

THE MAGNETO-OPTIC METHOD OF CHEMICAL ANALYSIS

by

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## THE MAGNETO-OPTIC METHOD OF CHEMICAL ANALYSIS

### I. Historical Background

It was found by Arago in 1811 that certain substances when placed between crossed Nicol prisms will rotate the plane of vibration of plane polarized light. About 60 solids and several thousand liquids having this property are known. Some rotate the plane in a clockwise and some in a counterclockwise direction. If plane polarized light that has been passed through one of these substances is reflected from a mirror and passed through the same substance in the opposite direction, the second passage will produce its own effect, and the angle of rotation will be doubled.

In 1845 Faraday (14) discovered that any transparent body, not itself optically active, will rotate the plane of polarization when placed in a magnetic field, the rotation being a maximum when the direction of the light is either in or opposite to that of the field, and zero when at right angles to the field. This phenomenon is commonly called the "Faraday effect". If the light is caused to retrace its path through a substance while in the field, the second passage will rotate the plane in the opposite direction so that the total rotation of the plane of

polarization is zero. This "magnetic rotation" takes place in solids, liquids, and gases, the latter having been first observed by Kundt and Roentgen in 1879. The magnitude of the rotation depends on the strength of the magnetic field parallel to the direction of the beam, on the character of the medium itself, and on the length of the light path in the medium. The "Verdet constant" of a substance is the rotation in minutes of arc per oersted per centimeter of path length when the field and the path have the same direction; it is commonly stated for sodium light.

Many attempts have been made to detect a possible time interval between the application of the magnetic field and the appearance of the Faraday effect, as well as between the removal of the magnetic field and the disappearance of the effect.

In 1873, Villari (22) rotated a block of glass between the poles of an electromagnet; when the speed exceeded 100 revolutions per second, the rotation of the plane of polarization became less and at 180 revolutions per second it was practically reduced to zero. He interpreted this as showing that a certain amount of time is needed for the development of the Faraday effect. Later, in 1889, Lodge (22) attempted to explain Villari's results on the assumption that the change in the amount of rotation was caused

by a state of strain in the glass due to centrifugal force, and that the reduction was caused by a mixture of small effects "not easily analysable nor precisely defined".

Abraham and Lemoine (25) devised a method for measuring time intervals of the order of  $10^{-8}$  sec. Their method was elaborated and perfected in 1927 by Beams and Allison so as to measure time intervals down to  $10^{-9}$  sec. This increase in sensitivity was sufficient to establish the fact that when polarized light enters carbon disulfide placed in a longitudinal magnetic field, the rotation of the plane of polarization does not begin until after the lapse of a time interval of this magnitude.

In their original apparatus, (see simplified diagram shown in Fig. 1) damped oscillations from the condenser circuit were passed across the spark gap, A, and thence to two solenoids,  $S_1$  and  $S_2$ , connected in parallel, with their polarities in opposite directions, and mounted so that they could be moved to and fro along their common axis. The solenoids were of identical dimensions and each was provided with one of two similar containers for the liquid medium. Both solenoids were placed between crossed Nicols,  $N_1$  and  $N_2$ . Since the magnetic fields of the solenoids cause the plane of polarization to rotate in opposite directions, a total rotation of zero may be expected. This would mean no light issuing from the

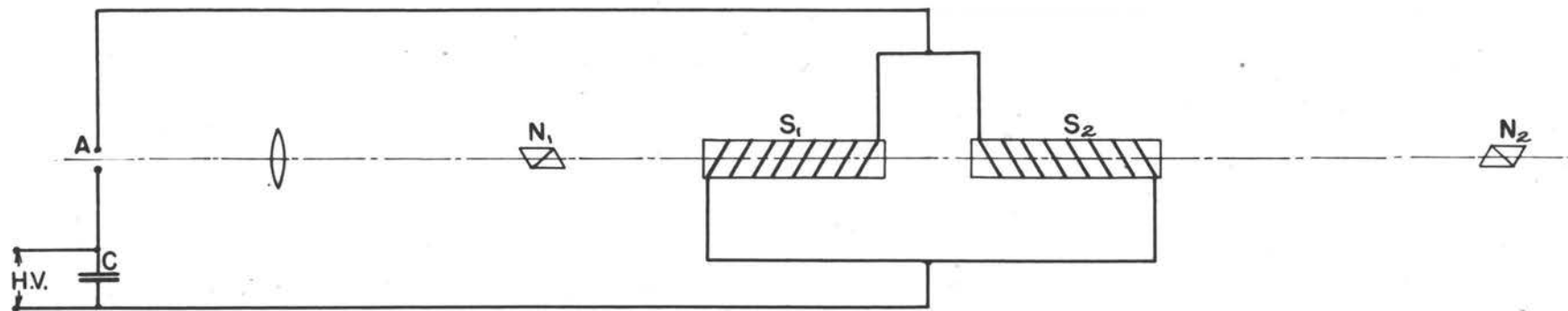


Figure 1.



analyzing Nicol. However, when both containers were filled with carbon disulfide, it was found that light usually emerged from the analyzing Nicol. Upon changing the distance between the solenoids a position could always be found such that, as expected, the light was extinguished by the analyzer.

This behavior cannot be explained by the mere reduction of the velocity of light in a liquid medium. If a definite time lag is postulated between the application of the field and the beginning of the optical rotation, an explanation can be given, and involves the following considerations: A surge or pulse of light emanating from the interrupted spark and polarized by the first Nicol has its plane of polarization rotated a definite amount by passing through the field of the first solenoid. This light surge then passes through the air gap to the second solenoid and may arrive (1) at the same time, (2) earlier than, or (3) later than the current surge. If the first condition holds, the second solenoid will offset the effect of the first, and no light will pass the second Nicol. Under the second condition the light has passed part way through the second solenoid by the time the magnetic field is established, and consequently the rotation given by the field is not sufficient to annul that given by the first solenoid,

so that some light will issue from the analyzer. If the third condition exists, the rotation due to the second solenoid will again not offset that due to the first so that some light will be passed by the analyzer. A change in the distance between the coils changes the time required for the passage through the air and thus enables the attainment of condition (1).

When the solenoids are in such a position that no light emerges from the analyzer, the substitution of another liquid for the carbon disulfide in one of the containers will again produce emergence of light because the time-lag in this liquid will be different from that in carbon disulfide. Extinction, or at least a minimum transmission, can be obtained by shifting the distance between the solenoids. A minimum rather than complete darkness will exist because the amount of rotation is a function not only of the field and path length but also of the substance. The change in the distance between the solenoids divided by the velocity of light in air represents the difference between the time-lags of the Faraday effect in the liquid and in carbon disulfide. After examining many substances and finding no identical time-lags, it was concluded that each substance has a characteristic time-lag. Later it was found that in a mixture each substance acts independently and retains its own individual time-lag.

