[CONTRIBUTION FROM THE CHEMICAL LABORATORY, MICHIGAN AGRICULTURAL EXPERIMENT STATION]

THE DETERMINATION OF ALUMINUM IN PLANTS. I. A STUDY OF THE USE OF AURINTRICARBOXYLIC ACID FOR THE COLORIMETRIC DETERMINATION OF ALUMINUM[1]

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Two types of methods, colorimetric and spectrographic, have been used for determining very small amounts of aluminum. The latter is of very recent origin. It has one decided advantage over other methods in that it requires no chemical reagents, a point which is particularly important in the estimation of aluminum since this element contaminates nearly all reagents. Unfortunately the necessary apparatus is so expensive that but few laboratories can afford to possess it.

Though known for many years, colorimetric methods for estimating aluminum have only recently assumed importance as the increased demand for micro methods has aroused interest in colorimetric methods in general. While affording many chances for inaccurateness, they can be used wherever a colorimeter is available and hence have tempted chemists to work for their perfection. Several such methods have been proposed, the most promising of which is the one making use of the ammonium salt of aurintricarboxylic acid—the dye commercially known as aluminon. Lundell and Knowles[2] used it for the detection of small amounts of aluminum in certain non-ferrous materials; Myers and co-workers[3] used it for the determination of aluminum in blood and animal materials, while Yoe and Hill[4] studied the reaction of aluminum with the dye under different experimental conditions and discussed its application to the colorimetric determination of aluminum in water. Some time previous to the above, Hammett and Sottery[5] studied the behavior of some of the common elements and ions with the dye, and Middleton[6] and Corey and Rogers[7] studied its behavior with some of the less common elements.

Yoe and Hill showed that during the formation of the aluminum lake intensity of color increased, within certain limits, with rise in tempera-

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[1] Published by permission of the Director of the Experiment Station as Journal Article Number 7 (n. s.) and Number 48 from the Chemical Laboratory.

[2] Lundell and Knowles, *Ind. Eng. Chem.*, **18**, 60 (1926).

[3] Mull, Morrison and Myers, *Proc. Soc. Exptl. Biol. Med.*, **24**, 476 (1927); Myers, Mull and Morrison, *J. Biol. Chem.*, **78**, 595 (1928); Myers and Mull, *ibid.*, **78**, 605 (1928); Myers and Morrison, *ibid.*, **78**, 615 (1928); Myers and Mull, *ibid.*, **78**, 625 (1928).

[4] Yoe and Hill, THIS JOURNAL, **49**, 2395 (1927).

[5] Hammett and Sottery, *ibid.*, **47**, 142 (1925).

[6] Middleton, *ibid.*, **48**, 2125 (1926).

[7] Corey and Rogers, *ibid.*, **49**, 216 (1927).

ture, length of time of standing and with the increase in the quantity of aluminum, dye, hydrochloric acid or ammonium acetate present. They also showed that the color decreased with increase in volume of solution and with the amount of ammonium hydroxide or carbonate added, and that the use of protective colloids made it possible to increase the concentration of the lake without having it precipitate.

Several attempts at determining aluminum in plants by the modifications of the method used by these investigators showed that none was entirely satisfactory in our hands. The following difficulties were encountered.

(1) The results of duplicate determinations did not always agree. (2) The color of some samples faded rapidly. (3) The necessity of having the amount of aluminum in the standard nearly the same as that in the sample required the preparation of several standards whenever a number of determinations were to be made. This wasted much time.

Hence it was decided to make a further study of the reaction between aluminum and the dye in an attempt to overcome these difficulties and if possible to adapt the method to our problem. Special emphasis was placed on determining suitable conditions (1) for the formation of a lake of maximum color intensity and (2) for destroying the color of the excess dye while retaining the lake color. Considerable time was also given to working out a procedure whereby the relationship between the amount of aluminum in a sample and the colorimeter readings could be represented by a curve. This would enable the analyst to compare all of the samples run at one time with one standard and to read the amount of aluminum directly from this curve.

