructed and imperfect apparatus, which showed variations in the number, length, and strength of the lines exhibited by some of the elements in the ultra-violet region. These photographs proved that by alterations in the exposure of the photographic plates certain impurities became visible in metals otherwise apparently pure, without any changes being noticeable in the spectra such as might be introduced by over-exposure. Thus by increasing the period of exposure three-fold the lines of iron were plainly seen in a spectrum regarded as that of pure aluminium. Gold obtained in as pure a condition as possible by parting gave evidence of the presence of silver. Two specimens of indium were examined: they both yielded the flame spectrum and the reactions usual with this metal; one of them showed no strong lines in the ultra-violet which could not be attributed to tin, lead, or cadmium; the other contained tin and cadmium in such proportions that the lines of these metals were more prominent than those of indium. A third specimen, prepared by Professor Richter, of Freiberg, yielded no spectral lines which could be attributed to any foreign metal.

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A striking fact was noticed which, as will be seen, is exemplified in the case of magnesium, namely, that it is not always what appears to be the strongest and longest lines which first make their appearance when an impurity is discernible; and it was considered that many observations were necessary to ascertain which are the most persistent lines in the spectra of the elements. It was proposed to extend these observations, but their importance at that time did not seem to be appreciated. Almost all varieties of spark spectra have since been investigated, with the object of applying spectrum photography to the purposes of chemical analysis. From time to time opportunities have occurred when the process which has been gradually developed and rendered practical has been advantageously put into operation for the solution of questions upon which it would have been difficult to arrive at a decision by other means. For instance, I employed photographs of spark spectra in an examination of the rare earth bases separated from the mineral rhabdophane, for testing the purity of certain cerium compounds, and for estimating the amount of beryllium contained therein (Journal of the Chemical Society, vol. xli., Transactions, 1882, p. 210). It may therefore be considered that the method is so far complete in detail that it may be with advantage described for publication, notwithstanding that it is manifestly capable of improvement.

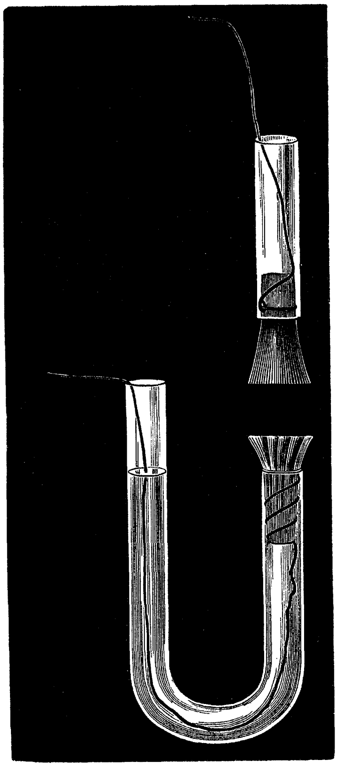
At an early stage of the inquiry it was found necessary to devise some convenient method of examining solutions of salts, and ascertaining the best material from which to form electrodes.

On a method of photographing spark spectra of the elements with solutions of their compounds.

In the examination of substances for the purpose of chemical analysis it is undesirable to use metallic electrodes even when this is possible, owing to the fact that alloys are not generally of a homogeneous character, and the sparks pass from only one or two spots situated at the surface of the electrodes. A better means of judging of the composition of a mass, whatever be its dimensions, is afforded by solutions, because the amount of metal volatilised by the spark from mere points of the substance is exceedingly small—according to Messrs. LOCKYER and ROBERTS not more than 0·0001 gram. ('Studies in Spectrum Analysis,' LOCKYER, p. 226). Messrs. PARRY and TUCKER ('Engineering,' vol. xxvii., pp. 127, 429; and xxviii., p. 141) in the examination of iron and steel have made use of the charcoal points first used by BUNSEN, and by dispensing with a Leyden-jar have photographed the lines characteristic of metallic solutions in such a manner as to render them comparatively free from the air spectrum. This method does not appear satisfactory to me, because a prolonged exposure is necessary, and with the reduced density of the spark, fluted spectra of air make their appearance while the metallic lines are too short. These bands or flutings are composed of a large number of fine lines, the distance between which increases with their increased refrangibility. They appear to be the spectrum of nitrogen of the first order. Messrs. PARRY and TUCKER'S photographs are representations of the less refrangible rays only, such as are transmitted by glass lenses and prisms. For obtaining sparks from solutions, M. LECOCQ DE BOISBAUDRAN uses a concentrated solution contained in a glass tube, through the bottom of which passes a platinum wire which is fused into the glass. The wire is connected with the negative pole of an induction coil, the positive pole terminating in a wire placed conveniently above this. A well-known modification of this is the tube of MM. DELACHANEL and MERMET (SCHÜTZENBERGER'S 'Traité de Chimie Générale,' vol. i., p. 284), but as the rays must necessarily pass through glass, it is not adapted to the examination of ultra-violet spectra. Any method is disadvantageous which necessitates the use of platinum electrodes, since the number of lines belonging to this element is embarrassing when they have to be eliminated from the spectra of other bodies. M. LECOCQ DE BOISBAUDRAN states that iridium points give no lines belonging to that metal, but this statement does not apply to photographed spectra of rays of high refrangibility obtained with a condensed spark, since about 180 lines have been counted in such a spectrum. Of all *metals* affording materials for electrodes gold appears to be the best; its spectrum is a weak one, containing comparatively few lines, it is an excellent conductor of electricity, and it is not attacked by solutions of metallic chlorides.

