

TABLE I (Concluded)

RUTHENIUM FOUND IN K_2RuCl_6 ;⁴ THEORETICAL, 25.89%
22.65, 23.91, 23.03, 24.10, 22.11, 24.64, 24.39, 24.64, 25.31, 24.69, 23.42, 24.47, 24.07,
24.27; average of 14 determinations, 23.99.

RUTHENIUM FOUND IN K_2RuCl_5OH ; THEORETICAL, 27.18%
24.675, 25.68, 26.64, 24.05, 25.68, 20.12, 25.54, 19.89, 24.84; average of 9 determinations
24.124.

Summary

This paper presents a simple method of determining ruthenium volumetrically, when present in small amounts, and of evaluating ruthenium solutions approximately.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA,
No. 41]

AN INVESTIGATION OF THE REACTION OF ALUMINUM WITH THE AMMONIUM SALT OF AURINTRICARBOXYLIC ACID UNDER DIFFERENT EXPERIMENTAL CONDITIONS, AND ITS APPLICATION TO THE COLORIMETRIC DETERMINATION OF ALUMINUM IN WATER

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Recently Hammett and Sottery¹ described a new qualitative test for aluminum in which the principal reagent is the ammonium salt of aurintricarboxylic acid, now sold under the trade name, "Aluminon." These authors studied the behavior of several of the elements and ions commonly dealt with in qualitative analysis which would be likely to interfere with the test. Middleton² and later Corey and Rogers³ have studied the behavior of several of the less common elements with "Aluminon." A brief summary of the results with respect to the final solution follows.

1. Silicic acid, salts of antimony, bismuth, lead, mercuric mercury, stannic tin and titanium give white precipitates. The qualitative test may be made without a separation.

2. Salts of cadmium, chromium, cobalt, germanium, indium, manganese, nickel, rare earths, thallium, thorium, zinc and zirconium give no precipitates.

3. Ferric salts produce a reddish-brown precipitate which is stable under the same conditions as the aluminum lake. Beryllium gives a lake which cannot be distinguished from aluminum. The gallium lake

⁴ For details see ref. 2.

¹ Hammett and Sottery, *THIS JOURNAL*, **47**, 142 (1925).

² Middleton, *ibid.*, **48**, 2125 (1926).

³ Corey and Rogers, *ibid.*, **49**, 216 (1927).

dissolves with difficulty in 2 *N* ammonium carbonate, leaving a red-colored solution.

4. Phosphates tend to prevent the formation of the lake, and reducing agents such as hydrogen sulfide, sulfur dioxide, etc., destroy the color.

Lundell and Knowles⁴ adopted the "Aluminon" reagent in preference to sodium alizarin sulfonate⁵ since "it requires less time and is more sensitive, particularly in the presence of precipitates such as stannic hydroxide." They found that the final color is unsatisfactory when the ammonium hydroxide-carbonate solution is added too rapidly, or in large excess; also when the amount of aluminum is very small and proportionately large amounts of precipitates are present.

A further investigation seemed well worth while, having for its purpose the study of the effects of changing the several factors in order to determine the optimum conditions for the reaction, with a view towards making a more general application in the field of quantitative analysis.

Apparatus and Reagents

The dark-room consisted of a wooden box of convenient dimensions mounted on a table. The inside of the box was painted a dull black and a curtain of heavy black cloth covered the open side and extended almost to the floor. The source of light was a Bausch and Lomb daylight lamp which was supported on a platform rigidly attached to the wall of the box. The legs of the lamp fitted snugly into holes in the platform and the source of light was thus kept in one position throughout the course of the work. Three strips of wood were screwed to the floor of the box in such a manner that they served as guides for placing the colorimeter always in the same position with respect to the lamp. A colorimeter of the Kennicott-Campbell-Hurley type was employed.

Carefully matched Nessler tubes of 50cc. capacity were employed, the dimensions of the tubes being those established by the American Public Health Association. The tubes were also marked to indicate a volume of 30 cc. The reagents were measured out with precision pipets of the desired capacity. The pipets were labeled so that a given pipet was always used for one solution only, and where necessary these were calibrated.

The purest chemicals obtainable were used in the preparation of the reagents, and the solutions were stored in the dark in Pyrex flasks which were carefully cleaned and steamed out just before being filled. Comparison solutions to which aluminum had not been added gave as a final color the characteristic yellow of the dye.

