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An attempt was made to set up an Allison Magneto-optic apparatus for the purpose of analyzing certain solutions whose ionic content is unknown. The apparatus as set up has proved to be unreliable as a research tool.

The results in this respect coincide with those in many other laboratories in which similar conclusions have been reached.

Certain physical modifications were made in an attempt to explain the effect on the basis of well known principles which have hitherto not been applied. There are four known principles which might be responsible for the effect. These were treated in the following sequence. First, the Faraday effect; the results of Slack's investigation were accepted in which he found the Faraday effect

not responsible for Allison's observation. Second, magnetic double refraction; this was eliminated because of its negligible magnitude under the conditions of observation. Third, resonance effects; these effects were not investigated because of the extended nature of the problem. Fourth, electric double refraction; this was shown by qualitative investigation to be too weak to produce an observable effect under the condition existing in Allison's experiments.

ALLISON'S METHOD OF MAGNETO-OPTIC ANALYSIS

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ALLISON'S METHOD OF MAGNETO-OPTIC ANALYSIS

In 1845 Faraday (7) found that a transparent medium placed in a magnetic field has the power of rotating plain polarized light. The light is rotated in a plane perpendicular to the magnetic lines of force. The direction and magnitude of this rotation depends on the nature of the medium and on the direction and intensity of the magnetic field. The amount of rotation also depends on the length of the light path in the medium. The rotating power of a mixture depends on the nature of its components. If two substances with opposite rotations are mixed in the right proportions a medium with zero rotation may be obtained.

The question early arose as to whether this rotatory power is established instantaneously or whether there exists a time interval between the establishment of the magnetic field and the rotation of the light. In 1926 J. W. Beams and Fred Allison (3) reported the results of a study on this problem from the University of Virginia. Since all observations have indicated that the time lag, if any, is of almost infinitesimal duration, their method of attack was designed to utilize the speed of light or electricity as a means of measurement of time, and instead of measuring the time lag itself to measure the difference in the lag encountered in different media. By their method they found these differences to be of the order of 10^{-9} seconds with an estimated accuracy of 3×10^{-10} seconds.

Later experiments (2) with this difference of time lag seemed to show that it was a specific property of the two substances compared, and if comparison was made between some standard pure substance and a mixture, each component of the mixture retained its individual characteristic time lag. This observation, if substantiated, would make the method a very important and powerful tool for chemical analysis and it was from this standpoint that the present investigation was initiated.

The apparatus which has been used for chemical analysis in Allison's laboratory is fundamentally the same as that originally used by Beams and Allison. A diagram is shown in Fig. 1. The two Nicol Prisms are crossed and the spark is allowed to jump across the gap S. The light leaves S, is converged at L, goes through F, is polarized at N, and enters B_1 at

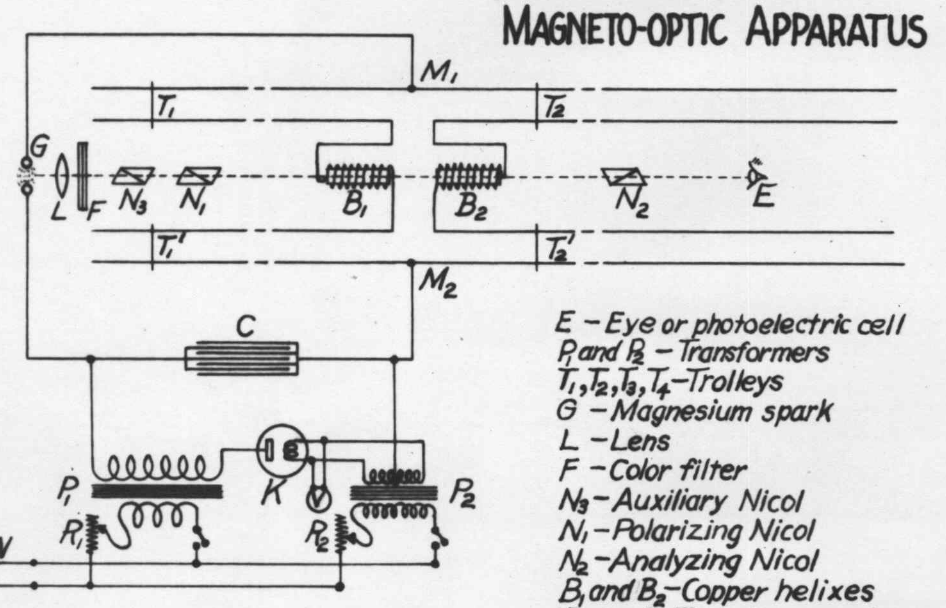

FIGURE 1.