There is no very simple method of obtaining spectra free from air lines without resorting to either an inconveniently short or a too prolonged exposure, and if such existed it would be of doubtful advantage, since the number of the air lines in the ultra-violet region is not exceedingly large, and from their character they are easily recognisable. They are, in fact, a positive advantage, since by their well known appearance and positions they serve to fix the position of other lines. A simple and elegant apparatus devised by my colleague, Professor O'REILLY, consists of a metallic wick composed of a few twists of platinum wire, by which a BUNSEN flame is fed with the solution to be examined. Wicks of gold wire have been used by me, the metal projecting about one-eighth of an inch above the surface of the solution.

Of all elementary substances hitherto photographed, graphite yields the simplest spectrum ("Note on Certain Photographs of the Ultra-Violet Spectra of Elementary Bodies," Journal of the Chemical Society, vol. xli., p. 90). It shows lines and the edges of bands due to the air-spectrum to the number of sixty-six, of rays assignable to carbon it contains but twelve. Graphite being an excellent conductor of electricity, electrodes are made in the simplest possible manner by cutting plates of good Ceylon or Siberian graphite, tapering from one-fourth to one-eighth of a inch in breadth and three-eighths of an inch in length. Deep grooves or scratches are made in the sides of the lower electrode, which is inserted into the end of a small glass U tube containing the solution. The upper pole may be of metal or of graphite, either being fused into a glass tube or held in a screw clip. Platinum terminals from the coil are connected with these. Capillary attraction keeps the lower electrode moist at its upper surface. Such electrodes have been constantly in use for producing sparks from which photographs of the spectra of saline solutions have been taken. Fresh electrodes have generally been made for each solution, but they may be used over again repeatedly provided they be well washed with hydrochloric acid and water. They wear away rather quickly, but their durability may be indicated by the fact that the same points have actually been employed continuously for a period of ten hours. Each of the two pieces of graphite should be sharpened so as to resemble a chisel, the edge of the one being exactly superposed above that of the other, while both are placed in a line with the slit; the movement of the spark is thus restricted to a direction backwards and forwards, but always in front of the slit and not to one side or the other.



Graphite electrodes (actual size).

The only two lines of a foreign element plainly visible in the spectrum of graphite are the first and third of the quadruple group in the magnesium spectrum, with wavelengths 2794·4 and 2801·1. Faintly seen are the second and fourth lines, wavelengths 2796·9 and 2789·6. This specimen of graphite came from Ceylon, and it was thought worth while to submit it to the ordinary method of analysis. Accordingly a considerable quantity was incinerated, and the ash was found to contain only magnesium and a trace of iron. After some hundreds of electrodes had been cut from a lump of the material, it was found that the points showed more or less unmistakable indications of the presence of iron.

From this it appears that the same piece of the mineral may be of unequal purity.

Alterations in spectra caused by moistening the electrodes.

When electrodes of graphite are moistened with water, the only alteration remarkable in the spectrum is a lengthening of the short carbon lines, with wave-lengths 3590·0, 3583·5, 2836·8, 2836·0, 2511·6, 2508·7, and 2478·3, so that they extend from pole to pole. The other lines of carbon do not appear to be more than slightly lengthened, and in addition the line 4266·3 is much weakened. This change would receive a natural explanation by assuming the formation of some gaseous or at least volatile carbon compound. If it be due to carbon dioxide, a similar change should occur when the electrodes are surrounded by pure oxygen. In order to put this matter to the test of experiment, pure dry oxygen was passed for some time through a glass tube in which were fastened electrodes of graphite, the end of the tube being closed by a plate of quartz. The change seen in the spectrum under these circumstances is the following :—

Wave-lengths.	
4266·3	This line does not appear altered.
3919·5	This line remains short.
3875·9	This line remains short.
3590·7	This line remains short.
2836·8 2836·0	These lines are so lengthened as to be rendered continuous from pole to pole.
2746·6 2640·0	These lines are somewhat lengthened.
2511·6 2507·8 2478·3 2297·6	These lines are lengthened so as to be rendered continuous.

