

XIV. *On the Quantitative Analysis of certain Alloys by means of the Spectroscope.*
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IN certain researches on Spectrum-Analysis, the results of which have already been communicated by one of us to the Royal Society, it has been shown that the spectroscope may be employed to distinguish minute differences in the composition of certain alloys. We have therefore instituted a series of experiments with the view to ascertain the degree of accuracy of which the method is capable, and now submit the results which we have already obtained.

In the researches above referred to, an electric-spark-current was used to volatilize the alloy under examination, and the image of the spark was thrown by means of a lens on the slit of a spectroscope; the phenomena observed indicated that a change in the percentage of any constituent of a metallic alloy ordinarily causes a change in the character of lines exhibited in the resulting spectrum, in length, brightness, or thickness; and the percentages of the constituents, it was stated, might be determined by comparison with the spectra of pieces of metal of known composition.

It may be remarked that changes are exhibited in the spectra in various ways, thus:—

1. Changes in the lengths of lines of one constituent.
2. Changes in the position of the point at which lines belonging to different metals in the alloy show equal brightness or thickness.
3. Changes in the relative lengths of a pair of lines belonging severally to the constituents of the alloy.

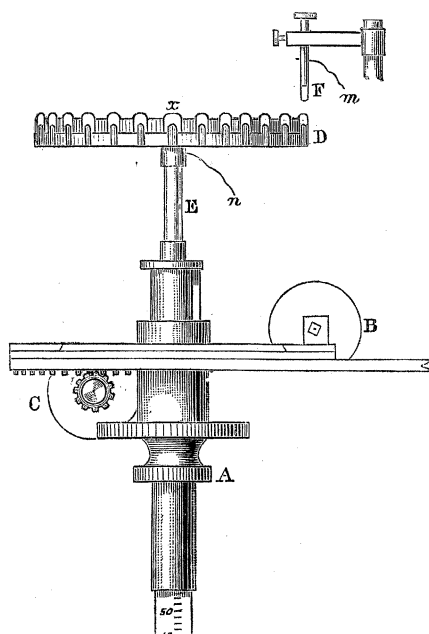
Any of the above changes may give the requisite information, and all are due to the same cause, which evidently is the difference of alloys as regards volatility. Thus in the case of gold and copper, the former being less volatile than the latter, there will be a minimum of metallic vapour with pure gold and a maximum with pure copper; and when alloys are employed, there will be a regular gradation between these two limits.

In the experiments about to be detailed, unknown alloys and check pieces of known composition having been arranged on a suitable stand (as shown in the diagram, p. 496), they were in turn brought immediately under the fixed electrode F (of aluminium or iridio-platinum).

We were soon convinced that it was necessary to regulate with extreme accuracy the length of the spark by which the incandescent vapour of the alloy was produced; and

the following experiments were made with a view to determine what details of manipulation would give the most satisfactory results.

In the first attempts a fragment of the alloy of a more or less irregular shape was simply held in a suitable clip, and a spark-current passed from the alloy to a similar



- A. Milled head of elevating-screw.
- B. } Horizontal adjusting-screws.
- C. }
- D. Revolving table.
- E. Insulating glass rod.
- F. Fixed terminal.
- x*. Series of assay-pieces.
- m, n*. Wires from induction-coil.

fragment of aluminium or other metal. We then adopted a method orally suggested to one of us by Professor STOKES, which consists in the passage of the spark-current in a vertical line across the shortest distance between two cylinders arranged in a horizontal position, with their axes at right angles to each other.

The use of these cylinders was attended with many difficulties, and we substituted for them strips of metal cut in the form indicated in the figure (at *x*).

The distance between the poles was at first adjusted by a gauge, and subsequently by a cathetometer; but the most accurate results were obtained by placing the portion of alloy in the field of a microscope furnished with a 3- or 4-inch objective, a simple mechanical arrangement, shown above, bringing the surface from which the spark would pass to the point of intersection of two spider-lines in the eyepiece of the microscope.

