tion formula theory, the additional mole of 8-hydroxyquinoline is held by secondary valence.[3]

It may also be noteworthy to mention that of the many elements which form precipitates with 8-hydroxyquinoline, thorium and uranium are the only two known which form an addition compound.

Summary

1. It has been shown that thorium and uranium 8-hydroxyquinolates form an addition compound with 8-hydroxyquinoline.

2. It has been shown that the additional mole of 8-hydroxyquinoline can be driven off by heating and that it will again recombine to nearly its former value.

3. An explanation of these phenomena on the basis of Werner's theory of secondary valence seems plausible.

(3) A. Werner, "New Ideas on Inorganic Chemistry." Translated from second German ed. by E. P. Hedley, Longmans, Green and Co., New York, 1911.

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[CONTRIBUTION FROM THE ALABAMA EXPERIMENT STATION]

Magneto-optic Nicol Rotation Method for Quantitative Analysis of Calcium

BY EDNA R. BISHOP, C. B. DOLLINS AND IRENE G. OTTO

The magneto-optic method[1] of analysis detects the presence of minute traces of a compound regardless of the presence of other compounds. A quantitative method[2] for the determination of calcium depending on dilutions has been described. It offers a means of analysis of samples containing less calcium than could be detected by other methods, but the determination is slow and requires a high degree of skill to operate the apparatus and great care to prevent contamination.

Allison and Murphy[3] early investigated the effect of concentration on the amount that the analyzing nicol could be rotated and the minima still be seen. They found an increase in the angle of rotation with increase in concentration of the solution examined but the variation in angle was less than 2° for a change in concentration from 10^{-11} to 10^{-3} g./cc.; hence, it did not lend itself to quantitative use. Similar determinations were made recently with like results.

In the meantime, however, Allison, Christensen and Waldo[4] predicted and found that the characteristic minima could also be produced if the

(1) Allison and Murphy, THIS JOURNAL, **52**, 3796 (1930); Allison, *Ind. Eng. Chem., Anal. Ed.*, **4**, 9 (1932).

(2) Bishop and Dollins, THIS JOURNAL, **54**, 4585 (1932).

(3) Work unpublished.

(4) Allison, Cbristensen and Waldo, *Phys. Rev.*, **40**, 1052 (1932).

current was passed through both coils of the apparatus (Fig. 1) in the same direction, with the analyzing nicol set parallel to the polarizing nicol. This arrangement was investigated and found suitable for quantitative analysis by nicol rotation.

Arrangement of Apparatus.—The optical train of the present arrangement is shown diagrammatically in Fig. 1. Light from the magnesium spark G is rendered parallel by the lens L and then passes through the color filter F, control nicol N_3, polarizing nicol N_1, cell containing carbon disulfide in the helix B_1, cell containing the solution studied in helix B_2, and analyzing nicol N_2. N_3 is mounted so that it can be rotated at will to give the light intensity at which minima can be most easily detected. N_2 is mounted in a circle calibrated to hundredths of a degree in a counterclockwise direction and is set crossed with respect to N_1 at 90° on the circle. The current flows counterclockwise through both B_1 and B_2.

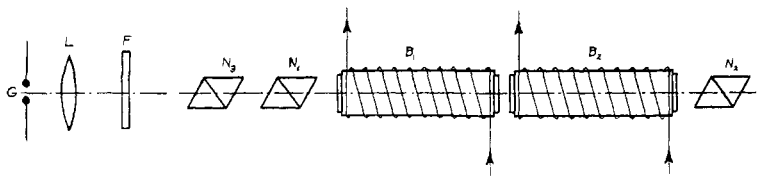

Fig. 1.—Optical train of magneto-optic apparatus for quantitative analysis by nicol rotation.

Production of Maxima and Minima.—At the characteristic scale settings of the trolley, solutions of compounds in B_2 produce maxima of light intensity when N_2 is set at 90° and minima of light intensity when it is set at 0°. If N_2 is rotated from either position, the maxima or minima persist through considerable angles. The amount of rotation of N_2 possible before the maxima or minima disappear is dependent on the concentration of the compound in B_2 but varies over a wider angle when N_2 is rotated from a position parallel to N_1 than from a position crossed with respect to N_1. Minima are more easily read than maxima and therefore the former are used for quantitative work.