The simple diagram shown in Fig. 1 would be very difficult to build, as it is practically impossible to wind coils, for example, with complete symmetry. Wires, as shown in Fig. 2, are necessary to adjust the electrical path-lengths to equality. The introduction of these wires enables (1) a verification of the natural assumption that for this type of circuit the speed of the current is practically that of light, and (2) a simplification in the manipulation in that the distance between the solenoids can be kept constant and the electrical path lengths altered by sliding bridges along the wires. The positions of the bridges can be readily noted on a scale placed conveniently near the wires.

It is found in practice that the distance these bridges must be moved to effect minimum transmission is equal to the distance through which the solenoids had been moved. This serves to show that the velocity of an impulse along the wires is very closely equal to the velocity of light.

In 1930 Allison and Murphy (7) announced this method of using the apparatus as the "magneto-optic method of chemical analysis". The method has been developed both qualitatively and quantitatively and has been used mainly in research involving the detection of minute quantities of substances.

## II. Controversial Nature of Field of Investigation

The magneto-optic method of chemical analysis has been severely criticized by a number of physicists and chemists. A number of favorable and unfavorable comments will be cited and discussed.

As stated, the magneto-optic method of chemical analysis was announced by Allison and Murphy (6). Unknown substances can be analyzed by merely subjecting them to a beam of light in a magnetic field. The method is extremely sensitive and for this reason somewhat difficult to master, but it will detect minute quantities of substances, down to a few parts in  $10^{12}$  parts of water.

Dr. Allison has announced the discoveries of elements 85 (2) and 87 (2). Papish and Wainer (26), using spectral x-ray data, confirmed the existence of element 87. Hydrogen of mass two when first observed was thought to be an impurity (28) in water, but it was soon definitely determined to be the second isotope of hydrogen and was announced as such in 1932. Urey (32), using a spectroscopic method, made a similar announcement in 1932. Latimer and Young (2), using the magneto-optic method filled one of the cells with heavy water and found hydrogen of mass three; this was confirmed by Allison (28) on his own apparatus. Since then, Latimer and Young (21), for reasons

unknown, have withdrawn all of their data. However, the existence of  $H_3$  has been demonstrated in bombardment experiments. Allison and Goslin (5) determined the end product of radioactive potassium,  $_{39}K^{41}$ .

The magneto-optic method has shown the most promise in the field of chemistry. Minimum positions have been determined for both inorganic and organic compounds. Allison, Bishop, and Sommer (2) have used the method to determine the action of bromine, iodine, and element 87 toward certain reagents. Hughes and Hopkins (25) have used it to detect the concentration of various rare earths in certain ores. Ball and Crane (9) have detected intermediate states in the reduction of chromium from the chromate to the chromic ion. It has been employed by Yoe and Wingard (36) in the detection of the formation of formaldehyde from irradiated carbon dioxide and water. Sommer, Bishop, and Otto (3) have measured the formation of formaldehyde in the presence of chlorophyll. Jones and Goslin (19) have been able to trace the localization of uranium salts in the organs of rabbits. Wissink (34) has detected vitamin A in spinach juice, orange juice, and tomato juice. McGhee and Lawrenz (24) have checked the results on element 87.

The above researches were accomplished by visual observation, which is to some extent, subjective. The method has been made more objective in the following

investigations. Allison, Christensen, and Waldo (4) showed positive results using a photoelectric cell connected to a galvanometer. They report that galvanometer deflections produced by the amplified current located minima that coincided exactly with those determined visually. Wissink (34) used the photocell in working with vitamin A. At the present time Hughes (28) is using a rubidium photocell which is highly sensitive to blue light in conjunction with a cathode ray oscilloscope and reports consistent results.

The work of Hughes and Goslin (16) using a photographic method must be mentioned somewhat in detail. In this investigation, the analyzing Nicol was replaced by a Wollaston prism. Several hundred photographs were taken on and near the positions of known minima. The absolute change in the light intensity was found to be only 0.7 per cent. In further work the positions of the minima were determined photographically and were found to coincide with those determined visually. Minimum positions are characteristic of the substance under investigation.

At the present time Allison and Waldo (28) are replacing the analyzing Nicol by a Wollaston prism set so as to emit its two beams at practically equal intensities. A rubidium photocell is placed in each beam and their differential effect applied to a Compton electrometer after amplification.

The determination of the substances present in an unknown solution is the most successful method of showing that minima exist and that they are characteristic of the substances under observation. A number of investigators have reported the successful solution of unknowns. McGhee and Lawrenz (24) reported that Dr. Allison solved a solution containing twelve unknowns in three hours. Slack (29), although believing that he was unintentionally aided in some of the determinations, was able to solve unknowns with 80 per cent accuracy. Ball (8) has reported the correct solution of ten out of twelve unknowns. Cooper (13) has reported successful use of the apparatus in this matter, and has shown the probability of guessing correctly would be 1 in 7560. The work of Jones and Goslin (19) should also be cited at this point since various "blanks" unknown to the observer, were added in the determinations at various points to test the observer and the apparatus.

While working in Dr. Allison's laboratory with a solution containing cupric, aluminum, strontium, potassium and lithium ions, all five were detected. The content of the cell was diluted and observations were again made. Finally after several such dilutions one of the isotopes of potassium disappeared, which gave an indication of the relative abundance of the two isotopes. Further dilutions were made until the other minima disappeared one by one;

the relative concentrations of the different ions agreed with the composition of the solutions as prepared by Dr. Allison.

In sharp contrast to the positive results obtained by some investigators as discussed above, severe criticism and condemnation of the method has been meted out by others. Some have been unable to observe sharp minima. Others have been unable to correlate the minima with the positions of the bridges or with the substances under observation. The difficulties of the first class are probably caused by inequalities in the relative lengths of the wires. A great deal of care must be taken to see that the wires are practically of identical length. Another possible cause lies in the dimension of the Nicol prisms. If their cross sections are too small, it is very likely that when the spark exists between peripheral points on the electrodes, the light will not pass through both prisms properly and cause a large variation in intensity.

In regard to the second class of observers, those that see minima but do not find them characteristic of the substances under observation, the most likely fault is lack of cleanliness of the cells. Unless the most meticulous care is taken in cleaning the cells and in maintaining the cleanliness of the water still, various



contaminants are almost certain to foul the readings. Small Nicol prisms may also produce this fault by giving spurious or unstable minima as already explained. A third cause may lie in the irregularities of the spark itself. A practiced eye and ear can readily detect when the spark departs from its normal operation and becomes too unsteady.