Reagents

1. Hydrochloric acid, 1 *N* and 4 *N*. 2. Nitric acid, 5 *N*. 3. Ammonium hydroxide, 5 *N*. 4. Ammonium hydroxide-carbonate solution; 250 g. of ammonium carbonate dissolved in a liter of 6 *N* ammonium hydroxide. 5. Ammonium carbonate solution, 5 *N*. 6. Sodium hydroxide solution, 6 *N*. 7. Ammonium acetate solution, 3 *N*. 8. Standard aluminum chloride solution; 8.952 g. of pure aluminum chloride hexahydrate⁶ dissolved in distilled water and diluted to a liter. The mean of three

⁴ Lundell and Knowles, *Ind. Eng. Chem.*, **18**, 60 (1926).

⁵ Atack, *J. Soc. Chem. Ind.*, **34**, 936 (1915).

⁶ Dennis, *Z. anorg. Chem.*, **9**, 339 (1895); also, J. W. Mellor, "A Comprehensive Treatise of Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1924, Vol. V, p. 315.

closely agreeing analyses, carried out according to the method of Blum,⁷ showed that 1 cc. contained 0.999 mg. of aluminum. Ten cc. of this stock solution was diluted to a liter and mixed thoroughly. One cc. of the dilute solution contained 0.010 mg. of aluminum. 9. Solutions of the several salts which were used in studying the effects of ions were prepared so that 1 cc. would contain 10 mg. of the desired ion if the salt were completely dissociated. In the study of positive ions, chlorides or nitrates were used; in all other cases sodium salts were employed. 10. "Aluminon" reagent, 0.1% solution in water. The salt was obtained from the Fales Chemical Co., 74 Cortlandt St., New York City. 11. "Aluminon" reagent, 0.2% solution in water. 12. Methyl red, 0.05% solution in water. 13. Neutral litmus paper. 14. Starch solution, 1%. One gram of potato starch boiled in 100 cc. of distilled water for three hours, water being added from time to time to keep the volume at 100 cc. Transferred while hot to a sterilized, glass-stoppered bottle, and after allowing it to settle the clear supernatant liquid was pipetted out as needed.

Experimental

The order of addition of the reagents, as well as the quantities added, unless otherwise stated, was as follows. To the stated amount of aluminum in a Nessler tube were added 5 cc. of 1 *N* hydrochloric acid, 5 cc. of 3 *N* ammonium acetate and sufficient distilled water to bring the volume to the 30cc. mark. Then 5 cc. of the "Aluminon" reagent was added and the solution mixed thoroughly. It was allowed to stand for five minutes, reckoning the time from the beginning of the addition of the "Aluminon" to the beginning of the addition of the ammonium hydroxide, and 2 cc. of 5 *N* ammonium hydroxide and 10 cc. of 5 *N* ammonium carbonate were added slowly with constant stirring. The solution was diluted to 50 cc., mixed thoroughly and transferred to the colorimeter tubes just before comparison.

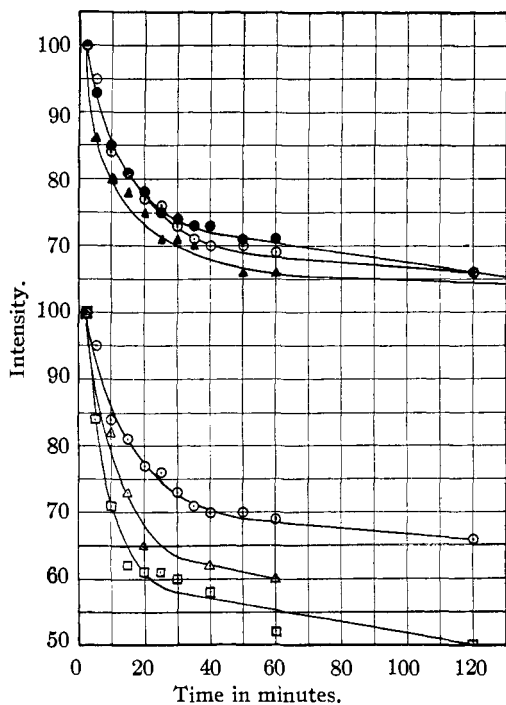
The measurements were carried out in such a manner that sufficient time was given for the operator's eyes to become adjusted to the dark before the readings were taken. Two "settings" of the colorimeter were made, one being made as the height of the adjustable column was increased, the other as its height was decreased. In order to obtain the best average value, the first reading was taken a few seconds before the end of the time interval and the second a few seconds afterwards. From the mean of the two readings the intensity was calculated by expressing the mean of the readings at the end of a given time interval as a percentage of the mean of the readings at the end of two minutes, the latter being considered as having an intensity of 100%. Beginning with the measurements on varying quantities of the reagents, the mean of the readings at the end of twenty-five minutes was adopted as the value corresponding to an intensity of 100%.