We were careful to select alloys which were homogeneous in character; and our attention was first devoted to observations on the zinc-cadmium alloy, one of a series of

alloys termed by MATTHIESSEN "solidified solutions of one metal in another." We next operated upon the gold-copper alloy, as its molecular arrangement appeared to render it peculiarly suited for the purpose of the research, the use of this alloy being attended with the additional advantage that the ordinary method of assay has rendered it possible to determine its composition with accuracy to the $\frac{1}{10,000}$ part of the original weight of the assay-piece, a degree of precision which will appear remarkable to all who are familiar with the ordinary methods of quantitative analysis.

We give in the accompanying curves (Plate XLI.) the results of our experiments with alloys of known composition, in which experiments the precautions to which we have referred have been taken. The results are represented graphically, the coordinates being the composition of the alloys as determined by the ordinary method of assay, and by the varying points of equal brightness as measured on the micrometer-scale of the lines at the wave-lengths stated in the diagrams. The micrometer is fixed to the eyepiece end of the observing-telescope. It is an ordinary wire-micrometer with movable horizontal wires. The micrometer-readings are represented by spots placed opposite the compositions as determined in the ordinary manner, a mean curve being subsequently constructed.

We have found that there are several variations possible in the method of observation, and we are yet uncertain which of these variations will afford the most satisfactory results.

Our method of procedure was upon each occasion to prepare such a curve by means of accurately known standards; and having this curve, to determine, by means of the micrometer-readings, the positions which various specimens of unknown composition would occupy on it. By carrying the eye from the curve to the side on which, as in those communicated to the Society, the parting assay determinations were shown, we were enabled to compare the places assigned to the specimens, on the curve, by the spectroscope with those determined by the parting assay which we then learnt for the first time. We do not think it necessary to give these curves, but may say that, as the result of many series of experiments with alloys of unknown composition, the difference between the spectroscopic and parting assays was but small so long as the conditions under which we experimented continued to be uniform.

Descriptions of Curves.

Curve No. 1.

A number of alloys of zinc and cadmium were synthetically prepared, and from these a series of five, the percentages of cadmium in which increased by 1 per cent. from 50 per cent. to 54 per cent., were carefully selected for the experiments. It is interesting to note that both the metals employed in the alloy are very fusible (zinc melting at 433° C. and cadmium at 228° C.); and observations by means of the spectroscope at once enabled us to arrange these alloys in their correct order.

Curve 2.

This comprises a series of alloys ranging from 900·0 to 922·5 parts of gold in 1000 of the alloy. It was obtained by measurements made by placing the micrometer-wires in a vertical position and measuring the base of the lowest visible portions of the spectroscopic lines under examination, a method which appeared to be better suited to wide ranges than observations made in the upper portions of the spectral lines; these latter were, however, found more suited to the study of narrow ranges, such as that shown in Curve 3. We should remark that, at this early stage of our inquiry, our attention was mainly devoted to ascertaining whether the curves would be continuous, and to determining at what point a curve deduced from any given lines in the spectrum would cease to be sensitive.

Curve 3.

The Curve 3 was constructed by means of observations made upon several specimens of gold-copper alloy, the composition of which had been determined to the $\frac{1}{10,000}$ part in the ordinary manner. Micrometer-readings for these specimens were taken, which, together with their known approximate compositions, furnished the coordinates to the curve.

It will be seen at a glance that with regard to the lower part of the curve a change of composition of $\frac{1}{10,000}$ gives a much greater change in the micrometer-readings than it does in the upper part. It is also to be remarked that, as in this more sensitive portion a change of $\frac{1}{10,000}$ part is represented by a change of 200 in the micrometer-readings, a true mean curve can only be constructed when the actual composition of the alloy is stated with much greater accuracy than that afforded by the present method of assay.