Specific criticisms will now be discussed. Dr. Slack (29) reports that he was able to observe minima on Dr. Allison's apparatus but that the observed minima on his own apparatus were not characteristic of the substances under observation. He believes that the consistency of the results obtained by some observers must have a physiological basis. Papish and Shuman (27) report that even though one of them (Shuman) spent two weeks studying the apparatus under Dr. Allison, the method was not a success in their hands. Slack and Peoples (30) state that they have obtained minima without the use of cells and also by the use of dummy solenoids. Jeppesen and Bell (18) report minima both with and without the substance in the cell. Farwell and Hawkes (15) have been unable to obtain minima of the type observed by Dr. Allison. Webb and Morey (33) have also been unable to see sharp minima.

Woodruff (35) reports negative results and attributes the minima to physiological and psychological effects. He mentions that in attempting to find minima for

hydrochloric acid he used a 0.001 N solution. This corresponds to 3.64 parts of acid in  $10^5$  parts of water. With a concentration as high as this, any minima that might be present, assuming symmetry of the apparatus, etc., would be so fuzzy or so flat that they would probably escape notice. The minima are sharp for concentrations bordering on 1 part in  $10^8$  or  $10^9$  parts of water.

MacPherson (23) reports using a photographic method with negative results. However, his apparatus was only sensitive to changes in light intensity of about 3 per cent. Hughes and Goslin (using a Wollaston prism) report that the change in light intensity near some minima is only 0.7 per cent.

Finally, the work of Latimer and Young (20)(21) should be discussed, as it was the author's privilege to visit their laboratory in Berkeley on numerous occasions. Although the apparatus was not in use during any of these visits, Dr. Latimer was kind enough to explain his method of observation. The movable bridges are not under the control of the observer. The observer looks at the analyzing Nicol for an instant; at a signal he looks away; an assistant moves the bridges two mm; upon another signal the observer again looks into the apparatus. The difficulties involved in such an arrangement are many. The

observer must remember the absolute value of the intensities; his pupil in all probability changes its diameter between successive observations. A change in intensity is far more readily determined if the change takes place during an observation; especially is this true for minimum positions. Since the change in intensity is only 0.7 per cent, it would seem that precautions similar to those used in photometry should be employed. As a minimum usually extends over several millimeters, the settings are usually obtained by averaging several values found by approaching from both sides.

As many observers who find fault with the method have used poor techniques in observing or have used too high concentrations, and as others complain of difficulties noticed and overcome by those who favor the method, it seemed worth while as a thesis project to set up an apparatus far from Dr. Allison's guiding influence and test it thoroughly.

### III. Apparatus

The brief description of the apparatus given in the preceding section is naturally restricted to its main features. Since its successful operation depends on careful construction and numerous refinements, as well as on proper manipulation, a detailed description of the present apparatus is necessary. The apparatus is very similar to the one in Dr. Allison's laboratory. The chief modifications are due to differences in the available parts and in the size of the research room. It is strongly advised that anyone interested in this field of investigation visit and handle some existing set-up before attempting to assemble his own.

A diagram of the assembled apparatus is shown in Fig. 2. The filament transformer, A, was designed to heat the filament of the Kenotron, K; it supplies a current of 12.38 amperes at a potential of 13 volts. Transformer B was made by the Thordarson Electric Company; it is a stock core-type, wireless transformer, Type R, 25,000 volt, 1 KVA. Each of these transformers is supplied, as indicated, with a sliding rheostat having a resistance of 44 ohms and a current carrying capacity of 3.1 amperes. The kenotron, K, is General Electric Company's type KR-3. This tube is designed for high voltage, half-wave rectifi-

cation with a maximum peak inverse voltage of 140,000 volts, and a load current of 30 milliamperes under continuous use. The kenotron charges condenser C which is a variable parallel plate air condenser made by mounting aluminum foil, 9 in. by 15 in., with beeswax on glass plates  $1/8$  in. thick, 15 in. wide, and 20 in. long. The condenser capacitance can be varied from 0.005 mf. to 0.01 mf.

G is a 2 mm spark gap made of  $1/8$  in. magnesium rods. L is an achromatic lens of focal length 21.6 cm. and is used to render the rays of light parallel. The light is made practically monochromatic by the use of two Wratten filters, F, Nos. 35 and 37.  $N_1$  and  $N_2$  are two 12 mm Nicol prisms.  $N_2$ , the analyzing Nicol is mounted so that it can be rotated and clamped in any position.  $B_1$  and  $B_2$  are two solenoids each of 56 turns of No. 16 double cotton covered copper wire wound on Bakelite tubing, outside diameter 3.5 cm., length 15 cm. The two solenoids are interchangeable with two similar solenoids wound with the same size wire, but on Amphenol (912-B) tubing,  $1\ 1/2$  in. outside diameter and  $1/8$  in. wall. One of each pair of these solenoids is wound clockwise, and the other counterclockwise. The cells, which hold the liquid under investigation, as stated before, lie inside the solenoids, and