It has not been possible to make any absolute measurements of light intensity, but Fig. 2 shows diagrammatically the apparent manner of variation of light intensity with nicol settings. The solid curve represents the effect produced with a concentrated solution and the dotted curve with a dilute one. Minima can be detected only when the light intensity differs from normal intensity, indicated by the line AB, by a definite amount. This amount, however, is characteristic of the individual eye and may correspond to a reduction to MN for one eye and to XY for another and hence produces the individual differences shown in Fig. 3. After passing this threshold value, the eye detects the minimum but is not capable of distinguishing the amount of change from normal, so that as soon as the threshold value of concentration or angle is passed the eye detects no change in the appearance of the minima. We are unable to interpret these results in terms of a Faraday rotation or to offer any other theoretical explanation.

With the arrangement shown in Fig. 1 and N_2 set parallel to N_1, the sensitivity or lowest concentration of calcium that can be detected is 3.74×10^{-12} g. of Ca/cc., which is the same as that previously reported[2] with current in the coils opposing and nicols crossed.

Calibration Curve.—Calcium chloride solutions ranging in concentration from 3.83×10^{-12} of aqueous solution to 0.089 g. of Ca/cc. of solution were prepared from stock solutions in which the calcium had been determined by permanganate titration. The limiting angle through which N_2 could be rotated and minima read was determined for

each. To do this, N_2 was rotated clockwise 10° at a time from zero until no minima were observed. This 10° range was then studied until two points were found 1° apart one of which would and one would not give minima. N_2 was set at the smallest angle

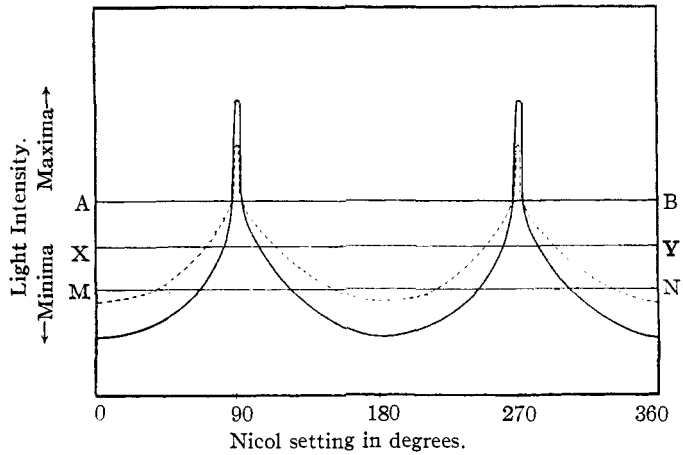

Fig. 2.—Effect of nicol rotation on maxima and minima: solid curve, concentrated solution; dotted curve, dilute solution; AB, normal light intensity; XY and MN, light intensity at which a given eye sees minima.

where minima were not visible and rotated by a fine adjustment screw until each minimum just appeared. The angle for each isotope was read and the average of these two values was used. The results are shown in Curve I and Curve II, Fig. 3.