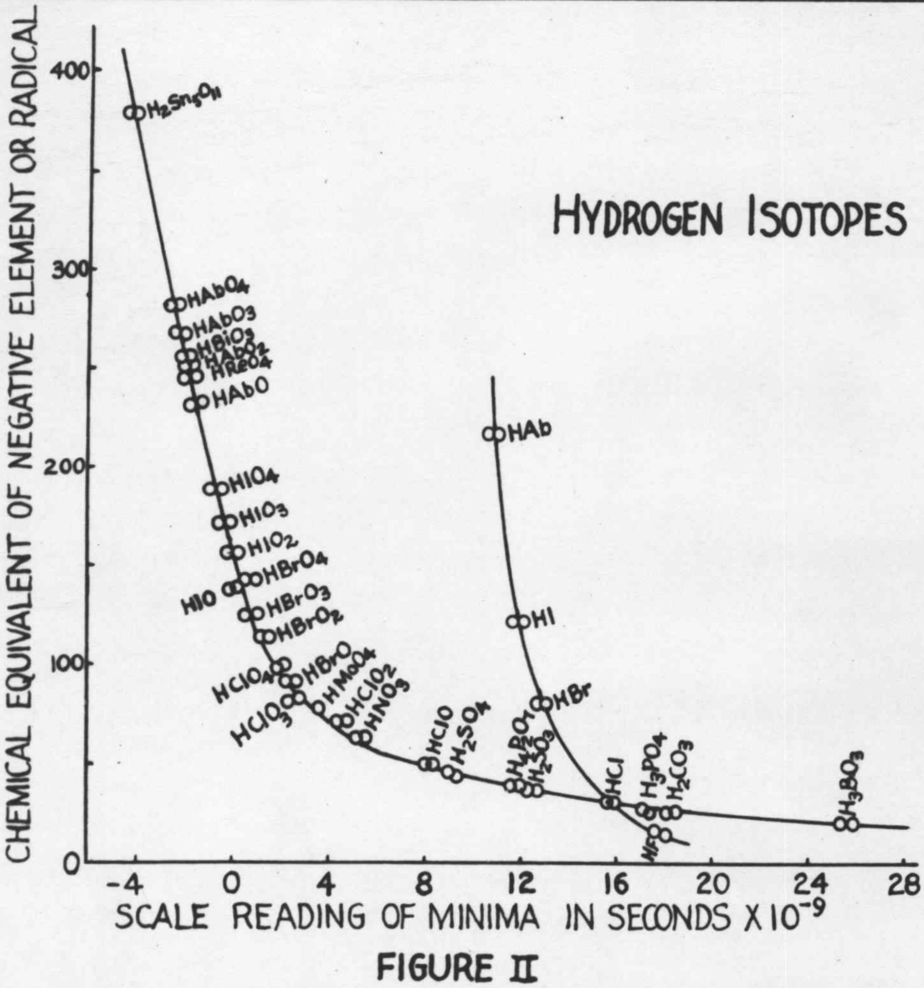

FIGURE II

the same time the electric pulse has reached B_1. The plane of polarization of the light is rotated due to the Faraday effect. When the light reaches B_2 the current pulse arrives just in time to rotate the light in the direction of the original plane and if B_1 and B_2 contain the same substance no light reaches the observer. This state of affairs, however, gives no indication of the postulated lag in time between the establishment of the magnetic field and the establishment of the optical rotation since the two tubes are identical in that respect. Now, if a substance with a longer or shorter time lag is put into B_2 some light will be seen by the observer because the light which was rotated in B_1 will either not have reached B_2 when the rotatory effect is established, or it will have gone through B_2 before the rotation takes place. However, if T_2 is shortened or lengthened a position may be found such that the rotatory effect in B_2 begins just as the light arrives and the light is again reduced to a minimum. The difference between the two readings of T_2 is proportional to the difference in time lags of the two substances used. Allison found, furthermore, that the positions of T_1 and T_2 corresponding to light minima were specifically characteristic of the equivalent weight of the compound present. Expressed in units of 30 centimeters trolley length which is approximately equivalent to 10^{-9} seconds time lag, for example, the readings for HCl are given as 15.75, and 15.85, for HBr 12.95, and 13.10 and for HI 11.90 and 12.05. (3) Each acid studied has two minima corresponding to the two isotopes of hydrogen. It is interesting to note that the existence of two minima for every acid led Allison to postulate the presence of a heavy isotope of hydrogen--a fact which has now been established by other methods, but which was not known at the time he made his experiments. In Allison's laboratory also, were found for the first time Alabamine and Virginium by this method.

The method has been most highly developed in the laboratories of Allison and his co-workers. It has been used not only qualitatively but quantitatively. (1) It has been used to detect vitamin A. (14) Successful use has been reported from the Chemical Laboratory at Washington University, (4) St. Louis and the Chemical Laboratory of the University of California. (8) Unfortunately the fact that Allison's interpretation of the theory is open to serious question has operated to lessen confidence in the experimental results. Furthermore, in many laboratories the experimental facts cannot be duplicated even after a careful attempt to duplicate exactly the Allison set-up.