During the course of the earlier measurements a new standard was prepared for each comparison. However, it was found that considerable time could be saved by preparing a standard solution of the desired strength and allowing it to stand for several hours. After this period the rate of change of color intensity is small, and without appreciable error from this source a whole series of measurements could be made against the same standard. In order to obtain the reading corresponding to an intensity of 100%, 50 cc. of a fresh solution was prepared and allowed to stand for two minutes or twenty-five minutes, depending upon whether the results were to be expressed in terms of the intensity at the end of two minutes or that at the end of twenty-five minutes. At the end of this time the fresh standard was compared with the solution which had stood for several hours, the height of the column of the latter being taken as the reading

⁷ Blum, THIS JOURNAL, 38, 1282 (1916); also *Sci. Paper* No. 286, U. S. Bureau of Standards, 1916.

corresponding to an intensity of 100%. A similar comparison was made at the beginning of each series of measurements.

"Aging."—The decrease in color intensity with time after the addition of ammonium hydroxide, or "aging," was studied both in the light and in the dark. In both cases the solutions were allowed to stand in the colorimeter; in the former the colorimeter was removed from the dark room after each reading and placed in the diffused light of a well-lighted laboratory, while in the latter the colorimeter was left in the dark



○ 2 cc. NH_4OH in light; □ 5 cc. NH_4OH in light; ● 2 cc. NH_4OH in dark; ▲ 0.2% "Aluminon" in dark; △ 2 cc. $\text{NH}_4\text{OH}-(\text{NH}_4)_2\text{CO}_3$ in light.

Fig. 1.—"Aging."

of 0.1% solution, and when the ammonium hydroxide-carbonate reagent was used.

Effect of Varying the Quantities of the Reagents.—The quantities of the reagents were varied one at a time, all other conditions being kept constant. In each instance the temperature was 23° . All solutions were "aged" for 25 minutes and the intensity is given in terms of the intensity of the standard at the end of 25 minutes. The results are shown in Figs. 2 and 3.

Conditions During Lake Formation.—Three variable conditions were

room. The results are shown in Fig. 1. The results for two concentrations of ammonium hydroxide are given. When 1 cc. of ammonium hydroxide was added in the neutralization, in which case the final solution was just neutral to litmus paper, the color intensity was about 20% higher than when 2 cc. was used. For higher concentrations of ammonium hydroxide, Fig. 3 may be studied. Measurements were made on solutions containing different aluminum concentrations. The results were identical, and, unless otherwise stated, an aluminum content of 0.1 mg. has been adopted as the standard in all measurements.

For comparison, curves are shown in Fig. 1 for "aging" when 0.2% "Aluminon" solution was employed instead

studied, namely, (1) the time allowed for the lake to form, (2) the temperature at which the lake was formed and (3) the volume of the solution at the time the lake was formed. In (2), Nessler tubes containing the mixture of aluminum, hydrochloric acid and ammonium acetate solutions were permitted to stand in a water-bath for ten minutes before the addition