A map to the scale of wave-lengths is appended (Plate 3).

In addition to the above, the following lines are seen with difficulty, a pair with wave-lengths about 3168·0 and 3166·3 is much lengthened, and a very nebulous ray, extending from about 2995 to 2990 ($\lambda=2993$) is rendered much larger and more distinct. It will be seen that the two spectra differ considerably; it does not, therefore, seem at all probable that the change is due to the cause suggested. Indeed, it is not, as may be learnt by a study of the action of the spark on metallic electrodes. When photographs are taken of dry electrodes of copper the lines in the spectrum with lesser wave-lengths than 2766·2 and extending to 2243·5 are all short lines. When the electrodes are moistened with a solution of a metallic chloride, with hydrochloric acid, or even with pure distilled water, these lines are greatly lengthened, some of them so much so as to become continuous. When platinum, iridium, and gold electrodes are partially immersed in water, the same lengthening of the short lines takes place as in the case of copper and graphite. The lines of iridium yielded by dry electrodes extend no more than one-fourth the distance towards the opposite pole. When one pole is a point of iridium and the other of copper, the two series of short lines are seen, but those of iridium only are visible when that metal constitutes the negative pole, though the copper lines are weak, but still visible, at the positive pole.

When an iridium point, as the negative electrode, is partially immersed in water all the short lines are increased in length, so that they stretch four-fifths of the distance towards the copper; if the copper be negative and immersed in water the copper lines are lengthened, and but few of those belonging to iridium are discernible. The same lengthening of short lines takes place when gold electrodes are moistened. We have but few facts which serve to indicate the constitution of the electric spark and the circumstances under which it is altered in character. It may, however, be affirmed, with some degree of truth, that an increased intensity of the spark, such as is gained by placing a jar in circuit, which is usually considered to correspond to an increase of temperature, causes an increased length in the short lines, and also that the more volatile the metal the longer the lines. It was considered necessary to ascertain the effect of heating the electrodes, and accordingly two points of iridium wire were taken as suitable. When the spark passed at the ordinary temperature, a photograph which received five minutes' exposure showed, beside the large number of short lines, a continuous band of rays extending through the whole spectrum. On the same plate, and immediately beneath this, another photograph was taken while the negative electrode was heated to the most brilliant incandescence by the oxy-hydrogen blowpipe. The spark continued to pass during the whole period of five minutes, as was made evident by the scintillations visible at the cooler electrode. This latter was kept at a temperature sufficiently low as to show no signs of redness. The passage of the spark, but for the scintillations, was otherwise invisible and almost noiseless. On turning down the gas the spark appeared of a pale blue colour, the electrode being at a red-heat, and it now emitted a moderate crackling sound, similar to that caused when no jar is in circuit. On turning the gas out the spark grew brighter as the metal became colder, till finally the usual brilliancy and the sharp crackling noise were resumed. The second photograph, with the same exposure of five minutes, showed barely a trace of the iridium spectrum; some feeble rays emitted by the flame of the blow-pipe were visible, but the chief feature of the photograph was the beautiful group of nitrogen lines seen when the spark is passed between points without a jar in circuit. The wave-length of the line at the commencement of one of these groups was 3369, the commencement of the second group was a line with wave-length 3211·6, the spectrum terminating with a line with wave-length 3062·4.

At a low red-heat the spark passes with only a moderate crackling sound, and the spectra photographed under these conditions consist of the two spectra of air—namely, those of the first and second order superposed.

The same photographs are obtained when only a small jar is used and the electrodes are cold.

From these experiments it is evident that cooling the electrodes intensifies the spark, and consequently lengthens the short lines, just as heating them causes the reverse effect. The reason why heating the negative electrode acts so powerfully upon the spark is because the high temperature of the pole discharges the jar (GUTHRIE'S 'Magnetism and Electricity,' p. 84).

In addition to the lengthening of the carbon lines, hydrochloric acid and solutions of metallic chlorides yield a weak continuous spectrum, and also a series of closely placed lines or flutings, further details concerning which are given on page 59. The continuous rays are most noticeable in spectra of solutions of chlorides of the alkali metals and of aluminium chloride; the flutings, however, appear most prominent in concentrated solutions of aluminium chloride and of zinc chloride.