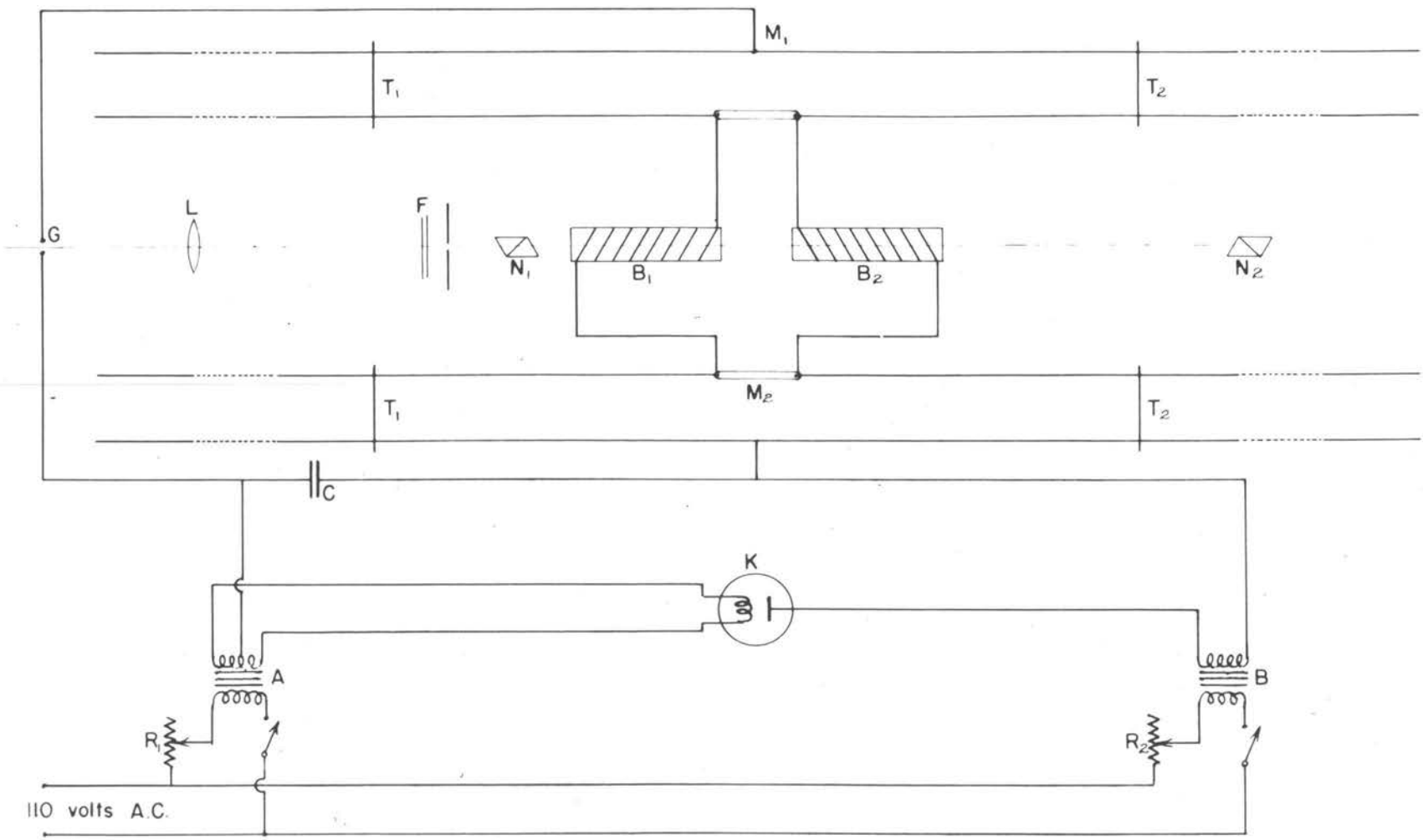


Figure 2

are made of pyrex tubing, 2.5 cm. outside diameter and 12.7 cm. long. The ends of the tubes were ground perpendicular to the axis, and closed by No. 2 microscope cover glasses, the cement used being sodium silicate for carbon disulfide and similar substances, and picein for aqueous solutions. Each tube is provided with a filling hole 0.4 to 0.5 cm. in diameter.

The wire path system fills the longest dimension of the laboratory which has a floor area of 9 ft. by 25 ft., and can best be described by reference to Fig. 3. There are two banks of wires vertically above each other at a distance of 15 cm. Each bank consists of four No. 18 bare copper wires 15 cm. apart. Since Fig. 3 is a diagram and not a perspective drawing, the wires of the upper and lower banks are designated respectively by unprimed and primed numerals. As indicated, each wire is provided with a 3 inch glass insulator and a turnbuckle at each end. The turnbuckles provide a means for lining up the centers of the wires as well as for equalizing their tensions. In addition, as shown, all wires except No's. 1' and 4' are provided with 15 cm. glazed porcelain insulators, which separate them into two portions having lengths 495 cm. on the right hand or moving trolley side and 195 cm. on the left hand or fixed trolley side. This lack of sym-

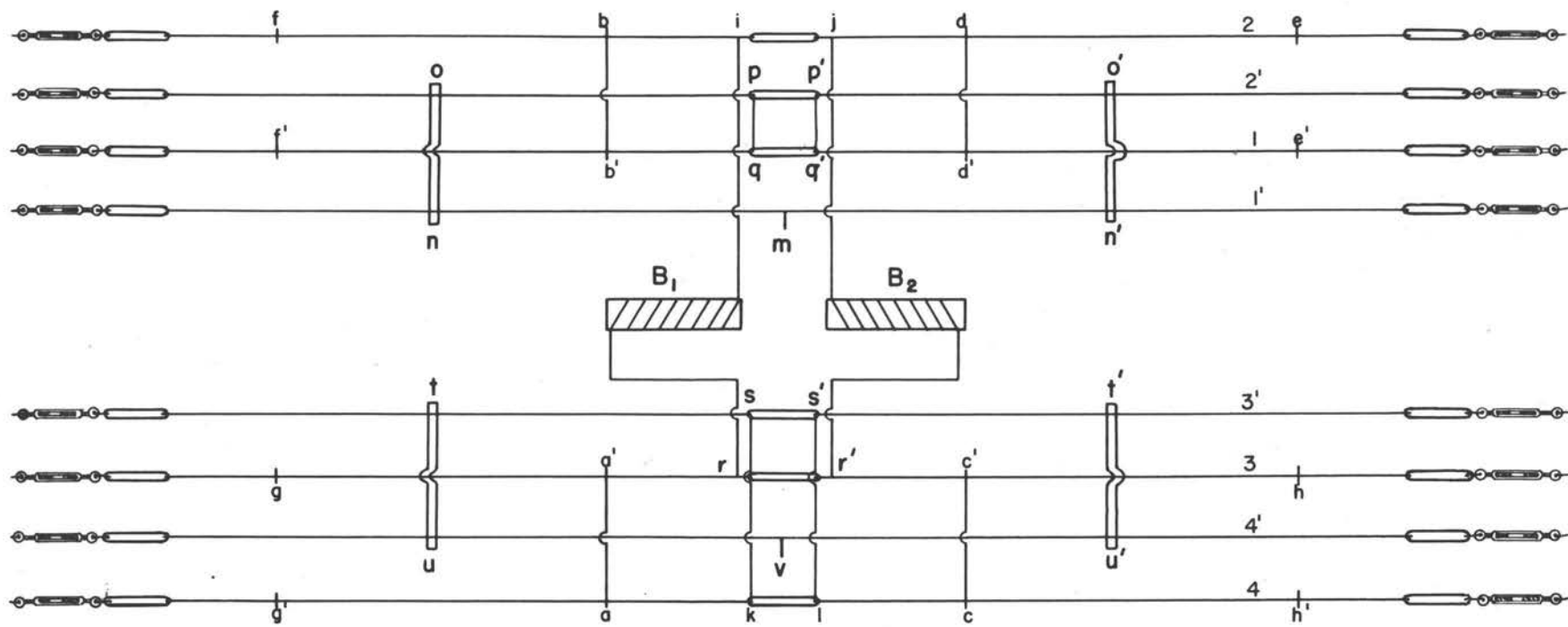


Figure 3



metry is necessary because the laboratory is too small to permit equal lengths of 495 cm. each. It may be mentioned at this point that Professor Allison first called attention to the fact that 15 cm. is a convenient length to use as a unit of distance in constructing this apparatus. Time differences of the order of  $10^{-9}$  seconds must be measured. Since the speed of light and also the approximate speed of electromagnetic waves along a wire is  $3 \times 10^{10}$  cm. per sec., the waves will travel 30 cm. in  $10^{-9}$  sec. Half of this will be the real determining distance, as part of the path lies on each side of the central insulators. The distance of 15 cm. is consequently frequently referred to in this type of work as an Allison unit.