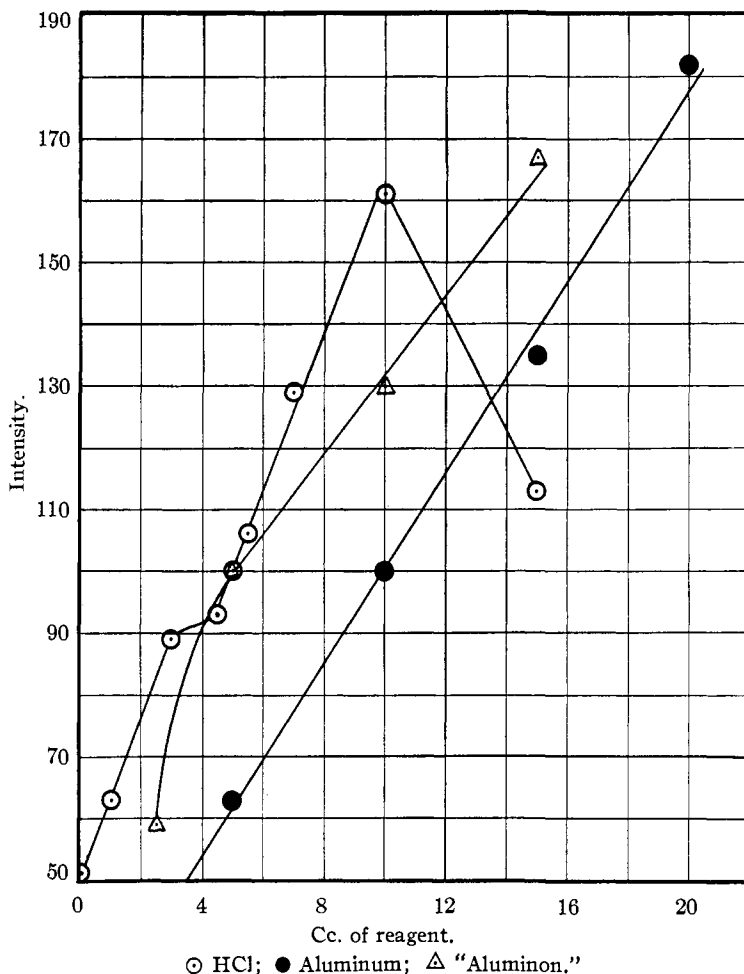


Fig. 2.—Variation in quantities of reagents.

of the dye, which was also at the temperature of the bath. Upon the addition of the ammonium hydroxide, the Nessler tubes were removed from the bath and placed in the rack until time for comparison. The results are shown in Figs. 4 and 5.

Presence of Other Ions.—The stated quantities of the ions were added to Nessler tubes containing 0.1 mg. of aluminum just before the

addition of the hydrochloric acid. The intensity of solutions containing 150 mg. of iodide, nitrate, nitrite and sulfate ions, respectively, was sensibly the same as that of the standard containing only aluminum. The effects

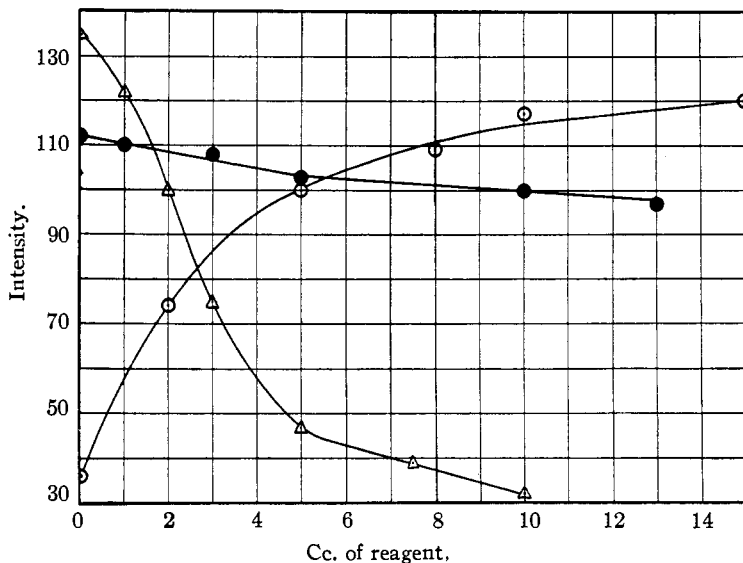


Fig. 3.—Variation in quantities of reagents. ○ NH₄Ac; ● (NH₄)₂CO₃; △ NH₄OH.

of the orthophosphate ion and silica are shown graphically in Fig. 6, while that for iron is given in Table I. The intensity of the solution containing 0.01 mg. each of iron and aluminum was too weak for com-

TABLE I
EFFECT OF IRON ON THE COLOR INTENSITY

| Mg. of iron | Mg. of aluminum | Intensity |
|-------------|-----------------|-----------|
| 0.00 | 0.10 | 100 |
| .01 | .10 | 100 |
| .03 | .10 | 121 |
| .01 | .01 | ? |

TABLE II
EFFECT OF CERTAIN COMMON IONS ON THE COLOR INTENSITY

| Ion | Intensity 1 mg. of ion | Intensity 10 mg. of ion |
|--------------------------------|---------------------------|----------------------------|
| Cu ⁺⁺ | 100 | ... |
| CrO ₄ ⁻⁻ | 112 | Too intense for comparison |
| Co ⁺⁺ | 110 | Too intense for comparison |
| Mn ⁺⁺ | 117 | Very turbid |
| Ni ⁺⁺ | 108 | 138 |
| Ca ⁺⁺ | 102 | Very turbid |
| Mg ⁺⁺ | 102 | 115 |
| PO ₄ ⁻⁻⁻ | (5 mg.) 107 (turbid) | Very turbid |

parison in the colorimeter but comparison in the Nessler tubes showed a distinct difference. An attempt was made to prevent the iron lake from forming by the addition of citric acid, with the result that neither the iron nor the aluminum lake was formed in its presence. The results for several other ions which were studied in less detail are shown in Table II. The presence of 0.01 mg. of sulfur as sodium sulfide did not alter the intensity appreciably, but with 0.1 mg. present the intensity was reduced to 94.