Dry electrodes in air showed in some instances a total absence of the lines, with wave-lengths 4266·3, 3919·5, 3881·9, 3875·7, 3870·7, 3590·0, 3585·0, 3583·5, 2746·6, and 2640·0, while 2836·8 and 2836·0 were exceedingly faint. These lines are marked on the map with a star. No reason can be assigned at present for this difference in the spectrum, as the lines 4266·3, 3919·5, 3881·9, 3875·7, and 3870·7 are visible when the atmosphere surrounding the poles is carbon dioxide, and the photograph was perfect as regards the other part of the spectrum. A difference in the strength of the spark may occasion some similar alteration, but such a cause did not operate in this case.

On the spectra of solutions of binary compounds.

A complete series of photographs of metallic salts, chiefly chlorides, corresponding to the electrodes already enumerated and examined, was executed (Journal of the Chemical Society, vol. xli., p. 90). The reason for taking chlorides was that as a rule they are among the most soluble of salts. The solutions examined consisted of the chlorides of magnesium, zinc and cadmium, aluminium, thallium, iron, cobalt and nickel, arsenic, copper, strontium and tin. The cadmium, copper, and stannous chlorides were made by dissolving the electrodes used for the series of photographs of the elements. The zinc chloride was made from a very pure specimen of distilled zinc, the only impurity it betrayed being a trace of cadmium. The arsenic trichloride was obtained from a very carefully purified specimen of arsenious oxide. The ferric chloride was prepared from fine pianoforte wire. The thallous chloride was a particularly pure specimen made from the metal used as electrodes.

Some preparations of barium and strontium chlorides made with great care were found to contain calcium. They were purified by treating saturated solutions with an equal volume of strong hydrochloric acid, whereby the chlorides are precipitated in a crystalline form, and by filtration through a plug of asbestos the acid liquid is separated therefrom, the crystals are washed with strong acid twice, after which they are dissolved in water, and if necessary treated again in the same manner. Aluminium chloride was prepared from an especially pure specimen of ammonia alum, the aluminium hydroxide was precipitated by ammonia and most thoroughly washed with hot water, it was then dissolved in hydrochloric acid. The cobalt chloride was a carefully prepared laboratory specimen. This series of solutions is very complete, inasmuch as spectra of almost every character are represented and may be referred to. For instance, there are comparatively few lines in the magnesium spectrum, but these are of a strongly marked character and they are closely grouped together. Exceedingly short and some straggling and long lines occur in the zinc spectrum, while in cadmium we see the position of two of the lines to be so near together that there is some difficulty in distinguishing them. In the iron and cobalt spectra there is a multitude of long and short lines crowded together in groups. In arsenic and antimony we have examples of metalloid spectra, with a considerable amount of diffused rays and lines distributed with tolerable regularity throughout the whole ultra-violet region.

By the juxtaposition of spectra on the same plate, the lines assignable to each metal were compared with those yielded by a solution of its chloride. With but two exceptions the two series of spectra are identical line for line; in the case of iron the number of lines reproduced is over 600, and in that of cobalt over 500. The group of five fine lines constituting the most refrangible group in the spectrum of magnesium were exactly reproduced by the solution of the chloride along with the other lines characteristic of the metal. The dual lines of cadmium were in like manner plainly seen. The one sole difference between the spectra of metallic electrodes and those from the salts of the metals was the greater degree of continuity of the lines shown by the salts. Thus all the lines discontinuous in the spectrum of iron were continuous in that afforded by a solution of ferric chloride. The short lines of the metals potassium and sodium, which are weak, appear as short lines in the spectra of their chlorides, likewise some of the shortest lines which are at the same time strong lines in the spectrum of aluminium are seen as short lines in the spectrum of a concentrated solution of its chloride. These lines form a triplet group with wave-lengths 3612·7, 3601·2, and 3584·5. This last line appears to be strongest in the aluminium spectrum. Whether the short lines appear or not depends upon the amount of metal present in the solution.

Regarding the two exceptional cases above-mentioned, they are referable to two distinct causes—the first to the extreme shortness of the lines, and the second to the presence of an impurity. Zinc is a metal with a number of lines in its spectrum so short that they can be described as merely dots. Their wave-lengths are the following: 2526·3, 2521·3, 2514·7, 2508·7, 2490·4, 2485·9, 2427·0, and 2418·8. All specimens of zinc yield these very short lines, but solutions made from them do not. As anhydrous zinc chloride contains only 65 per cent. of the metal, and as no solution of the chloride used in the spark apparatus contained more than 25 per cent. of this salt, it is easy to see that the absence of these lines may be accounted for by the small quantity of metal in the spark.

When zinc electrodes are moistened these very short lines become somewhat lengthened.