Papish (10) at Cornell found that the number of minima is limited only by trolley length and that by suitably lengthening the trolley minima could be obtained corresponding to elements beyond uranium in atomic weight. This is shown graphically in Fig. 2 in which his results are reproduced.

Three quite extensive investigations of this system of analysis have been reported since this investigation was started, in all of which negative results were obtained. Slack (12) concluded that if a time lag does exist in the Faraday effect it would not be characterized by sharp boundaries, but instead would gradually change over a large portion of the trolley. He carried out a large number of experiments which seemed to show that the sharp minima apparently obtained are due to physiological or psychological causes. In other words he believes the system of magneto-optic analysis is imaginary.

H. G. McPherson (9) used a photographic method which gave a comparison of the spark intensity and the intensity of the beam from the optical system. He obtained a sensitivity of from 1 to 3 % depending, in part, on the number of exposures averaged. He estimates the visual sensitivity at 3%. It is interesting to note here that the minima found by Latimer and Young (Private communication to E. C. Gilbert) were characterized by a 2% decrease of intensity. Their observations were made with a photoelectric cell. Farwell and Hawks (7) by an ingenious photometric device have been able to compare directly the intensity of the spark with the light that has gone through the Faraday cells. They found no reproducable minima but mention random fluctuations in the spark.

In summarizing the examples which have been mentioned, it may be seen that the magneto-optic method is at present in a controversial condition. Strongly supported evidence that it can serve as a most delicate and sensitive method of chemical analysis has been published from some laboratories, while many other investigators have not only been unable to confirm the method, but they have reported much evidence to indicate that it will not be confirmed. It is of utmost importance especially to chemists that, if such a method exists, it be worked out to the fullest extent and its basic theory developed.