We should observe that as in several cases duplicate and even triplicate readings were made with the same specimens, the number of spots placed opposite any figure in the vertical column does not necessarily indicate the number of pieces of that composition under examination. If we examine the Mint specimens, of which the composition is stated to be 916·4, it is seen that the maximum departure from the curve is less than $\frac{1}{20,000}$ part; and in this case it is impossible to say that any error has been made by the spectroscope, because, were the composition of all the alloys in question to be what the spectroscope states them to be, they would still be called 916·4 on the parting assay. Again, if we consider the specimens 916·6, it will be seen that while in those two with micrometer-readings 150 the departure is not more than that previously stated, $\frac{1}{20,000}$ part, on the other hand the composition of the two the micrometer-readings of which were 250 would carry them into a region of the curve which would spectroscopically indicate their composition to be less than 916·5. The departure in this case was so great that it was considered advisable to make a fresh determination of their composition by the ordinary method; and it was satisfactory to find that the parting assay determination, as revised, was almost identical with that given by the spectroscope.

Curve 4.

The range of alloys is the same as those given in the preceding curve; but the method used was that employed in obtaining Curve 2, and it is interesting as illustrating the change introduced into the form of the curve by varying the method by which the spectral lines were observed.

Practical Considerations.

It is impossible to foresee to what analytical operations the new method may be found to be applicable; but as the experiments hitherto have been mainly directed towards the development of a new method of assaying gold, it is advisable that attention should be limited to the relative advantages of the old and new methods.

We ascertained by careful experiment that the amount of alloy actually volatilized during an observation in no case exceeds 0.0001 grm.; and it is interesting to compare this with the amount of metal usually employed in assaying gold, which varies from 0.5 to 1 grm.

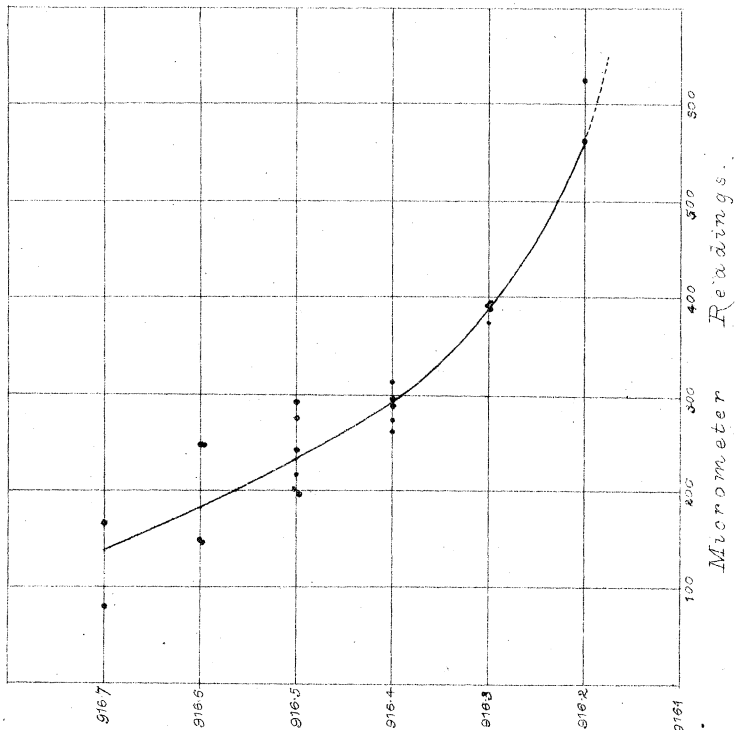
It may be objected that the amount of metal employed in the new method is very small; but granting the accuracy of the method and the homogeneity of the alloy, there is of course no reason why the composition of a gold ingot may not be ascertained by it as accurately as by the old method.

It is now well known, as previously mentioned, that the existing method is usually accurate to the $\frac{1}{10,000}$ part of the portion of metal operated upon, the process possessing in addition to its accuracy many incidental advantages, not the least of which is the possibility which it affords of detecting, at different stages of the work, the presence of metallic impurities, such as iridium.