Experimental Part

Apparatus and Reagents.—The lakes were developed in 50-cc. volumetric flasks. The colors were compared in a Duboscq type of colorimeter using a daylight lamp in a dark room or ordinary daylight. The reagents used in the preliminary work were not standardized but were approximately as follows: (1) hydrochloric acid, 1.5 *N;* (2) ammonium acetate, 5 *N;* (3) ammonium carbonate, 3 *N;* (4) ammonium hydroxide, *N* and 5 *N;* (5) 10% ammonium carbonate in ammonium hydroxide (1–2); (6) ammonium salt of aurintricarboxylic acid, 0.1 and 0.2%; (7) standard aluminum solution. This was prepared by dissolving 1.0000 g. of aluminum metal (99.976% Al) in as little hydrochloric acid as possible, diluting to 1 liter with distilled water, taking 10 cc. of this solution and again diluting to 1 liter. Each cc. of this final solution contained 0.01 mg. of aluminum. The reagents used in the later work were standardized and were as follows: (1) hydrochloric acid, 1.5 *N;* (2) ammonium acetate, 5 *N;* (3) ammonium carbonate, 3.2 *N;* (4) ammonium chloride, 5 *N;* (5) standard aluminum solution, same as above.

Color Development

The Dye.—Before attempting to find the optimum conditions under which a lake of maximum color could be obtained, it was deemed advisable to make a similar study of the dye alone.

To ascertain the effect of acidity on the dye several samples of varying PH were prepared by adding hydrochloric acid to distilled water, then adding 2 cc. of 0.1% dye to 25 cc. of these solutions and allowing them to stand for forty-five minutes for the color to develop. The PH of each solution was determined colorimetrically using phenol red, the color intensities were compared with the standard described above and calculated to a uniform basis giving the standard an arbitrary value of 100. The results are shown in Table I.

TABLE I

COLOR INTENSITY OF DYE AT DIFFERENT PH READINGS

Solution	1	2	3	4	5	6	7	8	9
PH	6.9	6.0	5.5	4.9	4.5	3.9	3.3	2.8	1.8
Color intens.	54	65	100	118	143	169	126	Yellow	Dye pptd.

The data in Table I show that the color intensity of the dye increased with the acidity of the solution until approximately PH 4.0 was reached and that the dye was precipitated at about PH 1.8.

Work on the other factors which, according to Yoe and Hill, influenced the intensity of the lake, showed that the intensity of the color reached a maximum and the dye separated at a slightly higher PH in the presence of ammonium acetate. It also showed that the intensity of color increased with increase in temperature or dye concentration.

The Aluminum Lake.—In order to determine the PH and quantity of ammonium salts that would produce the maximum color of the lake, a number of solutions were prepared, each of a different PH and containing a different amount of ammonium acetate. These were adjusted to PH 6.0, 5.0, 4.5 and 4.0 with hydrochloric acid. To 25 cc. of each at room temperature were added 3 cc. of the aluminum solution and 2 cc. of 0.1% dye, both having first been adjusted to the same PH as the solution to which they were added. After standing for forty-five minutes for the color to develop they were compared. The relative color intensity was also determined on a check containing 5 cc. of 5 *N* ammonium acetate, 2 cc. of 0.1% dye but no aluminum. The concentrations of ammonium acetate, the PH readings and the relative color intensities calculated as in Table I are given in Table II.

TABLE II

EFFECT OF VARYING PH AND CONCENTRATION OF AMMONIUM ACETATE ON COLOR INTENSITY

Soln.	$(NH_4)_2C_2H_3O_2$, cc.	Relative color intensity PH 6.0	PH 5.0	PH 4.5	PH 4.0
1	Check	8[a]	15[a]	19[a]	Yellow[b]
2	None	23	55	74	Yellow
3	2	24	64	75	Yellow
4	5	26	66	77	Lake pptd.
5	7	27	67	76	Lake pptd.

[a] These readings are only approximate. The colors differed from the standard.