When aluminium electrodes were employed to obtain a photograph of its spectrum (Journal of the Chemical Society, vol. xli., p. 90), a number of short lines were exhibited which did not appear in the spectra of solutions of the chloride. The wave-lengths of the aluminium lines as seen in solutions are the following: 3960·9, 3943·4, 3612·7, 3601·2, 3584·5, 3092·2, 3081·5, 3056·8 (faintly), 2815·6, 2659·8, 2651·7, 2631·0 (a group of five lines), and lastly 2567·5.

Nearly all the remaining short lines are caused by the presence of iron, a fact which may be easily ascertained by prolonging the exposure of the photographic plate. Commercial aluminium may contain as much as 2 per cent. of iron, and as the iron lines are strong, this quantity modifies the appearance of the spectrum to such a degree as to give it a considerable resemblance to that of iron, but there is the widest possible difference between the spectra of the two metals. J. L. SCHÖNN, who examined the ultra-violet spectra of several metals with Iceland spar prisms and a fluorescent eye-piece, has remarked on what he believes to be a similarity between the aluminium and iron spectra (WIEDEMANN'S Annalen, vol. ix., p. 483; vol. x., p. 143). It is possible that the likelihood of iron being contained in the aluminium had escaped his notice, or that he was not prepared to recognise the iron lines when they were somewhat altered in appearance by the metal being present in small quantities.

Mr. J. NORMAN LOCKYER, referring to the differences in the appearances of the spectrum of the same element under different conditions, has shown that by diminution of pressure under which the spark is taken, certain short lines disappear, while longer lines remain. Further, he states in reference to the spectra of chemical compounds: "It was found in all cases that the difference between the spectrum of the chloride and the spectrum of the metal was :—*That under the same spark conditions the short lines were obliterated, while the air lines remained unchanged in thickness*" (Phil. Trans., clxiii., p. 253, 1873).

It is obvious that this statement cannot be applied to solutions of chlorides examined in the manner described in the preceding pages, and the reasons for our different conclusions are the following. The short lines are not visible in the spectra of dry metallic chlorides, because the quantity of metal present in the spark is too small. Thus the spark does not pass from the chloride because it is a very bad conductor, or through it because it does not form a continuous and homogeneous covering to the metallic electrode, but only past or between the particles of the salt from the surface of which portions are volatilised. The conditions are quite different when metallic solutions are used; the salt is equally diffused throughout the liquid, which forms a continuous coating to the electrode through which the spark must pass, and as the electrode is nearly immersed in water the intensity of the spark is increased. Hence, though the quantity of the element present in the solution might be insufficient to render the short lines visible with dry electrodes, the opposite effect introduced by the presence of water is sufficient to compensate for this.

In order to ascertain whether the elements oxygen and sulphur in combination could yield spark spectra, and whether insoluble compounds could be made to yield metallic lines to the spark, ferric oxide and ferrous sulphide were examined. The substances were finely powdered and mixed with glycerine to prevent them being dispersed by the spark too rapidly. No iron lines were detected on the photographic plate exposed to the action of the spark for the normal period of two minutes, though there was a good photograph of the graphite electrodes and the air spectrum.

To test the behaviour of insoluble but volatile substances, thallous chloride was treated in the same way, and the lines with wave-lengths 3778·4 and 3518·8 were rendered weakly. In no case did the non-metallic constituents cause any variations in the spectra. Hence we may conclude that :—*Insoluble and non-volatile compounds do not yield spark spectra when diffused in liquids.*

Several attempts to obtain a spectrum from selenium, selenic acid, and sodium selenate have proved unsuccessful.

On the spectra of ternary compounds.