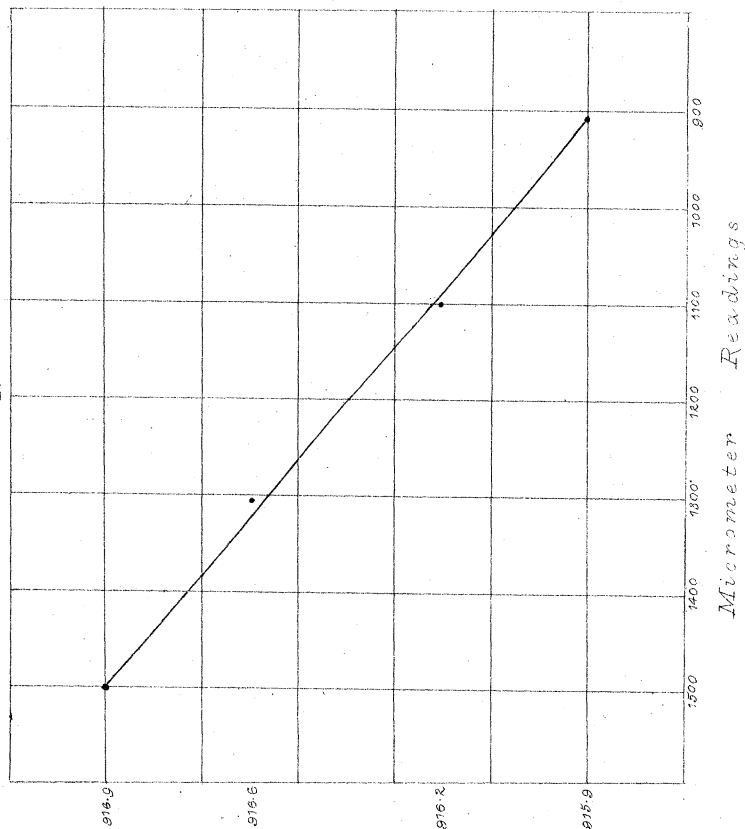
On the other hand, it should be observed that the method now in use comprises six distinct operations, and two hours are occupied in ascertaining the final result of the assay; and as it is frequently important to determine the value of an ingot of gold with rapidity, it will be obvious that the new method possesses marked advantages in this respect, for by its aid a result may be obtained in a few minutes.

In conclusion, we would submit that experience alone can show whether this new process may be made as trustworthy as the existing method; and we would draw attention to the fact that hitherto there has not been absolute identity in the conditions under which the several experiments were made; for instance, the intensity of the current employed to volatilize the metal varied from time to time; and this, together with other defects, mainly arose from the fact that we have as yet considered the problem solely from its scientific aspect, and have not provided ourselves with instruments well adapted for satisfying all the conditions which may arise in practice.

