tests made with no carbon bisulphide, and with smaller coils surrounding the solutions. Minima were also observed with the trolley at rest unknown to the observer. Various modifications in the apparatus were made, and others were planned, but the results were so uncertain that only data taken with the conventional set-up were used.

Conclusions: (1) Minima occur. (2) Some minima check with Allison's data. (3) Most of the minima obtained can be explained by probability on the basis of random settings. It should be pointed out that the two not explainable in this manner check with Allison. However, one of these was obtained with the coils shorted. (4) The minima may be psychological, physiological, or a function of the electrical circuit. (5) Since minima which are in good agreement with published data are found with wrong solutions and with the coils shorted, the minima here observed are not a function of the solutions in the cells.

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Observations on the Allison Magneto-Optic Apparatus

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The Allison magneto-optic apparatus has been subjected to critical tests by the checking of minima reported from other laboratories, by the working of unknowns and by the distribution of scale readings over a given range. About 300 of Allison's minima have been checked. Two sets of three unknowns, prepared in such a way that there was one chance in six of a fortuitous correct solution, have been successfully analyzed. One set in which three salts were chosen out of a list of seven was correctly analyzed after the three had been mixed. The chances were 34 to 1 against a lucky selection of the correct combination. A second set of three out of seven, similarly run, resulted in the identification of only one constituent. The overall average shows 10 out of 12 correctly reported. All unknowns were given to the observer at concentrations of 1 part in 10^7 of water and they were diluted to 1 part in 10^{10} before subjecting to analysis. A statistical study has been made of the distribution of 1698 scale readings, made over a period of three years by five different observers. The readings were plotted against the number of times they were observed and definite peaks are evident in the curve. 84.2 percent of all readings fall within the limits of experimental error of a peak, and 30.1 percent fall on a peak. This is contrary to the results of Slack and of MacPherson, who found only chance distribution.

THE magneto-optic method of analysis has been the subject of a very heated controversy since its discovery by Dr. Fred Allison several years ago. Recently a paper by Francis G. Slack[1] has shown data purporting to prove that the distribution of observed minima, when hydrochloric acid is placed in the observation cell, is similar to that obtained when numbers are drawn at random from a box. In plotting these data the method of Ball and Cooper[2] and of Ball and Crane[3] was followed in which the scale readings for minima are plotted against the number of times they are observed. It is true that Slack's data show nothing more than a random distribution of readings.

An abstract of a paper by H. G. MacPherson[4] read before the Los Angeles meeting of the American Physical Society, Dec. 21 and 22, 1934, in Los Angeles, shows the same results, both by optical and photographic means. The magneto-optic apparatus is admittedly a difficult instrument to use and unless great care is used

[1] Slack, J. Frank. Inst. **218**, 445 (1934).
[2] Ball and Cooper, J. Am. Chem. Soc. **55**, 3207 (1933).
[3] Ball and Crane, J. Am. Chem. Soc. **55**, 4860 (1933).

[4] MacPherson, Phys. Rev. **47**, 254A (1935). Complete paper, Phys. Rev. **47**, 310 (1935).

in its construction and long hours are spent in mastering the technique of its operation, negative results are sure to follow. About one year was spent in this laboratory to construct the apparatus and perfect the technique.

The following data are presented with a view of adding something to the positive side of the controversy as to whether minima are real or merely psychological or physiological.

In the progress of our investigations it has been necessary for us to repeat some of Dr. Allison's work, either because we wished to confirm the data, or with a view of satisfying ourselves that our apparatus was properly calibrated to read directly in Allison units. In all, 162 of these minima have been checked on our apparatus by Mr. S. S. Cooper and 224 by Mr. R. E. Wingard. Most of Mr. Cooper's data are duplicated in the 224 readings of Mr. Wingard, but there are enough which are not duplicates to bring the total number of points checked to about 300. Except for some confusion between cobalt and nickel minima, discussed by Ball and Cooper in the article referred to above, our results have been practically 100 percent confirmatory of Allison's. It might be mentioned that our trolley system differs from Allison's in that it has three banks of wire instead of two. This was necessary because of the small room in which our apparatus had to be placed.

In February, 1933, solutions of three different substituted benzoic acids, at concentrations of one part in 10^9 were taken to Auburn by the author, and three different observers who knew nothing regarding the position of the minima which had been found in our laboratory by Mr. Cooper, checked the results to within 0.01 to 0.02 Allison units. In making these tests the trolley was set about a foot off the position of the minima and the observer was told which way to move the trolley. No other information was given. In all, six minima were checked by each of three observers. These acids had not been studied at Auburn.