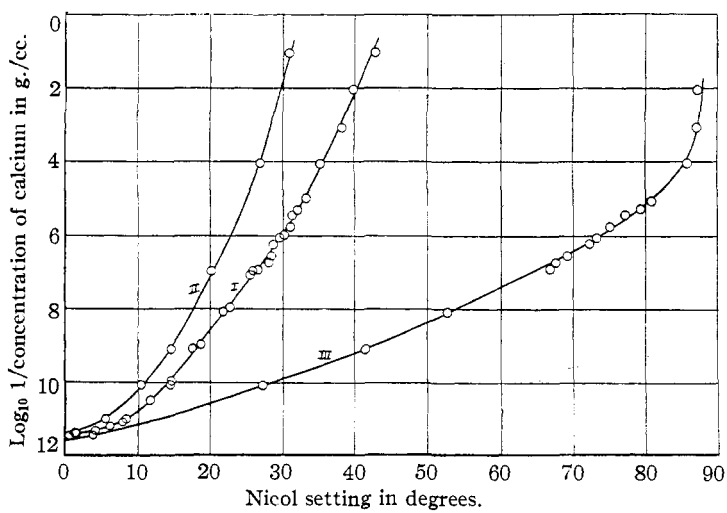

Fig. 3.—Calcium calibration curves: Curve I, direction of nicol rotation opposite to flow of current (Dollins); Curve II, direction of nicol rotation the same as flow of current (Dollins); Curve III, direction of nicol rotation opposite to flow of current (Otto).

Each point on the curve represents the average of at least four readings which were made on at least two different days and with all parts of the apparatus completely readjusted. Settings of N_2 were reproducible to 0.20° or less except for concentrations of 1×10^{-3} g. of Ca/cc. or greater where the variation increased to one degree. Hence, if a preliminary examination showed a calcium content in this range a dilution was made and the angle of rotation determined for the diluted solution which comes on a more accurate part of the curve. A new circle and nicol were installed during the progress of the work but produced no change in the results obtained.

Extensive determinations were also made starting with the minima just visible and rotating the nicol until they could not be seen. It was harder to recognize the point of disappearance than of appearance of the minima and variations as great as 0.50° were obtained.

If either the direction of the current in the coils or the direction of rotation of the nicol is reversed, the angle of rotation for a given concentration becomes less as is shown in Curve II of Fig. 3. Hence, it is important that the nicol should be rotated in a direction opposite to that of the flow of the current.

Variation of the capacity or resistance of the circuit or of light intensity does not affect the results as long as these factors are kept within the limits that produce easily detected minima.

Effect of the Presence of other Compounds.—The presence of excess chloride, nitrate, sulfate, phosphate, hydrogen, magnesium, sodium or ammonium did not affect the limiting angle at which the minima could be detected, and in the presence of an excess of all four cations the minima of each of the four calcium compounds were read at the same angle. These results are similar to those found for the dilution method.[2] Experiments with nicol rotation also checked the former results[2] that the rate of solution of calcium from the glass is not great enough to interfere with the use of the method.

Personal Factor.—The angle of rotation, however, depends not only on the concentration but on the observer. Dr. Fred Allison, Mr. R. E. Wingard, Mr. Roy Goslin and Mr. Louis Baisden have also made a considerable number of determinations of this nature. Each finds consistent and reproducible results, but at a different circle reading for a given concentration, so that each observer must determine his own calibration curve. This personal variation is shown in Fig. 3, where Curves I and III were obtained in exactly the same manner by Mr. C. B. Dollins and Miss Irene Otto, respectively.

Determination of Calcium in Vegetables.—Analyses were made of samples of plant ash prepared as previously described.[2] The solutions were then analyzed by nicol rotation. For example, in solution Number 56, Mr. Dollins saw the minima at 30° but not at 31°. The nicol was then set at 31° and he turned the fine adjustment screw as he

TABLE I

THE PERCENTAGE OF CALCIUM IN VEGETABLES AS DETERMINED BY DIFFERENT METHODS

		Magneto-optic determinations						Dilution calcium, %	Permanganate titration calcium, %
			Nicol rotation in degrees		Nicol rotation Concn. g. Ca/10^6 cc.		Calcium, %			
Vegetable	Soln.	Dried vegt./10^3 cc.	Dollins	Otto	Dollins	Otto	Dollins	Otto		
New Zealand spinach	56	0.1489	30.43	74.67	1.38	1.32	0.926	0.885	0.973	0.900
	63	.1282	30.20	74.41	1.15	1.22	.900	.954	.994	
Turnip tops	57	.1187	31.25	76.53	2.54	2.29	2.13	1.93	2.01	2.04
	55	.1607	31.59	77.56	3.31	3.09	2.06	1.93	2.00	
Chinese cabbage	1	.0818	30.70	75.28	1.68	1.58	2.05	1.93	..	1.88
	88	.1170	31.04	76.45	2.19	2.24	1.87	1.92	..	
Onion tops	59	.0670	28.86	71.15	0.454	0.447	0.676	0.667	..	0.663
	79	.0902	29.36	72.14	.631	.616	.700	.684	..	