In an examination of ternary compounds the salts examined were sulphates, nitrates, and phosphates of magnesium, cadmium, zinc, aluminium and iron. The bases of these salts were, as in the former case, prepared from the metallic electrodes, the aluminium and iron compounds being prepared from pure aluminium hydroxide and ferric oxide. The ferric oxide was obtained by heating pure ferrous sulphate with sodic sulphate, lixiviating with hot water, and washing many times therewith by decantation. The oxide was then dissolved in the requisite acids. The observations recorded in the case of metallic chlorides apply equally well to sulphates and nitrates, while the difficulty of obtaining a spectrum from ferric phosphate diffused in glycerine was equal to that in the case of the sulphide. When dissolved in hydrochloric acid the phosphate displayed the lines of iron only. A similar observation was made with cerous phosphate. Ammonium chloride was made into a saturated solution, and its spectrum photographed. There was no striking alteration in the spectrum of the graphite poles, but a careful examination showed that a group of lines which appear to be caused by the presence of nitrogen was greatly strengthened and made more prominent. These lines or flutings extend from about wave-lengths 3881·8 to 3829·0. The following facts point to their origin. They are never seen when metallic electrodes are used, wet or dry ; they are therefore not air-bands. They are not seen when carbon electrodes are immersed in oxygen, and cannot therefore be due to carbon dioxide. They are always seen when solutions are used with carbon electrodes, and are particularly strong when the carbons, wet or dry, are immersed in pure and dry nitrogen. When the negative pole is a metallic wire immersed in water, and the positive a point of carbon, the lines are strongly developed at the positive pole only. When the current is reversed the spectrum is not so strong. The bands not being traceable to carbon dioxide, to a hydrocarbon or to air, and being at the same time produced with great intensity when graphite is surrounded by pure and dry nitrogen, they must belong either to a modified spectrum of carbon or to a compound of carbon with nitrogen, such as cyanogen. In order to test the probability of these flutings belonging to the cyanogen spectrum, it was thought desirable to try the effect of cyanides in solution, using for the purpose metallic electrodes. A sample of perfectly pure cyanide of potassium was prepared by dissolving the commercial salt in alcohol and crystallising it therefrom. A saturated solution of the salt gave no sign of the bands when submitted to the spark passed between gold electrodes. A hot saturated solution of mercuric cyanide was similarly treated, the negative electrode being gold and the positive carbon, the gold being all but immersed in the solution. A strong mercury spectrum was obtained, but the flutings were absent except at that point where they might be expected under ordinary circumstances, namely, at the positive carbon electrode, and even here they appeared as faintly as if water and not a saline solution had been used. Cyanides therefore do not yield this spectrum.

It is remarkable that certain solutions which do not contain nitrogen in any form favour the formation of these bands, as for instance chlorides generally and zinc chloride as a saturated solution particularly. In order to ascertain whether the strength of the spectrum is dependent on the proportion of saline matter present, I examined a series of solutions containing varying proportions of calcium chloride, from $\frac{1}{100}$th to $\frac{1}{10000}$th, with the result that the strength of the bands was found to increase with the strength of the solutions.

There are two lines in this spectrum of graphite (Journal of the Chemical Society, vol. xli., p. 90) which apparently commence these flutings; their wave-lengths are 3875·7 and 3870·7, and yet two others which are absent from the spectrum of carbon when taken in oxygen with wave-lengths 3585·5 and 3584·0.

Professors LIVEING and DEWAR give the general appearance of the cyanogen spectrum as observed by them (Proc. Royal Soc., vol. xxxiv., p. 123), and the group of lines between K and L, extending from 3883 to about 3830, much resembles the first group mentioned above, while the second series near N, lying between 3580 and 3590, approximate closely to the second pair of lines to which I refer; nevertheless I cannot attribute these lines to cyanogen because they are not obtainable from cyanides.

That these lines are absent from the carbon spectrum when taken under certain conditions is not conclusive evidence that they are not carbon lines, because, as I have already shown, the lines 4266·3, 3919·5, 3881·9, 3875·7, 3870·7, &c., are occasionally absent, yet these unquestionably belong to the carbon spectrum.

Borates and silicates.—When soluble borates or boracic acid, soluble silicates, silicofluorides, or hydrofluosilicic acid are submitted to the spark, line spectra of the elements boron and silicon result, as I have already shown in a paper submitted at a recent date to the Royal Society. I then showed reason for suspecting that several lines attributed to carbon by Professors LIVEING and DEWAR (Proc. Roy. Soc., vol. xxxiii., p. 403) are in reality lines of silicon. In their communication, to which I have had to refer for a description of the cyanogen spectrum, I find (*loc. cit.*, vol. xxxiv., p. 123) a list of lines seen in the arc spectrum which they assign to carbon. I give for comparison with these the wave-lengths of the most prominent lines in the spectrum of silicon.

Approximate wave-lengths of carbon arc-lines (LIVEING and DEWAR).	Wave-lengths of silicon lines (HARTLEY).
2434·8	2435·5
2478·3	...
2506·6	2506·3
2514·1	2513·7
2515·8	2515·6
2518·8	2518·5
2523·9	2523·5
2528·1	2528·1
2881·1	2881·0

From this it seems probable that the only carbon line in the ultra-violet arc spectrum is the strongest of the series with wave-length 2478·3.

On spectra obtained from dilute solutions and on alterations caused by prolonged exposures.

The effect of prolonged exposure of the sensitive plate to the spark produced from weak solutions is a lengthening and strengthening of the metallic lines. It is reasonable to suppose that the density of the lines, or otherwise the intensity of chemical action, is a function of the concentration of the liquid and the period of exposure in all cases, but with very dilute solutions this certainly appears not to be exactly the case. Thus a solution containing six per cent. of calcium chloride exposed for half a minute, yields a spectrum with the calcium lines, showing a greater density than that produced by a solution containing one per cent. of the salt exposed for three minutes. Probably the conducting surface of the electrodes is not large enough to be kept constantly moistened, and so maintained in a condition capable of presenting a sufficient quantity of the solution to the spark. It has been observed in all cases that the effect of diluting solutions is to weaken the metallic lines; and, further, with one or two exceptions, to shorten even the longest and strongest lines until they finally disappear.