Limits of the Test for Colorimetric Work.—With 0.001 mg. of aluminum in a 50cc. Nessler tube the color could not be distinguished from that of a "blank" which contained no aluminum. A faint pink was perceptible when 0.002 mg. of aluminum was present. The lake did not settle out with 0.5 mg. of aluminum present but the solution was too highly colored

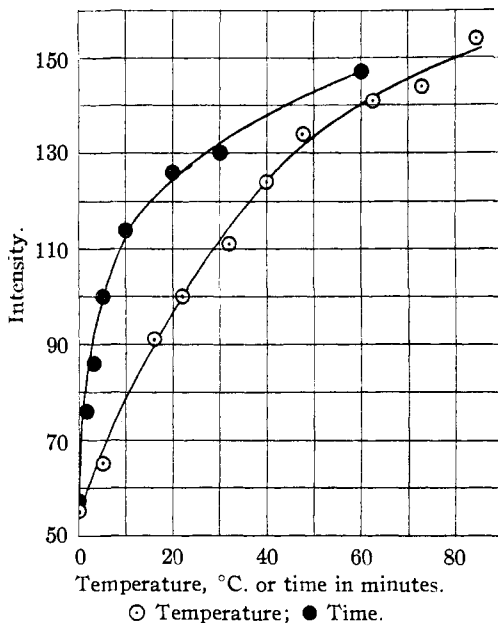


Fig. 4.—Time for lake formation and temperature.

○ Temperature; ● Time.

for comparison with the colorimeter employed in this work. With 1 mg. of aluminum a slight coagulation was observed after one hour, with 3 mg. the lake had coagulated at the end of ten minutes, and with 5 mg. the coagulated lake had begun to settle at the end of ten minutes. In these

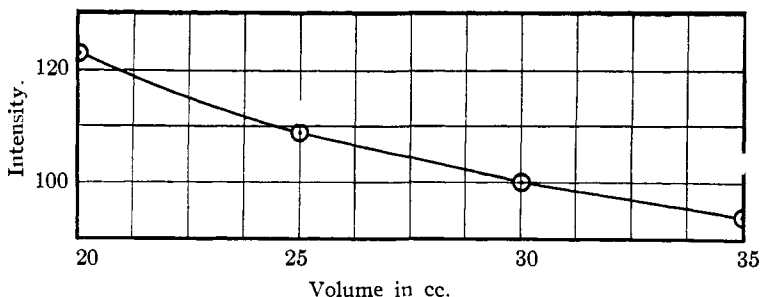


Fig. 5.—Variation in volume at lake formation.

experiments 2 cc. of ammonium hydroxide was added. An increase in the quantity of alkali hastened the process of coagulation.

A few observations were made on the effect of adding starch as a pro-

TECTIVE COLLOID just before the addition of the ammonium hydroxide, with a view towards stabilizing the lake with the higher concentrations of aluminum. The results for 3 mg. of aluminum are summarized below.

| Time in minutes | 1% starch solution added | | |
|-----------------|--------------------------|-------------------|----------------------|
| | No starch added | 5 cc. | 10 cc. |
| 10 | Coagulated | Suspended | Suspended |
| 20 | Settled | Began coagulating | Suspended |
| 180 | ... | ... | Signs of coagulation |

The effect of starch on the stability of the color intensity was determined using 0.1 mg. of aluminum.

| | | | | | |
|---|------|-----|-----|-----|------|
| Cc. of 1% starch solution added..... | 0.00 | 0.5 | 1.0 | 5.0 | 10.0 |
| Intensity of color after 25 minutes.... | 100 | 106 | 106 | 100 | 82 |

In the determination of the "sensitiveness" of the test, the experimental method of Horn and Blake⁸ was used. A series of five solutions was

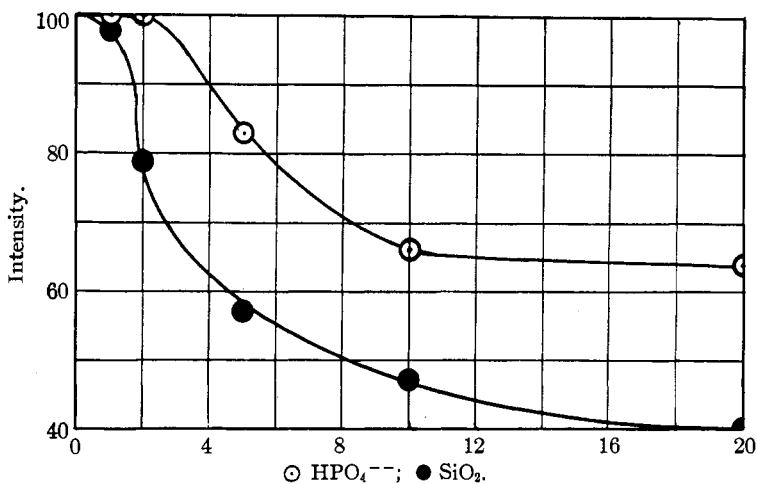


Fig. 6.—Orthophosphate ion and silica.