[b] These differed so much from the standard that no attempt was made to read them.

The data in Table II show that the color intensity due to the lake and the excess dye which did not enter the lake increased with the acidity of the solution until the point was reached where the lake separated which, in the presence of 5 cc. of 5 *N* ammonium acetate, was at about *P*H 4.0. Since the color of the dye was only a small part of the total color, the above phenomenon was caused mostly by the lake. The data also show that the intensity of the color increased slightly with the addition of ammonium acetate until about 5 cc. had been added. Therefore this concentration of the salt should be used for making aluminum determinations.

To show the temperature at which maximum color was produced, two solutions, each containing 5 cc. of 5 *N* ammonium acetate for every 25 cc., were prepared and adjusted to *P*H 5.0 and 4.5, respectively. Three cc. of the aluminum solution and 2 cc. of the 0.1% dye were added to 25-cc. portions and, after holding the solution at given temperatures for ten minutes, the color intensities were compared. The figures for the *P*H of the solution, the temperature at which the color was developed and the relative intensities calculated as before are given in Table III.

TABLE III

EFFECT OF VARIATION IN TEMPERATURE ON COLOR INTENSITY

Solution		1	2	3	4	5	6
Temp., °C.		27	65	80	85	Boil 1 min.	Boil 3 min.
Rel. color intensity	*P*H 5.0	87	107	112	111	112	112
	*P*H 4.5	94	114	120	121	120	121

Table III shows that under the conditions of the experiment maximum color intensity was obtained when the solution was heated to about 80° for ten minutes or when boiled for one minute.

The effect of the time of standing at room temperature on the development of the color was shown by adjusting a number of solutions to *P*H 5.0 as in the preceding experiment, developing the colors and comparing their intensities after standing for different lengths of time. The results are shown in Table IV, which gives the relative color intensity expressed in percentage of maximum intensity (obtained by boiling for one minute) corresponding to each different length of time the solution was allowed to stand.

TABLE IV

EFFECT OF VARIATION IN LENGTH OF TIME OF STANDING ON COLOR INTENSITY

Soln.	1	2	3	4	5	6	7	8
Temp., °C.	27	27	27	27	27	27	27	Boiling
Standing, hrs.	$^1/_6$	0.25	0.5	1	1.5	18	60	1 min.
Col. intens.	63	64	66	69	73	90	92	100

Table IV indicates that with the given amount of dye and aluminum approximately 64% of the possible maximum color (obtained by boiling for one minute) was developed in fifteen minutes, that it continued to develop at a decreasing rate but that the maximum color obtainable was not reached in sixty hours. Other experiments showed that with a sufficient increase in the dye concentration it was possible to obtain maximum color at room temperature in about twenty-four hours.

From the work done on color development it appeared that maximum intensity of color was obtained when the lake was developed in the presence of 5 cc. of 5 *N* ammonium acetate in 25-cc. solution at *P*H 4.5 and allowed to stand for ten minutes at 80° or to boil for one minute.

Decolorization of Excess Dye and Permanency of Lake Color.—Since the color of the dye alone in acid solution and that of the lake are quite similar, it was found impracticable to make quantitative determinations of aluminum by comparison of the intensity of the color of the unknown with that of the standard until after the solution was neutralized and the excess dye decolorized. Hence the next step in this work was to try to find optimum conditions for destroying the color of the unused dye while retaining the color of the lake.

The Dye.—In order to determine the *P*H at which the dye decolorized and the effect of ammonium salts on this *P*H, several solutions of 25 cc. each were prepared containing salts as shown in Lines 2 and 3 in Table V. Hydrochloric acid to give a *P*H of 4.5 and 2 cc. of 0.1% dye were added to each of these and they were allowed to stand for forty-five minutes for the color to develop. Ammonium carbonate[8] was now added slowly until the color began to fade, after which the addition of small amounts of the carbonate was continued at intervals until the color entirely disappeared. The *P*H was then determined colorimetrically. The results are given in Table V.