On the presence of impurities in certain spectra.

It has been noticed that when solutions are photographed with a Leyden-jar in circuit, and when these solutions are concentrated, two very fine and continuous lines of a strong character, which have been identified with the metal calcium, are occasionally seen. Their wave-lengths are 3967·6 and 3933, and they are designated H and K of the solar spectrum on M. CORNU's map. Sometimes a second pair of lines, with wave-lengths 3736·5 and 3705·5, are visible. They appear in strong solutions of cadmium chloride, ferric chloride, cobaltic chloride, and ferric nitrate. They are of very feeble intensity in strontium chloride and barium chloride, and then only the first pair are visible, attenuated and shortened.

They appear as short lines and rather feeble in photographs taken from electrodes of SIEMENS-MARTIN steel, and from electrodes of iridium. The most remarkable fact about these lines is, that they are not visible in the spectra of the alkaline chlorides, lithium, sodium and potassium, which were prepared from neutral solutions. Nor are they to be seen in the spectrum of aluminium chloride. They do not appear in photographs of the spectra of graphite points, either when dry or moistened with water, but they are seen as very faint and short lines when graphite points are moistened with hydrochloric acid. They are fairly well seen in solutions of ferric sulphate, prepared by dissolving the oxide in sulphuric acid. For some time the origin of these lines was a source of some perplexity, for although they had been ascertained to be calcium lines, yet they made their appearance on occasions when they were least expected, and when their presence could not be accounted for. Acids were always found to contain traces of calcium, and particularly hydrochloric acid; but the quantity was so minute as to be capable of detection only by photographing the spectrum. A quantity of pure hydrochloric acid was distilled in a previously very carefully cleaned glass retort and collected in a glass receiver. The operation was so conducted that by no possibility could any of the liquid have been carried over, except in the form of vapour. Still, in photographs of the spectrum of the distillate, the calcium lines were detected but little diminished in intensity. When platinum wire was substituted for graphite electrodes the lines were again present.

There is much evidence that the action of the acid upon the glass vessels dissolves out of the glass a small portion of calcium. The calcium lines are particularly strong, while those of the alkalies are just as weak. It is probable that the aluminium which does not appear would be less likely to enter into solution, and at the same time as the lines are not so strong as the calcium lines they would not be so easily rendered visible. Messrs. PARRY and TUCKER found that various samples of iron, after solution in hydrochloric acid and further chemical treatment, gave evidence of the presence of calcium. In this case the calcium probably was introduced by the acid, or at least a portion of it, and the strength of the lines was increased by the concentration of the solutions. It must, however, not be overlooked that both SIEMENS-MARTIN steel and dry iridium electrodes yielded spectra with the calcium lines. In the case of the steel, either minute traces of slag are diffused through the metal or traces of calcium occur as one of its constituents. The iridium points were new, and it is just conceivable that traces of lime from the crucible in which the metal was fused were adhering to its outer surface. The specimens of graphite contained magnesium and iron, but no calcium. This conclusion was the result of spectrum observations, and likewise of a careful analysis of the ash made by the usual methods. Many of the photographs of solutions of metallic chlorides, as for instance the chlorides of copper and manganese, show no trace of the calcium lines. I have now no doubt that when the calcium salt is not derived from the action of acids on glass vessels, the spectra are contaminated by dust floating in the air, and that the calcium lines are to the ultra-violet region in this respect what the sodium lines are to the visible spectrum.

The alkali-metals yield but feeble ultra-violet spectra, otherwise the sodium lines would likewise be ever present.

The evidence that the calcium lines are due to dust is the following: two metallic electrodes, alloys of copper and silver, were filed up so as to present bright points; they were each opposed to a graphite electrode, and the spark was made to pass from the metal to the carbon; in the one case the calcium lines were either very faint or invisible, but in the second they were very strong. The interval of time between the taking of the photographs was not more than half a minute. The calcium lines were strongest at the metallic or negative pole.

The following facts have been established by the foregoing observations :—

When carbon or metallic electrodes are moistened the short lines are lengthened.

With very few exceptions the non-metallic constituents of a salt do not affect the spark spectra of solutions.