The apparatus at Oregon State College was designed to be as nearly as possible like the one used by Allison. This is difficult as most publications on the method have apparently studiously avoided giving the exact details of any single working set. It was first assembled without a kenotron as Allison reported that minima had been observed thay way. The arrangement of this preliminary set-up is represented by Fig. 1, with the exception that the kenotron and the filament circuit were omitted and the secondary of the high voltage transformer was connected directly across the condenser. The condenser consisted of 24 plates of glass 14.5 by 23 centimeters. Sheets of tinfoil were placed between alternate plates. The tinfoil extended out on one end for connection but on the other three sides sufficient margin was left to prevent spark-over. Zinc plates were arranged to slide between the alternate glass plates, thus allowing the capacity to be adjusted to any desired value. The glass plates were held apart, so that the zinc slid freely by glass strips cut from lantern slides. These strips were 3 to 4 millimeters wide and about 4 centimeters long and spaced to allow for oil movement. The whole condenser was assembled under oil and bolted between bakelite sheets. The zinc plates were soldered to a cross strip at the outer end so that they operated as a unit, and the whole condenser was permanently immersed in oil. The maximum capacity of the condenser was about 0.0065 micro-farads and it could be adjusted to any value between this and zero. A Thordarson 25000 volt spark-type transformer was used as the source of potential. The coils B_1 and B_2 shown in Fig. 1 were wound on bakelite tubes 2.8 centimeters in diameter and 12 centimeters long. They contained 60 turns of number 20 copper annunciator wire. One coil was wound in the right hand direction and the other oppositely. They were connected into the circuit so that the magnetic rotatory effect was in opposite directions. Other combinations of windings were tried with no apparent improvement in their operation. Pyrex cells were made to fit snugly inside of these coils. They were made by cementing plane glass plates to the carefully ground ends of pyrex tubes. A hole was drilled in the side to permit filling. For the carbon bisulphide cells one of the best cements was found to be Insolute (Titanium oxide and Sodium Silicate) and for the HCl tubes, Picein wax. For nitro benzene, nitro cellulose served most satisfactorily. Each part of the trolley system T_1 and T_2 was 21 feet long, insulated by pyrex insulators, and rigidly supported one above the other. Slides which made contact between the pairs of trolley wires could be adjusted from the observer's position. The rheostat for the primary circuit of the transformer, and the condenser were also under the observer's control.

The Nicol prisms and lenses were taken from a polariscope. The analyzer and eyepiece were mounted on a wooden support which could be adjusted to and fro so that the distance between the coils could be varied. The spark gap was constructed of magnesium rods about 3 millimeters in diameter. The width of the gap could be adjusted to any value by a rack and pinion.

This apparatus was assembled in the spring of 1934 and the first attempt was made to see sharp minima. The general procedure was to move the trolley very slowly and watch for a visual decrease in the light intensity. The method of moving the trolley in steps was also used. The observation tubes were usually filled with carbon disulfide and hydrochloric acid as their minima are reported to be the most pronounced. No sharp minima were observed that were definitely confined to any fixed position on the trolley. When carbon disulfide was used in both tubes a very broad minimum was seen, the approach to which could be noticed over almost the entire trolley and its center could not be located to less than two or three feet. Imposed upon this, however, was a more noticeable effect due to the resistance of the trolleys. This effect was characterized by an approximate inverse proportionality between trolley length and light intensity. Failure to see any minima at this time was attributed to the lack of a kenotron in the circuit. During the summer of 1934 through the courtesy of Dr. Linus Pauling and Dr. J. H. Sturdivant of the California Institute of Technology, the facilities of their laboratory were made available, and it was possible to have constructed there a 100 kilovolt kenotron which was then incorporated into the apparatus. This required a low voltage filament transformer insulated for 100 kilovolts. A ring type transformer with a large air gap between primary and secondary winding was constructed in our own laboratory for this purpose and its characteristics were determined through the courtesy of F. O. McMillan of the Electrical Engineering Department.

After the apparatus was adjusted the search for sharp minima was again resumed. Both continuous and stepwise movement of the trolley was used. Sometimes an apparent minimum was seen, but upon sliding the trolley back over the position it could not be re-located. The positions of some of these apparent minima were marked and their intensity was compared to that in nearby positions by having an observer report whether the light was brighter or dimmer when an assistant set the trolley on or away from the mark. Table 1 gives a sample of data on such minima using carbon bisulfide in B_1 and 0.1N hydrochloric acid in tube B_2. When the observer could see no difference the comparison was not counted.

Table I

Minimum	A Bright	A Dim	B Bright	B Dim	C Bright	C Dim
Obs. 1.	7 (times)	6	5	7	2	7
Obs. 2.	2	2	2	3	1	4

Table II

Mimimum	D Bright	D Dim	E Bright	E Dim	F Bright	F Dim
Obs. 1.	6	11	4	10	5	10
Obs. 2.	6	5	15	11	8	10

The striking difference between the observers in Table 2 might be attributed to unconscious cues given in the tone of the voice of the person setting the trolley, etc. The observations in Table 2 were taken with carbon-disulfide in B_1 and .001N hydrochloric acid in B_2. These readings were taken several weeks after those in Table 1. The chemicals used in this run were specially purified to insure reliability. The observer was in a dark compartment and he did not know what adjustments were being made by the assistant. These minima, moreover, did not coincide with the positions for HCl recorded by