TABLE V

EFFECT OF AMMONIUM SALTS ON THE *P*H AT WHICH DYE DECOLORIZED

Sample	1	2	3	4
5 *N* NH_4Cl, cc.	0	5	0	5
5 *N* $NH_4C_2H_3O_2$, cc.	0	0	5	5
Average *P*H	8.0	6.9	7.0	7.0

The figures in Table V indicate that the dye was decolorized at a lower *P*H in the presence of ammonium salts and that under these conditions the dye decolorized at *P*H 6.9–7.0. It should also be stated that the use of a larger quantity of dye or the development of the color at a higher temperature had no effect upon the *P*H at which the color changed.

The Lake.—The maximum *P*H at which the lake color would remain was determined by preparing several solutions containing 5 cc. of 5 *N* ammonium acetate, 2 cc. of 0.1% dye and 0.03 mg. of aluminum and

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[8] Similar results were obtained when dilute ammonium hydroxide or 10% ammonium carbonate in ammonium hydroxide (1–2) was used.

developing the colors as in the preceding experiment. An equal number of similar solutions was prepared but with the dye omitted. The quantity of neutralizing agent necessary to bring each of these latter solutions, respectively, to *P*H 7.0, 7.1, 7.2, 7.3, 7.4 and 7.5 was carefully determined and these amounts were added to the solutions containing the dye. After standing for thirty minutes for the excess dye to decolorize, the color changes were noted at intervals over a period of two hours and are recorded in Table VI.

TABLE VI

EFFECT OF *P*H OF SOLUTION ON PERMANENCY OF LAKE COLOR

Sample	1	2	3	4	5	6
*P*H	7.0	7.1	7.2	7.3	7.4	7.5
Color intens.	Const.	Const.	Const.	Faded v. sl.	Faded sl.	Faded rapidly

From Table VI it will be seen that the lake color remained practically constant until after the solution was raised above *P*H 7.3 and that it decolorized more rapidly as the *P*H increased above this point. Other experiments showed that the quantity of dye used or the temperature at which the lake was developed had no effect upon this.

Now it seemed important to know whether or not the *P*H of the solution at which the lake color was developed had any effect on the final color intensity of the lake after the dye had been decolorized. Therefore, a number of solutions were prepared as in the preceding experiment, the lakes developed at *P*H 5.5, 5.0 and 4.5 and after standing for forty-five minutes the solutions were brought to *P*H 7.2 with ammonium carbonate. After these neutralized solutions had stood for thirty minutes to allow the excess dye to decolorize, they were compared. The relative color intensities are given in Table VII where *a*, *b* and *c* under each number represent similar solutions each adjusted to the corresponding *P*H shown in the table.

TABLE VII

EFFECT OF DEVELOPING THE LAKE AT THREE DIFFERENT *P*H'S ON THE FINAL INTENSITY OF COLOR

Sample	1*a*	1*b*	1*c*	2*a*	2*b*	2*c*	3*a*	3*b*	3*a*
*P*H of col. dev.	5.5	5.0	4.5	5.5	5.0	4.5	5.5	5.0	4.5
Rel. final intens.	90	100	101	115	130	129	90	100	97

The results in Table VII show that the lakes developed at *P*H 4.5–5.0 gave rise to maximum final color intensity.

Other experiments not reported here showed that increasing the amount of dye used in developing the lake increased the color intensity of the final solution and made it possible to increase the concentration of the lake without having it separate. However, the yellow color formed when the excess dye was neutralized gave rise to varying tints which made reading the colorimeter very difficult; therefore, the data on this work are omitted.