prepared in marked Nessler tubes of 50cc. capacity, such that the aluminum content of each solution differed from the one immediately before it in the series by a constant amount, the concentration of aluminum in the third solution being that at which the sensitiveness was to be determined. After standing for 25 minutes the tubes were arranged out of their regular order, and four men, separately and unaided, attempted to rearrange them in their proper order. Several such sets of tubes were prepared in which the difference in aluminum content was constant for a given set, though differing from series to series, until finally a series was obtained which could barely be rearranged with certainty by four different persons. The aluminum increment in this series was taken as the amount

⁸ Horn and Blake, *Am. Chem. J.*, 36, 195 (1906).

of aluminum necessary to produce a difference in the color intensity barely perceptible with certainty at the concentration of the third tube in the series. According to Horn's definition, the reciprocal of this increment in milligrams is the sensitiveness at the given concentration. This procedure was repeated at several concentrations. The results are shown in Table III,

in which, according to the nomenclature of Horn, V is the volume in liters of the solution which contains one gram atom of aluminum; B is the milligrams of aluminum in 50 cc. of the solution; Δ is the amount of aluminum in milligrams necessary to produce a perceptible difference in the intensity of 50 cc. of a solution containing B mg. of aluminum; S is the sensitivity and equal to the reciprocal of Δ and $B' = B + \Delta$. The sensitivity curve for aluminum is shown in Fig. 7, in which the square roots of V and S have been employed for convenience in plotting.

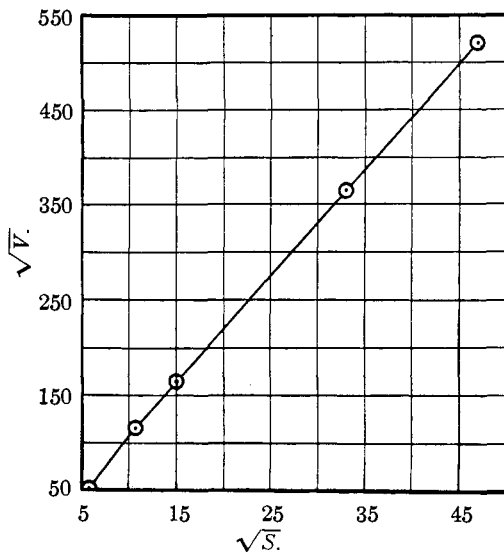


Fig. 7.—Sensitivity curve.

TABLE III
SENSITIVENESS

| V | B | Δ | S | B' | Δ/B' | \sqrt{V} | \sqrt{S} |
|-----------|-------|--|------|--------|-------------|------------|------------|
| 1,355 | 1.000 | Too intense for determination | | | | | |
| 2,710 | 0.500 | 0.025 | 40 | 0.525 | 0.048 | 52 | 6.3 |
| 13,550 | .100 | .009 | 111 | .109 | .083 | 116 | 10.6 |
| 27,000 | .050 | .0045 | 222 | .0545 | .083 | 165 | 15.0 |
| 135,000 | .010 | .0009 | 1111 | .0109 | .083 | 365 | 33.2 |
| 271,000 | .005 | .00045 | 2220 | .00545 | .083 | 520 | 47.0 |
| 1,355,000 | .001 | Matched solution to which no aluminum had been added | | | | | |

Determination of Aluminum in Water.—Four samples of water of different iron content were analyzed for aluminum by the three methods described below. The results in parts per million are given in Table IV.

1. The aluminum was determined gravimetrically according to the method given in "Standard Methods of Water Analysis," American Public Health Association, 6th ed., New York, 1925, except that the hydroxides of aluminum and iron were precipitated by adding 5 N ammonium hydroxide until the solution was just neutral to methyl red. The iron was determined colorimetrically by the thiocyanate method.