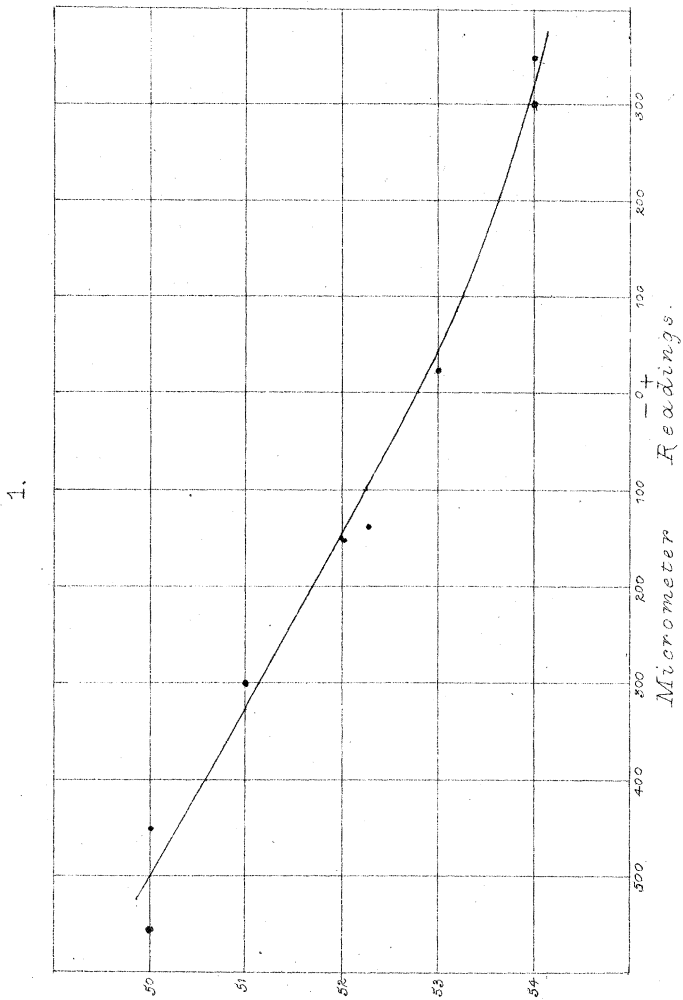
Whether this new method be found preferable to the old one or not, the fact has been clearly established that it is possible to detect, by its means, differences in the composition of the gold-copper alloy as minute as the $\frac{1}{10,000}$ part of the whole mass.



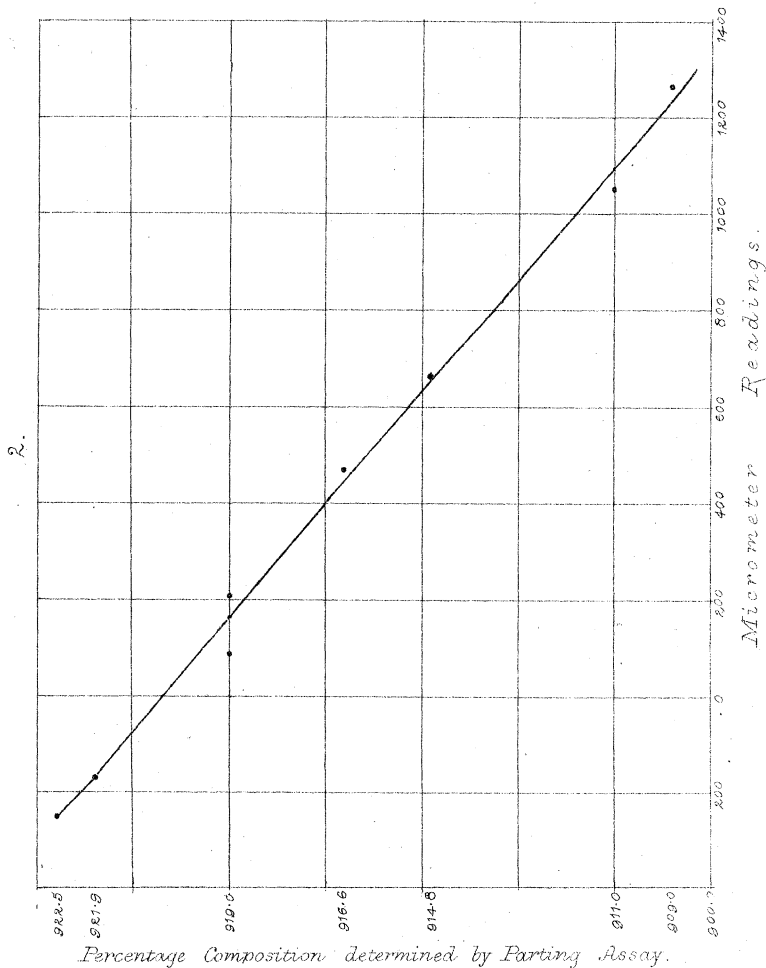
Percentage Composition determined by Parting Assay.



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