From the work done thus far it appeared that the maximum final color intensity for practical purposes was obtained when the lake was developed in the presence of 5 cc. of 5 *N* ammonium acetate at *P*H 5.0 heated at 80° for ten minutes or boiled for one minute and neutralized to *P*H 7.1–7.3. It was found that 5 cc. of 1.5 *N* hydrochloric acid added to the solution gave the desired acidity (*P*H 5.0). In neutralizing the solution with ammonium hydroxide it was found necessary to use a dilute solution (about 1 *N*) and add it very slowly with vigorous shaking in order to get concordant results. Apparently a more concentrated solution (5 *N*) gave rise to localities of momentary high *P*H where some lake color was destroyed. There appeared to be no advantage in adding the ammonium hydroxide–ammonium carbonate solution which some analysts have used. It was found that 5 *N* ammonium carbonate could be used without loss of color if added slowly (about 5 cc. in 20 sec.) with gentle shaking. Ammonium chloride has a slight buffer effect in the range near *P*H 7.2 and the addition of 5 cc. of a 5 *N* solution of this salt before neutralizing made it possible to control more easily the acidity of the solution at this point. Therefore, ammonium chloride and ammonium carbonate were used in the remainder of this work and it was found that 5 cc. of a 3.2 *N* solution of the carbonate brought the lake to *P*H 7.2. The formation of carbon dioxide bubbles on the prisms of the colorimeter and occasionally in the bottom of the cups was sometimes quite annoying. This was largely avoided by allowing the cups to stand a few moments after the solution had been poured into them. The presence of bubbles could easily be recognized by the altered color of the solution.

The procedure developed thus far was now used for making a number of determinations on synthetic aluminum solutions. The results of these determinations are given in Table VIII, which also shows the percentage error.

The data in Table VIIIA show that the method gave good results providing the amount of aluminum in the standard was very nearly the same as that in the sample. Otherwise the results were not good, as is more emphatically shown by the determinations in Part B, for which several standards were chosen differing considerably in composition from the samples. These results show that the color intensity is not a linear function of the amount of aluminum present, that when the standards contain more aluminum than the sample the results are high and *vice versa* and that the greater the difference between the amount of aluminum in the standard and the sample, the greater is the error.

Now it appeared safe to assume that if the variable factors in the method (temperature, time, quantity of reagents, etc.) were carefully controlled and if the colorimeter readings of the standard were kept constant, the relation between the colorimeter readings and the amount of aluminum

TABLE VIII

DETERMINATION OF ALUMINUM IN SYNTHETIC SOLUTIONS

	Sample	Aluminum in standard, mg.	Aluminum Present, mg.	Aluminum Found, mg.	Error, %
A	1	0.0300	0.0300	0.0306	+ 2.0
	2	.0200	.0200	.0200	0.0
	3	.0500	.0500	.0496	− 0.8
	4	.0500	.0500	.0480	− 4.0
	5	.0400	.0400	.0413	+ 3.2
	6	.0300	.0320	.0328	+ 2.5
	7	.0500	.0520	.0516	− 0.8
	8	.0400	.0420	.0420	0.0
B	1	.0300	.0050	.0084	+68.0
	2	.0300	.0100	.0151	+51.0
	3	.0300	.0200	.0231	+15.5
	4	.0300	.0300	.0300	0.0
	5	.0300	.0400	.0359	−10.2
	6	.0300	.0500	.0449	−10.2
	7	.0100	.0050	.0067	+34.0
	8	.0100	.0200	.0189	− 5.5
	9	.0200	.0100	.0110	+10.0
	10	.0200	.0200	.0197	− 1.5

present might be represented by a curve plotted to show this relationship. Furthermore, it should be possible to read directly from this curve the quantity of aluminum present in unknowns.

In order to determine the correctness of this assumption, several series of determinations were made, taking solutions containing 0.005, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06 and 0.07 mg. of aluminum for each series and reading each of these against 0.03 mg. of aluminum as the standard. The readings were made with the standard set at 30 or when this was not practical they were calculated to this value. The results are shown in Table IX, which gives the amount of aluminum in the solution, the corresponding colorimeter readings and the averages of these readings.