2. A direct determination of the aluminum was made using "Aluminon;" 100–200

cc. of the sample, after the addition of 1-2 cc. of 4 *N* hydrochloric acid, was evaporated to dryness on the water-bath, and the residue ignited at dull redness for a few minutes to destroy any organic matter. After cooling, the ignited residue was taken up with a few drops of 4 *N* hydrochloric acid and 5 cc. of hot water and filtered in order to remove the small amount of silica which had separated. After washing the filter three times with small portions of hot water, the combined filtrate with washings was made neutral to litmus paper by adding 4 *N* hydrochloric acid and transferred to a 50cc. Nessler tube. After the addition of 5 cc. of 1 *N* hydrochloric acid, 5 cc. of 3 *N* ammonium acetate and sufficient distilled water to bring the volume to 30 cc., 5 cc. of 0.1% "Aluminon" solution was added and mixed. When the solution had stood for five minutes, 5 cc. of 5 *N* ammonium hydroxide and 10 cc. of 5 *N* ammonium carbonate were added slowly with constant stirring. The solution was now diluted to 50 cc. and mixed, and after standing for twenty minutes it was compared against standard aluminum solutions in Nessler tubes which were prepared and "aged" in a similar manner. In order to correct for the iron, a quantity of iron equivalent to that found in (1) was added to the standard.

3. In this case the aluminum was separated from the iron. A 300-550cc. sample of the water was treated as stated in (1) above until the precipitates of aluminum and iron hydroxides were filtered the first time. This precipitate was dissolved in 5 cc. of warm 5 *N* nitric acid by pouring the acid through the filter three times, and finally washing the filter three times with small quantities of hot water. The combined filtrate with washings was evaporated on the hot-plate to 1 cc., made strongly alkaline with 6 *N* sodium hydroxide, brought to boiling and filtered through a very small filter paper. The filter was washed three times with small quantities of hot water, and the filtrate with washings, after being made neutral to litmus paper by the addition of hydrochloric acid, was transferred to Nessler tubes and cooled. The procedure was completed from this point in (2) above.

TABLE IV
DETERMINATION OF ALUMINUM IN WATER

| Sample | Iron (p.p.m.) | Aluminum (p.p.m.) | | |
|--------|---------------|--------------------------|---------------------------|-------------------------------|
| | | Method 1, gravimetric | Method 2, direct detn. | Method 3, separation of Fe |
| I | 0.00 | 0.05 | 0.05 | 0.05 |
| II | .66 | 1.03 | .22 | 1.09 |
| III | .23 | 0.51 | .10 | 0.41 |
| IV | 5.00 | .59 | .12 | .62 |

Discussion

The results for "aging" with 2 cc. of ammonium hydroxide, where the solutions were "aged" in the light and dark, respectively, are represented graphically in Fig. 1. There is little difference at any time between the intensities in the two cases. Although the curves diverge from each other in the manner which is to be expected if light has an appreciable effect on the stability of the color, the maximum difference of about 2% is within the limits of the experimental error. Thus, the rate of decrease in intensity appears to be independent of the diffused light of the laboratory.

The lower curves in Fig. 1 show the effect of the concentration of the ammonium hydroxide. Here, as in each case studied, the period of "aging" may be divided into two parts according to whether the slope

of the curve is "steep" or "flat." With the addition of ammonium hydroxide a comparatively short interval begins, in which the rate of decrease in intensity is very rapid. This period merges into the second and comparatively long period of slow change in intensity. With 2 cc. of ammonium hydroxide the first stage is 35 minutes long, while with 5 cc. this time is almost halved; however, in the latter instance the intensity is decreased by about 15% in the second period.

In Figs. 2 and 3 are shown the effects of varying the quantities of the reagents. The intensity increases with the concentration of hydrochloric acid to a maximum value, then drops rapidly on a further increase in the acid concentration. With an increase in the quantity of ammonium hydroxide, the intensity decreases along a curve which is very similar to the curves for "aging." The effect of ammonium carbonate is least of all, being a decrease in intensity of about 15% for 13 cc. of the reagent. In the case of the other three reagents the intensity increases with the concentration.

For the colorimetric determination of aluminum with "Aluminon" a procedure has been given which is in accord with the facts brought out in the foregoing curves. The quantities of the reagents, the time given for lake formation and all other conditions have been chosen, where possible, so that slight variations in the several factors will produce a minimum effect on the final color intensity and, therefore, a minimum error in the determination. Since the test is fairly sensitive to a change in the acid concentration, the solution to be examined for aluminum must be neutral at the time the hydrochloric acid is added. Furthermore, since the curves for the change in intensity with temperature and the time at lake formation are quite steep, it is obvious that the unknown solution and the standards must be at the same temperature during lake formation, and that the time intervals must also be of equal length. Where the analyst has the time, something in accuracy may be gained by giving a longer period for the lake to form.