The lower bank of wires carries two trolleys, each of which reaches across all four wires. Each trolley consists of a wooden strip carrying two copper bridges; each of these bridges connects two adjacent wires.  $T_1T_1$  Fig. 1 is the fixed trolley which is moved only during calibration.  $T_2T_2$  is the movable trolley to which motion is imparted by a fish line passing over a system of pulleys and a large hand wheel within reach of the observer.

The scale for measuring the position of the movable trolley reads directly in Allison units; its zero is at

point *i*. Units are numbered, and tenths of units are indicated. By means of a vernier carried on the trolley, hundredths of an Allison unit may be measured.

A diagram of the wire-path system is shown in Fig. 3. *aa'*, *bb'*, *cc'*, and *dd'* are short-circuiting wires that are made by placing Fahnestock clips on the ends of wires 15 cm. long. Stubs, i.e. short pieces of wire about a half inch long, are soldered so that they project at right angles to the wires at the points just mentioned and at *e*, *e'*, *f*, *f'*, *g*, *g'*, *h* and *h'*. By means of these short-circuiting wires, the relative length of either side may be varied in relation to the other. The lengths *ib*, *jd*, *ka*, and *lc* are all equal to three Allison units. Lengths *bf*, *de*, *a'g*, and *c'h* are each equal to 10 units.

The movable contacts or trolleys *n o*, *t u*, *n' o'*, and *t' u'* connect wires 1' with 2', and 3' with 4' (all in the lower bank). The condenser discharge is applied to this system at points *m* and *v* on wires 1' and 4'. At *m* the current divides into two parts, one flowing to the left and the other to the right. The left hand current takes the following path *m n o p q b' b i B<sub>1</sub> r a' a k s t u v*, while the right hand current follows a corresponding path.

It is evident that since the two circuits are in

parallel, moving the short circuiting wires  $bb'$  and  $aa'$  ten Allison units to the left (thus lengthening these wires) is equivalent to decreasing the lengths of the right hand parts of these wires by the same amount. After such a change, it takes a longer time for the current to reach solenoid  $B_1$  than solenoid  $B_2$ . The difference in time is the time it takes the current to move a distance of 10 Allison units. Therefore if the trolley scale covered the range from zero to plus thirty units before the short-circuiting wires were moved, it would have the range minus ten to plus twenty units after the change. By the same reasoning a shortening of the right hand side is equivalent to a lengthening of the left hand side. By shifting the short-circuiting wires to different pairs of stubs any portion of the scale from minus 10 to plus 60 units may be used.

#### IV. Calibration and Operation

As already stated, the spark gap serves both as a source of light and as an interrupter for the current. The rapid discharges of the condenser across the spark-gap establish the fields in coils  $B_1$  and  $B_2$ . The fields are established simultaneously only when the parallel surges after leaving  $M_1$  Fig. 2 or  $m$  Fig. 3 reach the coils  $B_1$  and  $B_2$  at the same time. This condition can be true only when  $M_1T_1B_1$  Fig. 2 is the same as  $M_1T_2B_2$ . A movement of trolley  $T_2T_3$  toward  $M_1$  away from this position of electrical symmetry causes the field in coil  $B_1$  to be established later than in coil  $B_2$ .

The following method is suggested (13) for adjusting and calibrating the apparatus. The glass cells within the solenoids are filled with carbon disulfide, each solenoid is short-circuited, and the lens is removed from the optical path. With the Nicols parallel, the spark gap is brought into alignment; the lens is replaced. The spark gap is brought into the center of the field of view by moving the lens. The Nicol prisms are placed in the crossed position. With the trolleys approximately equidistant from the center of the apparatus, no light comes through the system.

The short-circuiting wires are removed from the solenoids. Since the two trolleys were not set at exactly symmetrical positions, light emerges from the analyzing Nicol. As has been stated, this condition arises from the fact that in general the surge of light which is undergoing rotation in  $B_1$  does not exist in  $B_3$  when the field is established there. Hence it will not be rotated back into the original plane by the field of  $B_3$ . The trolley may be moved until the light issuing from  $B_1$  is rotated back into the plane of  $N_1$  by the field of  $B_3$ . This is the position of exact optical and electrical balance. However, this position is very difficult to find experimentally; even with carbon disulfide in both cells, it cannot be located accurately without a great deal of practice.

An easier method for calibrating the instrument is the following. Find the approximate position of balance with carbon disulfide in both cells. Replace the cell in coil  $B_3$  with an aqueous solution of HCl, about 1 part in  $10^{11}$  parts of water. The two minima of HCl should, according to previous investigations, be located at 15.75 and 15.85. Taking these readings as calibration points, the movable trolley may be set and held stationary at each of these points in succession while the so-called fixed

trolley is moved until minima appear. The same result may be reached in a slightly different manner. If on the uncalibrated apparatus the two minima are found at 15.35 and 15.45, then the fixed trolley should be moved toward  $M_1$  by exactly 0.40 unit. Other known points may be checked similarly; for example if an ammonium chloride solution is used, a minimum should be found at 17.82. Standard scale readings for a number of substances are shown in Table 1.

The table of known positions of minima may be readily extended by making use of a generalization determined by a study of experimental results. Suppose, for example, that it is desired to locate the minima of cobalt sulphate,  $CoSO_4$ . The chemical equivalent of cobalt is  $58.94/2$  or 29.47. On looking in the table, minima are found for, say sodium sulphate  $Na_2SO_4$ , and copper sulphate  $CuSO_4$ . These metals are chosen because their chemical equivalents, respectively 23 and 31.78 lie on either side of that of cobalt. It has been found that the minima of any element combined with a radical lie between the minima of two other elements, each combined with the same radical, provided that the chemical equivalent of the element in which interest centers is intermediate to the chemical equivalent of the other two metals. Hence it is only