TABLE IX

COLORIMETER READINGS OF SIX SERIES OF SYNTHETIC ALUMINUM SOLUTIONS

Al, mg.	Colorimeter readings 1	2	3	4	5	6	Av.
0.0050	102.6	106.0	102.6	100.1	..	..	103.1
.0100	58.8	59.5	58.1	54.6	61.5	60.4	58.8
.0200	38.8	39.1	39.3	38.6	40.0	40.0	39.3
.0300	30.0	30.0	30.0	30.0	30.0	30.0	30.0
.0400	24.7	24.2	24.2	24.8	24.4	25.0	24.5
.0500	21.6	21.3	21.1	21.1	21.2	21.1	21.2
.0600	18.3	18.4	..	18.1	18.5	18.9	18.4
.0700	16.9	17.1	..	17.0	16.9	17.0	17.0

Figure 1 shows the relation between the aluminum and average colorimetric readings expressed in Table IX in the form of a graph.

Aluminum determinations were now made on several synthetic solutions by reading the results directly from the curve in Fig. 1. These data are given in Table X, which shows the colorimeter readings, the amount of aluminum present, the amount found and the percentage error.

The values in Table X show that aluminum can be determined colorimetrically by comparing the color intensities of the unknowns with that of one standard and reading the results directly from a curve which shows the relation between the colorimeter reading and the amount of aluminum present. These also show that the method is applicable to solutions containing from 0.0050–0.0700 mg. of aluminum and that the method is accurate to within about 5%. Other determinations which are not recorded here show this to be approximately the limit of error of the method. The result for Solution 7 in Table X indicates that if the curve were continued nearer the zero point for aluminum the method might be useful for solutions containing less than 0.0050 mg. of aluminum. In this case a fair approximation may be made but the color is very faint and if accurate results are desired it is better to make up a standard containing 0.0050 mg. of aluminum and calculate the results.

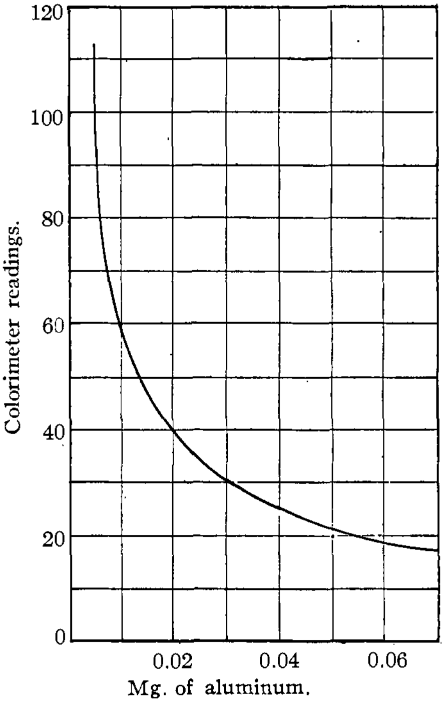

Fig. 1.—Relation between the colorimeter readings and the amount of aluminum.

Table X

Aluminum Determinations Read from Curve in Fig. 1

Soln.	Colorimeter reading	Aluminum Present, mg.	Aluminum Found, mg.	Error, %
1	31.4	0.0280	0.0285	−1.8
2	23.9	.0400	.0410	−5.0
3	20.5	.0530	.0515	−2.8
4	17.2	.0670	.0690	−2.9
5	34.1	.0250	.0250	0.0
6	100.9	.0050	.0052	−4.0
7	176.4	.0030	?	

The Method

The procedure recommended for making aluminum determinations is as follows: transfer the solutions, which should be slightly acid, to 50-cc. volumetric flasks and to each add water to make a volume of about 20 cc.; then add 5 cc. of 5 *N* ammonium acetate, 5 cc. of 1.5 *N* hydrochloric acid and 2 cc. of 0.1% dye and place in a water-bath at about 80° for ten minutes. Add 5 cc. of 5 *N* ammonium chloride, cool to room temperature, add 5 cc. of 3.2 *N* ammonium carbonate while shaking gently, fill to the mark with distilled water and mix. At this point the reactions should be P_H 7.1–7.3 and the red color of a blank should disappear in about fifteen minutes. (The exact concentration of the reagents is not important, but the final P_H is, and the amount of ammonium carbonate necessary to bring the solution to the above P_H should be determined by neutralizing similar solutions without adding the dye.) Simultaneously with the above, run a standard (or standards if necessary) containing a given quantity of aluminum. After standing for twenty minutes for the excess dye to decolorize, compare the color intensities and read the amount of aluminum from a curve plotted as described in the following paragraph.