moved the trolley over 18.66 until the minimum just appeared. The reading of the circle was 30.53. He then moved the trolley over 18.44 as he turned the screw until that minimum just appeared which was at nicol setting 30.33. This was repeated four times and the average value was used. The log of the reciprocal of the concentration which corresponded to this nicol rotation was read from the calibration curve. The concentration and percentage composition were then calculated in the usual manner. Table I shows the results obtained by two different observers employing this method, those obtained by the magneto-optic dilution method[2] and by permanganate titration. All samples were unknown to the observers and were designated simply by number. All circle settings were made by the second worker so that the observer merely decided whether minima could be seen or not without knowledge of the nicol setting. Duplicate determinations by the same or different observers check each other and the values obtained by permanganate titration within 10% error.

Limitations.—The actual observing time necessary to make a determination after preparation of the solution was about fifteen minutes. The eye, however, will not stand such steady observing and it was found necessary to take about an hour to a determination and four determinations a day were as much as one person could make. Two workers are needed, one to observe minima and one to watch the trolley movement. Considerable practice is necessary to obtain adequate skill in the operation of the apparatus. The determination of the individual calibration curve is a slow, tedious process. The error in this method is greater than that obtained by conventional chemical methods for solutions whose concentration is adapted to their use.

Advantages.—The magneto-optic determination of calcium, however, is useful over a very wide range of concentrations and at lower concentrations than any other known method. The solution analyzed undergoes no change. Complex mixtures may be analyzed without preliminary separations as there is no interference from the presence of any substance tested.

Possibilities.—Since none of the compounds tested affects the determinations and since the angle of rotation is the same for a given amount of calcium in every calcium compound studied, it seems probable that this method may be used for the determination of calcium in any type of sample by employing appropriate means for the preparation of a clear transparent solution.

Preliminary work supports the possibility that the same technique may be employed for the quantitative determination of any compound. Three requirements must be fulfilled. First, the location of the minima of the compound to be determined must be known. Those of many inorganic compounds are known and the approximate location of others can be predicted from equivalent weight relations and hence these can be located with comparative ease. The minima of very few organic compounds have been located and there is as yet little basis for predicting their location, so this may be quite a laborious task. Second, a calibration curve for the

angle of extinction *vs.* concentration must be prepared from solutions of known concentrations by the person who is to make the determinations. Third, the substance to be determined must yield a clear solution that will transmit light.

We wish to express our appreciation to Dr. Fred Allison for the use of his apparatus and for putting at our disposal the unpublished data of work which he did with Mr. Edgar J. Murphy, Mr. R. E. Wingard and Mr. Roy Goslin. We also wish to thank Dr. W. N. Arnquist and Mr. J. H. Christensen for helpful discussions and suggestions concerning the plotting of the curves.

Summary

A magneto-optic quantitative method for the determination of calcium by rotation of the analyzing nicol is described.

The range of concentration for which the method is best adapted is 3.74×10^{-12} to 1×10^{-3} g. of Ca/cc. More concentrated solutions are diluted to this range.

The angle through which the analyzing nicol can be rotated and the minima still persist depends on the concentration of calcium in the solution and on the observer. The results are not affected by the presence of any of the foreign substances tested, *viz.*, magnesium, sodium, ammonium, hydrogen, sulfate, nitrate or phosphate. Variations of the capacity and resistance of the circuit or of the light intensity used do not affect the results provided the adjustment of these factors is within the limits to produce good minima.

The limiting angle of rotation is the same for a given calcium concentration whether the minima are read for the chloride, sulfate, nitrate or phosphate.

Nicol settings are reproducible within a maximum variation of 0.20° under optimum adjustment of the apparatus and the concentration range employed.

Duplicate determinations by the same or different observers check each other and the values obtained by permanganate titration within 10%.

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