Certain substances interfere with the test, and in this connection the effect of several ions likely to be encountered in water analysis has been studied. One mg. of silica or 2 mg. of HPO_4^{--} may be present without the results being impaired. While the orthophosphate ion tends to give low results by preventing the formation of the aluminum lake, the normal phosphate ion causes a turbidity which tends towards high results. Similarly, calcium and manganese produce turbid solutions. Some numerical values for the permissible quantities per 50 cc. of solution are given in Table II.

The results in Table I seem to indicate that iron may be present with aluminum in the ratio of 1:10 without vitiating the results. However, if as much as a few hundredths of a milligram of iron is present, a separa-

tion is necessary regardless of the ratio, since the combined iron and aluminum lakes will give a solution which is too deeply colored for accurate comparison. A fairly rapid procedure for the separation of iron from aluminum has been described with which results have been obtained by the "Aluminon" method for several samples of water that agree closely with the values for the aluminum content found by the longer and more tedious gravimetric method.

With a colorimeter of the Kennicott-Campbell-Hurley type, quantities of aluminum less than 0.01 mg. in 50 cc. of comparison solution do not yield a coloration sufficiently intense for accurate comparison; and with amounts of the order of 0.5 mg. in 50 cc., a volume of less than 50 cc. must be used in the colorimeter. When 50cc. Nessler tubes are employed, the lower limit of the test is 0.002 mg. The lake is stable, that is, it does not coagulate until after 40-60 minutes when 2 cc. of ammonium hydroxide is used with 1 mg. of aluminum present in 50cc. of solution. With the higher concentrations of aluminum the lake may be stabilized by using starch as a protective colloid; thus, by using a type of colorimeter with which very small volumes of solutions can be compared the range can be extended to cover the more concentrated solutions.

A series of interesting papers on "Variable Sensitiveness in Colorimetry" have been published by Horn⁹ and by Horn and Blake.¹⁰ For convenience the sensitiveness is defined as the reciprocal of the weight in milligrams of the colored solute which is necessary to produce a difference in intensity in 50 cc. of solution that is just perceptible with certainty. These authors made a series of measurements with several colored salts over wide ranges of dilution in order to determine the way in which the sensitiveness varies with the total concentration of the colored solute. In connection with their study on copper sulfate solutions, the following conclusions were reached:

"1. The amount of copper that will produce, at different concentrations, a difference in color that can be just distinguished is not a constant weight, but is a constant fraction of the total weight of copper present. Exceptions occur when the solutions are too dilute or too concentrated."

Symbolically, Δ/B' is a constant.

"2. Whenever the difference in color between copper solutions is estimated as just perceptible, the ratio between the two quantities of copper in the solutions compared is always the same.

"3. The sensitiveness varies inversely as the total copper. $BS = B_1S_1 = B_2S_2 = \text{a constant.}$ "

In application to colorimetric analysis, it is suggested that, "every colorimetric method has at least one maximum of sensitiveness;" that

⁹ Horn, *Am. Chem. J.*, **35**, 253 (1906).

¹⁰ Horn and Blake, *ibid.*, **36**, 195, 516 (1906).

the best working range for a colorimetric method is that over which the ratio Δ/B' is constant; that the percentage error is the same for all concentrations within this range; and that on the basis of the psychophysical law known as Weber's Law, these relations are generally true throughout colorimetry.

The sensitivity curve for aluminum is shown in Fig. 7. This curve manifests a change in slope in the vicinity which corresponds to an aluminum concentration of 0.1 mg., and, in the light of the statements above, this is the upper limit of the range in which Δ/B' is constant. For comparison, the values for the ratios Δ/B' and B/B' found by Horn and those obtained for aluminum are given below.

| | CrO ₄ ⁻⁻ | Cu ⁺⁺ | [Cu(NH ₃) ₄] ⁺⁺ | Aluminum-lake |
|-------------|--------------------------------|------------------|--|---------------|
| Δ/B' | 0.08 ^a | 0.09 | 0.056 | 0.083 |
| B/B' | .7 ^a | .92 | .95 | .92 |

^a Calculated from Horn's data, Ref. 9.

Summary

An experimental study of the new reagent for aluminum, the ammonium salt of aurintricarboxylic acid, has been made and quantitative measurements of the effects of the following variables were obtained: (1) time, (2) temperature, (3) volume, (4) concentration of reagents and (5) the presence of other ions.

The range of the test has been determined for colorimetric work and a means of extending the range so as to include higher aluminum concentrations has been found. The sensitiveness of the test has also been determined.

Based upon the results of the experimental study, a quantitative method for the colorimetric determination of aluminum by the ammonium salt of aurintricarboxylic acid has been developed and applied to the direct determination of aluminum in potable water.

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