Latimer and Young, (8) and Allison (3). Minima E in Table 2 corresponded most closely to the theoretical location. It is interesting to note however, that between the time of obtaining Table I and Table 2, the apparatus was completely dismantled and rebuilt so that the trolley lengths were slightly different. However, the same approximate distance was found between the members of the second set of minima that had been found in the first set. The coils were tried with different windings, the trolley connections were changed, different optical systems were used, electrodes of different metals were tried, and several different circuits were arranged.

One modification is worthy of mention in some detail. A continuous source of light was used instead of the spark in the optical system, the spark being retained, however, in the electrical system. The continuous light source, of course, gave much less sensitivity since the rotatory effect due to the current oscillation existed for only a small part of the time. This difficulty was overcome with an electric shutter consisting of a Kerr cell between two crossed Nicols. The potential to operate the Kerr cell was drawn from across the coils so that only when the current was changing in the circuit would light be admitted to the optical system. It did not prove satisfactory for observation because of a lack of sufficient intensity. This could be overcome, however, by having a stronger continuous light source, a higher potential, or a longer Kerr cell.

Although the results are not susceptible of numerical tabulation and record, many hours were devoted to a systematic study of the effect of the several variables. In no case, however, were the results sufficiently consistent to give confidence in the minima found, so at this point it was deemed advisable to investigate some of the known physical principles that might be responsible for the phenomena in the hope that the source of our failure might be revealed.

To the writer's knowledge there are only three known physical effects by which a changing magnetic field can influence plane polarized light passing through a transparent medium. These effects are the Faraday effect, magnetic double refraction, and electric double refraction. If we add to this list resonance effects, which might change the characteristics of the circuit and indirectly the intensity of the light itself and also the amount of the first three effects, we have a complete list which in all probability will furnish an explanation of Allison's results if an explanation is to be found. Since Allison was working with the Faraday effect when he discovered the phenomena it is the only one of the four which has been extensively investigated. Slack (12) concluded from his investigation that the classical Faraday effect alone cannot be responsible for the phenomenon. In view of the thorough nature of his work no attempt was made in this laboratory to extend it.

Magnetic double refraction as a cause may also be eliminated for two reasons. First, the magnitude of the refraction in ordinary substances would be too slight to be seen with such weak magnetic fields. Second, the effect is a maximum when viewed perpendicularly to the magnetic field and zero when viewed parallel to the field; so this effect could not be seen at all when the coils are properly aligned.

It is possible that resonance (13) effects may exist in the tubes but it is very difficult to imagine how a resonance effect could be a basis for the experimental results attributed to Allison's apparatus. It is possible though that under the conditions of faint illumination Allison may see a <u>decrease in the intensity of the spark</u> itself caused by the absorption of energy in the coils instead of a decrease caused by a lag in the Faraday effect. This particular explanation has, so far as is known, not been suggested or investigated previously. It is interesting to note that this hypothesis is in agreement with most of Allison's experimental results and also can be reconciled with the work of most of the investigators who have failed to confirm his findings since they have, in general, used some means of comparing the light which has passed through the optical system with that coming directly from the spark. No systematic attempt was made to investigate this subject because it was felt that such a study would most properly be made first with a different type of apparatus.

In order for electric double refraction to exist there must be an electric stress on the liquid. It is a fact that if a metallic ring were placed symmetrically just inside one of the coils in Allison's setup there would be induced in it an electrical current. This current would flow around the ring, overcome resistance, and its energy will be dissipated as heat. The difference in this respect between a metallic conductor and a dielectric is that in a metallic conductor the electrons are free to move, so that if a gap were cut in the ring the inductive effects on the individual electrons all around the ring would be summed up to make a difference in potential across the gap but in the case of dielectrics the electrons are tightly held by the atoms so that the only effect will be a distortion of the atom or molecules. If, now the induced potential is great enough, the distortion will be apparent as electric double refraction. The magnitude of this induced effect can be compared to that of a static charge by imagining the potential induced in one turn of wire being applied to two parallel plates at a distance apart which is equal to the circumference of the turn of wire. If now a dielectric is substituted for the turn of wire in the same magnetic field it seems logical that it will be subjected to the same electrical strain as would be imposed on it if it were placed between the two plates in the previous arrangement. It is very difficult to visualize an electrical stress going around in a circle in a nonconductor. However, in reality, the same condition exists in the case of the metallic ring.