The only published report of the identification of unknowns by the magneto-optic method is by McGhee and Lawrenz.[5] They state that "in December, 1930, one of us (McGhee) handed out by number to Professor Allison twelve (to him) "unknowns" which were tested by him and checked by two assistants 100 percent correctly in three hours." As a further check upon the objectivity of the method and its reliability, four sets of unknowns were run in this laboratory in the fall of 1934. In the first set, the author received from Mr. S. S. Cooper and Mr. R. E. Wingard a list of three salts whose minima had been checked on our apparatus. Solutions of these were made up in separate flasks at concentrations of one part in 10^7. These flasks were numbered and left in the laboratory in the late afternoon after the two who were to make the identification had left. During the evening, these solutions, after dilution to one part in 10^{10}, were run separately by each observer and the name of the compound in each flask determined from the observed minima The report was made by telephone to the author's home on all three salts at once and the results were entirely correct.

In order to guard against the accusation made by Slack that in working unknowns at Auburn, a hint was given, unconsciously, by a second party, the one who made up the unknowns purposely absented himself from the laboratory while the tests were being made and had no contact with the observers after the list of salts was submitted. This applies to subsequent tests as well.

A second set of three salts or acids was run in exactly the same manner as the above and each solution was again correctly identified. There are six ways in which three solutions may be arranged so that the observers had only one chance in six of making a lucky guess on each set.

At a later date, a list of seven salts and acids was submitted by Messrs. Cooper and Wingard. Three of these were chosen at random by the author and solutions were made up containing one part in 10^7 in three flasks which bore no identification mark. The observers mixed the three and diluted the resulting solution so that each constituent was present in one part in 10^{10} of water. The search was then made over the scale regions in which the minima of each of the seven salts are known to be found, the observers knowing that three compounds would be present. In this test, one observer recorded the readings

[5] McGhee and Lawrenz, J. Am. Chem. Soc. **54**, 405 (1932).

of the other without informing him as to the settings he was making. They worked alternately at the instrument and when each had satisfied himself that he had read three groups of minima, their results were compared. The field of all seven salts was covered carefully but only three sets of minima appeared. Both observers had read the same minima and their results were reported by telephone. Again the report was correct. There are thirty-five combinations of three out of seven, making the odds 34 to 1 against a chance selection of the correct combination.

A second set of three salts out of seven was prepared and the tests carried out exactly as described above. This time, however, the results were not entirely satisfactory; one out of the three was correctly reported. There were some mitigating circumstances in connection with these tests which may partially account for the failure. However, we prefer to let it stand as it is without offering any explanation. Even with this failure, ten out of a possible twelve have been correctly identified giving an overall average of 83.3 percent. Previous tests by Ball, Crane and Cooper had shown about the same overall average on tests similarly carried out about two years ago. When it is considered that there was under observation 30 ml of a solution containing only one part of salt in 10^{10} of water, or 3×10^{-9} grams, it is doubtful if any other known method would be as successful in identifying the compounds present. In most published articles involving the recording of numerous data, those which are obviously wrong never find their way into print. It would be interesting to know what percentage of readings have to be discarded.

We have heard indirectly that the above method of preparing unknowns from a limited list has been adversely criticized on the ground that the observers knew what compounds were