When only a small number of determinations are to be made, prepare four standards containing 0.0100, 0.0300, 0.0500 and 0.0700 mg. of aluminum, respectively, and run these with the samples. Compare all of these solutions with the standard containing 0.0300 mg. of aluminum and calculate the results to a colorimeter reading of 30 for this standard. Arbitrarily give 0.0050 mg. of aluminum a reading of 100 and with this and the four readings on the standards plot a curve similar to Fig. 1. Read the quantity of aluminum in each sample from this curve. If a large number of determinations are to be made extending over a period of time, it is advisable to make determinations on several series of standards and plot a curve from the average of these results, as was done in obtaining the curve in Fig. 1. Having done this it is necessary to run only one standard each time determinations are to be made and read the results from the curve.

Summary and Conclusions

1. The colorimetric method in which aurintricarboxylic acid is used for determining aluminum has been modified so that samples ranging from 0.0050 to 0.0700 mg. of aluminum may be compared with one standard and the amount of aluminum in each sample may be read directly from a curve. The results are accurate to within about 5%.

2. Maximum color intensity was obtained in the presence of 10% of 6 *N* ammonium acetate when the solution was at approximately P_H 4.0 and held at a minimum temperature of 80° for about ten minutes.

3. In the presence of 5 cc. each of 5 *N* ammonium acetate and ammonium chloride the dye changed color at about P_H 7.0. A neutral or

alkaline solution of 2 cc. of 0.1% dye in a volume of 50 cc. was very nearly colorless.

4. The lake color remained sufficiently permanent for making determinations until the solution was raised to *P*H 7.4.
5. The presence of ammonium acetate and chloride as buffers was found advantageous for controlling the *P*H of the solution.
6. Ammonium carbonate was found more suitable for decolorizing the excess dye than either ammonium hydroxide or a solution of ammonium carbonate in ammonium hydroxide.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

PHOTOCHEMICAL STUDIES. IX. URANYL SULFATE AS SENSITIZER FOR THE PHOTOCHEMICAL DECOMPOSITION OF OXALIC AND MALONIC ACIDS

BY WILLIS CONWAY PIERCE

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The photochemical decomposition of malonic acid, both in the presence and absence of uranyl salts, has been the subject of a previous study,[1] while the decomposition of oxalic acid has been repeatedly investigated.[2] The results indicate that the mechanisms of the sensitized decompositions of the two acids may be different and the present work was undertaken in order to obtain a more thorough comparison between the two.

I. Temperature Coefficient

There is some discrepancy in the values given for the quantum efficiency of the oxalic acid decomposition but the generally accepted value seems to be one.[3,4] Various workers have reported a temperature coefficient of unity. The quantum efficiency for the decomposition of 0.05 *M* malonic acid with 0.0025 *M* uranyl sulfate was found[1] to be about 0.25, and to be in some degree at least independent of wave length. Büchi[3] attributed the effect of uranyl sulfate to complex formation in the case of oxalic acid. Müller,[5] on the other hand, has attributed the effect to collisions of the second kind between activated uranyl ions and oxalic acid molecules or oxalate ions. A somewhat similar explanation was suggested[1] for the

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[1] See Pierce, Leviton and Noyes, THIS JOURNAL, **51**, 80 (1929), for more complete references.

[2] See Kistiakowsky, "Photochemical Processes," The Chemical Catalog Co., Inc., New York, **1928**, for a review of this work.

[3] Büchi, *Z. physik. Chem.*, **111**, 269 (1924).

[4] Bowen and Watts, *J. Chem. Soc.*, **127**, 1607 (1925).

[5] Müller, *Proc. Roy. Soc. London*, **121A**, 313 (1929).