From these considerations it was decided to investigate the possibility of electric double refraction being responsible for Allison's results. The effect to be expected is not very pronounced. Approximate calculation shows that a potential drop of something over one hundred volts per cm. would be required to produce noticeable refraction in most non-electrolytes. It is interesting to note, however, that liquid crystals exhibit a million times greater effect than ordinary substances. It is impossible to predict what the effect would be in solutions of electrolytes where the ions and molecules may be hydrated and where the ions are free to migrate.

The maximum effect of electric double refraction is obtained when the light is viewed at right angles to the axis of the electric field and when it is viewed in a direction parallel to the field, the effect is zero. The effect is also zero when the plane of polarization of the light is either parallel or perpendicular to the field, a maximum value, therefore, being observed at an orientation forty-five degrees from the field. Now, since, if any electric field exists, it is circular when looked at in a direction parallel to the plane of polarization and the other where it is perpendicular. This dark cross would be masked to a considerable extent by the much brighter light transmitted due to a rotation caused by the Faraday effect. The time of existence of these two effects will be slightly different. The Faraday effect is a maximum when the current is at the maximum in the coil, but the electric double refraction is a maximum when the current is changing at its maximum rate. An attempt was made to minimize the Faraday effect and intensify the electric double refraction by the use of the electrical shutter previously described so that the dark cross would be visible but the attempt failed. Next, a large field polariscope was constructed from glass plates but no dark cross was seen. It was then decided to pass the light perpendicularly to the axis of the tube. A new tube was made with windows in the sides. A coil was wound upon this so that the light could be viewed perpendicularly to the magnetic field. In this direction the Faraday effect should not be seen but both magnetic and electric double refraction would be expected. However, since magnetic double refraction is roughly a hundred thousand times less pronounced than electric double refraction it would be negligible. Therefore, if this cell were put between crossed Nicols so that the magnetic field of the coil was at right angles to the direction of the light and at forty-five degrees to the plane of polarization, any light transmitted would be attributable to electric double refraction. When this effect was experimentally investigated, however, no double refraction could be found. After several attempts and under very favorable conditions a slight increase in the intensity of the light was observed. Under these extreme conditions it could not be determined with any degree of certainty whether the increased light was due to magnetic double refraction or to an increase in spark intensity caused by a decrease in the inductance in the circuit. Even if this increase in light was caused by electric double refraction the intensity change was so slight that it could not be seen when mixed with light rotated by the Faraday effect as is the case in Allison's experiments. Furthermore, in order to obtain greater intensity a wider spark gap and a greater potential drop across the coils were used in these experiments than were used by Allison. In view of these conditions and the further condition that nitrobenzene, which has a coefficient of birefringence eighty-one times that of water and one hundred times that of carbon disulfide, was used in most of these investigations it seems reasonable to conclude that electric double refraction cannot be responsible for the experimental results obtained in experiments on magneto-optic analysis.

Summary

An attempt was made to set up an Allison Magneto-optic apparatus for the purpose of analyzing certain solutions whose ionic content is unknown. The apparatus as set up has proved to be unreliable as a research tool.

The results in this respect coincide with those in many other laboratories in which similar conclusions have been reached.

Certain physical modifications were made in an attempt to explain the effect on the basis of well known principles which have hitherto not been applied. There are four known principles which might be responsible for the effect. These were treated in the following sequence. First, the Faraday effect; the results of Slack's investigation were accepted in which he found the Faraday effect not responsible for Allison's observation. Second, magnetic double refraction; this was eliminated because of its negligible magnitude under the conditions of observation. Third, resonance effects; these effects were not investigated because of the extended nature of the problem. Fourth, electric double refraction; this was shown by qualitative investigation to be too weak to produce an observable effect under the condition existing in Allison's experiments.

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