TABLE I

SCALE READINGS OF CHARACTERISTIC MINIMA AND DIFFERENTIAL TIME LAGS  
WITH REFERENCE TO CARBON BISULFIDE

Scale reading	Seconds X 10 <sup>-9</sup>	Scale reading	Seconds X 10 <sup>-9</sup>	Scale reading	Seconds X 10 <sup>-9</sup>	Scale reading	Seconds X 10 <sup>-9</sup>
HCl		HNO <sub>3</sub>		H <sub>2</sub> SO <sub>4</sub>		HOH	
15.85	-0.85	5.50	9.50	8.43	6.57	9.30	5.70
15.95	- .95	5.61	9.39	8.65	6.35		
LiCl		LiNO <sub>3</sub>		Li <sub>2</sub> SO <sub>4</sub>		LiOH	
16.22	-1.22	5.85	9.15	9.00	6.00	10.03	4.97
16.45	-1.45	5.95	9.05	9.10	5.90	10.18	4.82
AlCl <sub>3</sub>		Al(NO <sub>3</sub> ) <sub>3</sub>		Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>		Al(OH) <sub>3</sub>	
16.58	-1.58	6.10	8.90	9.66	5.34	10.37	4.63
MgCl <sub>2</sub>		Mg(NO <sub>3</sub> ) <sub>2</sub>		MgSO <sub>4</sub>		Mg(OH) <sub>2</sub>	
16.82	-1.82	6.20	8.80	10.04	4.96		
16.90	-1.90	6.25	8.75	10.40	4.60		
17.03	-2.03	6.30	8.70	10.62	4.38		
NH <sub>4</sub> Cl		NH <sub>4</sub> NO <sub>3</sub>		(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>		NH <sub>4</sub> OH	
17.82	-2.82	6.80	8.20	11.21	3.79	11.05	3.95
FeCl <sub>3</sub>		Fe(NO <sub>3</sub> ) <sub>3</sub>		Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>		Fe(OH) <sub>3</sub>	
17.96	-2.96	6.83	8.17	11.32	3.68	11.60	3.40
18.05	-3.05	6.90	8.10	11.45	3.55	11.74	3.26

TABLE I (Cont'd)

Scale reading	Seconds X 10 <sup>-9</sup>	Scale reading	Seconds X 10 <sup>-9</sup>	Scale reading	Seconds X 10 <sup>-9</sup>	Scale reading	Seconds X 10 <sup>-9</sup>
	CaCl <sub>2</sub>		Ca(NO <sub>3</sub> ) <sub>2</sub>		CaSO <sub>4</sub>		Ca(OH) <sub>2</sub>
18.44	-3.44	7.17	7.83	11.54	3.46	12.37	2.63
18.66	-3.66	7.20	7.80	12.05	2.95	12.57	2.43
	NaCl		NaNO <sub>3</sub>		Na <sub>2</sub> SO <sub>4</sub>		NaOH
18.73	-3.73	7.21	7.79	13.00	2.00	13.47	1.53
	AsCl <sub>3</sub>		As(NO <sub>3</sub> ) <sub>3</sub>		As <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>		As(OH) <sub>3</sub>
18.98	-3.98			13.17	1.83		
	CrCl <sub>3</sub>		Cr(NO <sub>3</sub> ) <sub>3</sub>		CrSO <sub>4</sub>		Cr(OH) <sub>3</sub>
19.15	-4.15	6.50	8.50				
	MnCl <sub>2</sub>		Mn(NO <sub>3</sub> ) <sub>2</sub>		MnSO <sub>4</sub>		Mn(OH) <sub>2</sub>
19.22	-4.22	7.29	7.71	13.67	1.33	13.95	1.05
	FeCl <sub>3</sub>		Fe(NO <sub>3</sub> ) <sub>3</sub>		FeSO <sub>4</sub>		Fe(OH) <sub>3</sub>
19.25	-4.25			13.90	1.10		
19.40	-4.40			14.20	0.80		
	CoCl <sub>2</sub>		Co(NO <sub>3</sub> ) <sub>2</sub>		CoSO <sub>4</sub>		Co(OH) <sub>2</sub>
20.15	-5.15	7.30	7.70	14.40	0.60	14.74	0.26
	NiCl <sub>2</sub>		Ni(NO <sub>3</sub> ) <sub>2</sub>		NiSO <sub>4</sub>		Ni(OH) <sub>2</sub>
20.30	-5.30	7.31	7.69	14.52	0.48	15.28	-0.28
20.40	-5.40	7.34	7.66	14.66	.34	15.60	- .60



TABLE I (Cont'd)

Scale reading	Seconds X 10 <sup>-9</sup>	Scale reading	Seconds X 10 <sup>-9</sup>	Scale reading	Seconds X 10 <sup>-9</sup>	Scale reading	Seconds X 10 <sup>-9</sup>
CuCl <sub>2</sub>		Cu(NO <sub>3</sub> ) <sub>2</sub>		CuSO <sub>4</sub>		Cu(OH) <sub>2</sub>	
20.48	-5.48	7.40	7.60	14.80	0.20	16.04	-1.04
20.68	-5.68	7.43	7.57	15.00	.00	16.35	-1.35
ZnCl <sub>2</sub>		Zn(NO <sub>3</sub> ) <sub>2</sub>		ZnSO <sub>4</sub>		Zn(OH) <sub>2</sub>	
21.08	-6.08	7.54	7.46	15.21	-0.21	16.27	-1.27
21.40	-6.40	7.56	7.44	15.42	- .42	16.52	-1.52
21.73	-6.73	7.67	7.33	15.75	- .75	16.93	-1.93
21.85	-6.85	7.70	7.30	16.03	-1.03	17.20	-2.20
KCl		KNO <sub>3</sub>		K <sub>2</sub> SO <sub>4</sub>		KOH	
22.50	-7.50	7.82	7.18	16.74	-1.74	19.54	-4.54
22.87	-7.87	7.84	7.16	16.98	-1.98	19.95	-4.95
SbCl <sub>3</sub>		Sb(NO <sub>3</sub> ) <sub>3</sub>		Sb <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>		Sb(OH) <sub>3</sub>	
23.30	-8.30			17.96	-2.96	19.65	-4.65
23.66	-8.66			18.13	-3.13	19.90	-4.90
SrCl <sub>2</sub>		Sr(NO <sub>3</sub> ) <sub>2</sub>		SrSO <sub>4</sub>		Sr(OH) <sub>2</sub>	
24.35	-9.35	8.00	7.00			20.33	-5.33
24.59	-9.59	8.30	6.70			20.92	-5.92

TABLE I (Cont'd)