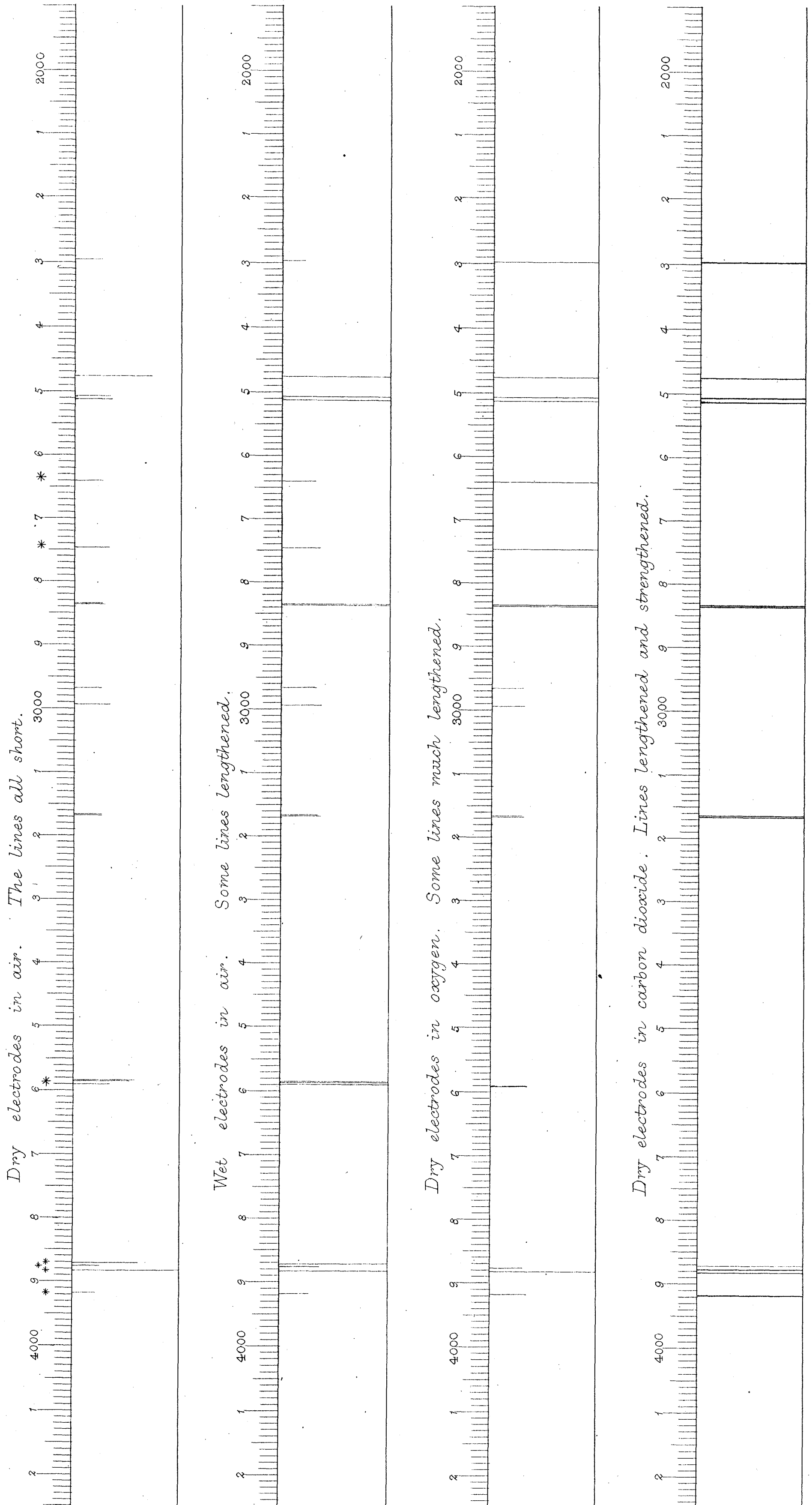
Insoluble and non-volatile compounds do not yield spark spectra.

The solution of a metallic chloride yields spectral lines identical in number and position with the principal lines of the metal itself.

Short lines become long lines, but otherwise their character is identical, whether the spectra are produced by metallic electrodes or solutions.

The effect of diluting solutions of metallic salts is first to weaken and attenuate the metallic lines, then with a more extensive dilution to shorten them, the length of the longest and strongest lines generally decreasing until they finally disappear.

Accidental differences in the passage of the spark or in the time of exposure of the photographic plate, when the normal period is from half a minute to five minutes, do not cause sensible variations in spectra obtained from the same substance.



The Spectrum of Graphite Electrodes under different Circumstances.

The lines and groups of lines marked thus * are occasionally absent.

Dry electrodes in air. The lines all short.

Wet electrodes in air. Some lines lengthened.

Dry electrodes in oxygen. Some lines much lengthened.

Dry electrodes in carbon dioxide. Lines lengthened and strengthened.

West, Newman & Co. lith.