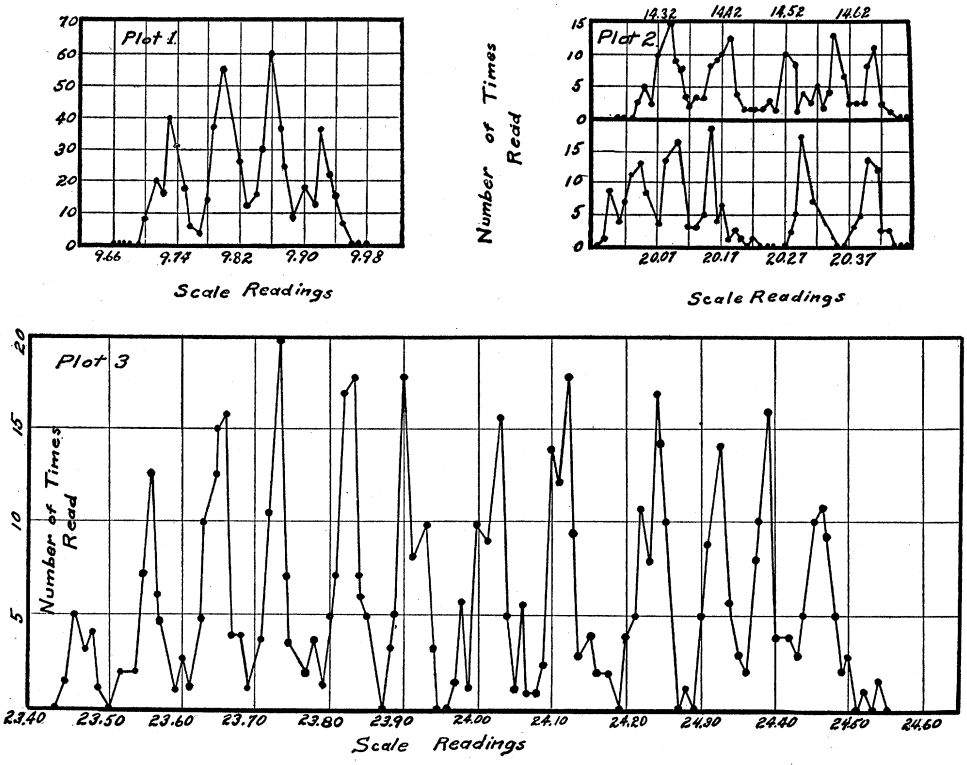

FIG. 1. Plot No. 1. Scale readings plotted against frequency of observation. Pentavalent chromium sulfate; Plot No. 2. Frequency distribution of readings for cobalt and nickel mixed sulfates (upper graph) and chlorides (lower graph); Plot No. 3. Frequency distribution of observations on oxidation products of stannous chloride.

present. This would scarcely need an answer if everyone were familiar with the method of operation. The full range in which minima might be found, if there were no limitation, would extend over 9.9 meters of trolley scale and the settings would have to be made within a space of 2 or 3 millimeters. Obviously this would be a very time consuming task.

Slack and MacPherson, whose work has already been cited, have found the distribution of observed minima merely one of chance. The accompanying plots of some of the data obtained in this laboratory show quite a different result (Fig. 1). Plot No. 1 shows a curve in which scale readings are plotted against the number of times they were observed. These readings were taken by Mr. Keith D. Crane in 1932 and have been interpreted as being due to pentavalent chromium sulfate. This curve has been published elsewhere, and since we are interested here in the distribution of minima only, we shall omit any chemical interpretation. In all, 615 readings are involved and 31 percent fall on a peak of the curve and 93.4 percent fall within 0.02 scale division of a peak. This is 3 mm. In getting the data, no reading was ever discarded. This applies to subsequent graphs as well.

The upper and lower graphs of Plot 2 show the distribution of readings for cobalt and nickel (mixed) sulfates and chlorides, respectively. These data were obtained by Ball and Cooper in 1933, with a few readings by Crane. There are 454 recorded settings and 81 percent fall within 0.02 scale division of a peak.

Plot No. 3 is made from the unpublished data obtained by Mr. Walter Wulfkuehler in this laboratory in 1934 in a study of the oxidation products of stannous chloride. The minima are interpreted as being due to the chloride of trivalent tin. There are 629 readings, 77.5 percent of which fall within 0.02 unit of a peak. In making the computation the small peak at the extreme left is disregarded, as all of the readings in that region were obtained on the first solution studied and they did not appear from the many other solutions involved in later readings. They may, therefore, be assumed to be due to something other than a tin salt.

An overall analysis of the data of these four plots shows that 1698 readings have been recorded from the work of four different observers, and that 84.2 percent fall within 0.02 scale division of some peak and 30.1 percent fall on a peak. It must be remembered that the trolley is moving at the time the observation is made and the physiological time lag in stopping the motion frequently causes the exact position of the minima to be over-shot. By approaching the position from both sides a very uniform distribution is obtained on either side of the peak.

There can be no doubt but that some of the readings recorded above are spurious and are due to deceptive spark flickers. We believe, however, that these are reduced to a minimum as it has always been our custom to re-explore the immediate region in which an indication of a minimum has been obtained and to disregard it unless it can be seen to recur. Thus, the 1698 minima which are recorded really represent from two to three times that many observations. There could be no preferential selection of readings by this method because each initial indication of a minimum is treated exactly like every other. Contrary to the conclusions of Slack and of MacPherson, the above graphs certainly show distributions that are not merely those of chance. The identification of unknowns also indicates that the positions of the minima are a function of the solution placed in the cell and are not merely the result of retinal fatigue as has been suggested by several critics. While we realize that our results have not been perfect, there is certainly incontrovertible evidence of the reproducibility and reliability of the magneto-optic method.