Scale reading	Seconds X 10 <sup>-9</sup>	Scale reading	Seconds X 10 <sup>-9</sup>	Scale reading	Seconds X 10 <sup>-9</sup>	Scale reading	Seconds X 10 <sup>-9</sup>
<chem>CdCl2</chem>		<chem>Cd(NO3)2</chem>		<chem>CdSO4</chem>		<chem>Cd(OH)2</chem>	
25.06	-10.06			18.50	-3.50		
25.28	-10.28			18.68	-3.68		
25.54	-10.54			18.81	-3.81		
25.90	-10.90			19.00	-4.00		
26.10	-11.10			19.17	-4.17		
26.25	-11.25			19.48	-4.48		
<chem>SnCl2</chem>		<chem>Sn(NO3)2</chem>		<chem>SnSO4</chem>		<chem>Sn(OH)2</chem>	
27.40	-12.40	8.70	6.30	20.10	-5.10		
27.58	-12.58	8.74	6.26	20.40	-5.40		
27.88	-12.88	8.80	6.20	20.62	-5.62		
28.25	-13.25	8.83	6.17	21.00	-6.00		
28.54	-13.54	8.88	6.12	21.27	-6.27		
28.82	-13.82	8.90	6.10	21.40	-6.40		
29.23	-14.23	8.95	6.05	21.80	-6.80		
29.55	-14.55	9.00	6.00	22.06	-7.06		
29.80	-14.80	9.12	5.88	22.54	-7.54		
30.10	-15.10	9.21	5.79	22.81	-7.81		
30.30	-15.30	9.28	5.72	23.22	-8.22		

TABLE I (Cont'd)

Scale reading	Seconds X 10 <sup>-9</sup>	Scale reading	Seconds X 10 <sup>-9</sup>	Scale reading	Seconds X 10 <sup>-9</sup>	Scale reading	Seconds X 10 <sup>-9</sup>
CuCl		CuNO <sub>3</sub>		Cu <sub>2</sub> SO <sub>4</sub>		CuOH	
30.38	-15.38	9.35	5.65				
30.68	-15.68	9.50	5.50				
BaCl <sub>2</sub>		Ba(NO <sub>3</sub> ) <sub>2</sub>		BaSO <sub>4</sub>		Ba(OH) <sub>2</sub>	
30.80	-15.80	9.45	5.55	23.55	-8.55		
31.18	-16.18	9.50	5.50	23.78	-8.78		
31.35	-16.35	9.58	5.42	23.98	-8.98		
31.65	-16.65	9.72	5.28	24.20	-9.20		
PbCl <sub>2</sub>		Pb(NO <sub>3</sub> ) <sub>2</sub>		PbSO <sub>4</sub>		Pb(OH) <sub>2</sub>	
36.90	-21.90	9.95	5.05	23.82	-8.82	19.18	-4.18
37.07	-22.07	10.08	4.92	24.36	-9.36	19.44	-4.44
37.30	-22.30	10.30	4.70	24.72	-9.72	19.65	-4.65
37.68	-22.68	10.46	4.54	25.10	-10.10	19.86	-4.86
AgCl		AgNO <sub>3</sub>		Ag <sub>2</sub> SO <sub>4</sub>		AgOH	
38.65	-23.65	10.60	4.40	26.17	-11.17		
39.18	-24.18	10.80	4.20	26.82	-11.82		

TABLE I (Cont'd)

Scale reading	Seconds $\times 10^{-9}$	Scale reading	Seconds $\times 10^{-9}$	Scale reading	Seconds $\times 10^{-9}$	Scale reading	Seconds $\times 10^{-9}$
HgCl		HgNO <sub>3</sub>		Hg <sub>2</sub> SO <sub>4</sub>		HgOH	
40.10	-25.10	10.82	4.18	27.75	-12.75	19.40	-4.40
40.42	-25.42	10.93	4.07	28.04	-13.04	19.60	-4.60
40.86	-25.86	11.01	3.99	28.30	-13.30	19.74	-4.74
41.12	-26.12	11.16	3.84	28.66	-13.66	20.00	-5.00
41.34	-26.34	11.28	3.72	29.06	-14.06	20.37	-5.37
41.65	-26.65	11.42	3.58	29.48	-14.48	20.70	-5.70
42.10	-27.10	11.52	3.48	29.88	-14.88	20.96	-5.96
TlCl		TlNO <sub>3</sub>		Tl <sub>2</sub> SO <sub>4</sub>		TlOH	
42.65	-27.65	11.15	3.85	30.20	-15.20	21.40	-6.40
42.95	-27.95	11.40	3.60	30.30	-15.30	21.70	-6.70

necessary to make a careful study of the regions indicated.

There are certain parts of the apparatus that demand particular attention. For example, the determination of the number of condenser plates is very important. If too many are used, the light will be too bright, and minima cannot be located with certainty. Other points that need attention are the width of the spark gap, the settings of rheostat  $R_2$ , and the atmospheric condition of the room. The best observations seem to be made when the relative humidity is between 50 and 60, the spark gap is 2mm, and the condenser capacitance 0.007 mf. It is evident that experience alone will make a person thoroughly conversant with this apparatus.

### V. Tests

To prove that minima exist and that they are characteristic of the substance, the following problem was undertaken. Solutions of five compounds, strontium chloride, lithium chloride, cobalt chloride, chromic chloride, and barium nitrate, were placed in individual bottles. A sixth bottle was filled with 100 milliliters of water. During the absence of the observer, a staff member prepared an "unknown" by taking 1 milliliter from some or all, or none of the five solutions mentioned, and diluting it to a predetermined volume. The observer was to determine the constituents.

To indicate the care necessary in preparing specimens for observation by this method, the entire procedure will be described in detail.

Water from a Barnstead still was redistilled in an all-pyrex still operated in a dust-proof cabinet. The still itself, after being made was washed for several hours with water from the Barnstead still. Thereafter a quantity of water was distilled and collected in pyrex flasks for use as wash water with which to clean pyrex storage flasks. After a series of these flasks were cleaned, more water was collected and used to give a final washing to the pyrex still itself. Great care was

taken to keep the cabinet as well as the room in which it was located, dust-free. Before collecting any water from the pyrex still for actual use, it is necessary to let the distilled water run for at least an hour in order to remove traces of dust that may have collected in the condensing column.

The cells and the cover glasses that are to serve as ends were washed thoroughly before assembly, with tap water, distilled water from the Barnstead still, and finally distilled water from the pyrex still. The three brushes used in these washings were never interchanged and were kept in a special dust-proof cabinet while not in use. All parts were dried in the dust-free cabinet by evaporation, and were then assembled with picein wax or water glass depending on the liquids that were to be used.

The glass stoppered bottles for storing the solutions were first rinsed a number of times with distilled water from the pyrex still and then filled and boiled for several hours. Ten milligrams of each of the different compounds were placed in each bottle and enough water added to make 100 ml. Pipettes were washed and then rinsed by allowing pyrex-distilled water to flow through them for 15 minutes. Four 200 ml. beakers were thoroughly washed with the three types of water, using three individual beaker brushes.

Immediately after washing, each article was placed in a dust-proof container.

The four beakers were labeled  $10^6$ ,  $10^8$ ,  $10^{10}$ , and  $10^{12}$ , indicating the concentrations of the solution that each will finally contain. Before introducing any chemicals, however, a careful test of the water and the beakers must be made. Into each beaker is poured 100 ml of pyrex-water. From the first beaker 1 ml is taken by means of a pipette and placed in the second. The contents of the second beaker are agitated and 1 ml taken and placed in the third beaker. Finally 1 ml is transferred from the third beaker to the fourth. The cell was then rinsed with water from the fourth beaker and finally filled. Observations were made to determine whether any minima characteristic of the compounds to be tested, exist. If any minima had been found, both the cell and its contents would have been discarded and a new cell used. If they had still persisted, the water would have been redistilled. However, no minima except those at 9.24 and 9.30, characteristic of water, appeared.

The unknown was prepared as already stated, using pyrex-water, and examined. Minima were found at 9.45, 9.50, 9.58, and 9.72, indicating that  $\text{Ba}(\text{NO}_3)_2$  was present; other minima at 20.04, 20.09, and 20.15, indicated the presence of  $\text{CoCl}_2$ . Four of the minima were verified by



Dr. Weniger. The "unknown" was correctly determined. The probability of guessing the correct combination is 1 in 32.

## VI. Conclusion

An apparatus for the application of the magneto-optic method of chemical analysis has been constructed, calibrated, and tested. The operation of the apparatus is admittedly somewhat difficult. Cleanliness is of prime importance, and the careful avoidance of all contaminants cannot be overemphasized.

A description of what minima look like cannot be undertaken except to say that the greenish yellow light passed by the filters becomes very faint, but does not as a rule become uniformly faint over the entire field. A prospective observer should see minima on an apparatus which is known to be operating satisfactorily.

The proof that minima exist, and that they are characteristic of substances has been illustrated by the correct determination of the metals placed in an "unknown" solution. This was done with dilutions far too high for determination by ordinary methods. The substances under test are of course not destroyed by the analysis.

The evidence obtained as a result of this investigation is definitely in favor of the validity of the method.

## BIBLIOGRAPHY

1. Allison, Fred. Magneto-optic method of chemical analysis as a new research tool. *Ind. and Chem. Eng. (anal. ed.)* 4:9-12, 1932.
2. Allison, F., Bishop, E. R., and Sommer, A. L. Concentration, acids, and lithium salts of element 85. *Jour. Amer. Chem. Soc.*, 54:613, 1932.
3. Allison, F., Christensen, J. H., and Waldo, G. V. Application of the photoelectric cell to reading minima in the magneto-optic method of analysis. *Phys. Rev.* 37:1003, 1931.
4. Allison, F. Christensen, J. H., and Waldo, G. V. Nature of phenomena underlying the magneto-optic method of analysis. *Phys. Rev.* 40:1052, 1932.
5. Allison, F. and Goslin, R. Transformation of products of potassium. *Phys. Rev.* 40:1015, 1932.
6. Allison, F. and Murphy, E. J. Magneto-optic method of chemical analysis. *Phys. Rev.* 35:124, 1930.
7. Allison, F. and Murphy, E. J. Magneto-optic method of chemical analysis. *Jour. Amer. Chem. Soc.* 52:3796-3806, 1930.
8. Ball, T. R. Allison's magneto-optic apparatus. *Phys. Rev.* 47:548-551, 1935.
9. Ball, T. R. and Cooper, S. S. Study of Isotopes of Cobalt by magneto-optic method. *Jour. Amer. Chem. Soc.* 55:3207, 1933.
10. Beams, J. W. and Allison, F. The difference in the time lags of Faraday effect behind the magnetic field in various liquids. *Phys. Rev.* 29:161, 1927.
11. Bhatnagar, M. J. and Mathur, J. Physical principles of magneto-chemistry. London, Macmillan Co., 1935.
12. Bishop, E. R. Radioactive families. *Phys. Rev.* 43:38, 1933.

13. Cooper, S. S. Magneto-optic method of chemical analysis. Journ. of Chem. Ed. 13: May, June, July, 1936.
14. Faraday, N. Experimental researches. Phil. Trans. XIX Series 47, 478, 1846.
15. Farwell, H. W. and Hawkes, J. B. Time lags in magneto-optics. Phys. Rev. 47:78-84, 1935.
16. Hughes, G., and Goslin, R. Photography in magneto-optic apparatus. Phys. Rev. 47:317, 1935.
17. Hughes, G. and Hopkins, B. S. Magneto-optic method of analysis. Jour. of Amer. Chem. Soc. 56:408, 1934.
18. Jeppesen, M. A. and Bell, R. M. Objective study of the Allison magneto-optic method of analysis. Phys. Rev. 47:546, 1935.
19. Jones, H. D. and Goslin, R. Some further remarks on the use of magneto-optic method. Jour. Amer. Chem. Soc. 55:3500, 1933.
20. Latimer, W. and Young, H. A. Isotopes of hydrogen by the magneto-optic method. Phys. Rev. 44:690, 1933.
21. Latimer, W. and Young, H. A. Nature of visual observations at low light intensities. Phys. Rev. 56: 963, 1939.
22. Lodge, O. Time lags in the Faraday effects. Phil. Mag. (5) 27:339, 1889.
23. MacPherson, H. G. Magneto-optic method of chemical analysis. Phys. Rev. 47:310, 1935.
24. McGhee, J. L. and Lawrenz, M. Scale readings of isomeric esters on magneto-optic apparatus. Jour. Amer. Chem. Soc. 55:2614, 1933.
25. Monk, G. S. Light. New York and London, McGraw-Hill Company, 1937.
26. Papish, J. and Wainer, E. Element 87. Jour. Amer. Chem. Soc., 53:3818, 1931.

27. Papish, J. and Shuman, A. C. Beyond uranium with the magneto-optic method of analysis. *Science*, 74:636, 1931.
28. Private Communication.
29. Slack, F. G. Magneto-optic method of chemical analysis. *Jour. Frank. Inst.* 218:445, 1934.
30. Slack, F. G. and Peoples, S. A. Magneto-optic method of chemical analysis. *Phys. Rev.* 45:126, 1934.
31. Sommer, A. L., Bishop, E. R., and Otto, I. G. Detection of Formaldehyde within the cell of a green plant by the Allison apparatus. *Plant Physiol.* 8:564, 1933.
32. Urey, H. A hydrogen isotope of mass two. *Phys. Rev.* 39:164, 1932.
33. Webb, J.S. and Morey, D. R. Time lags in the Faraday effect. *Phys. Rev.* 44:589, 1933.
34. Wissink, G. M. Magneto-optic method of determining vitamin content of various substances. *Physics*, 5:31, 1934.
35. Woodriff, R. Allison method of magneto-optic analysis. Thesis, Oregon State College, 1935.