THE COLORIMETRIC DETERMINATION OF ACETYLENE.

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1. Introduction.

In the course of experiments on the qualitative detection of small amounts of water[2] it was found that the addition of alcohol or acetone containing dissolved acetylene to a solution of curpous chloride, or the absorption of acetylene in a cuprous chloride solution containing alcohol or acetone, resulted in the formation of a clear colloidal solution of an intense red color. The formation of a red colloid when a small amount of curpous chloride is added to a solution of acetylene in water was observed by Küspert,[3] but no attempt to use the reaction for analytical purposes appears to have been made by him or others. Since the reaction appeared to present possibilities as a direct colorimetric method for the determination of water, an effort was made to apply it for this purpose. The results first obtained were very discordant and it soon became apparent that a careful examination of all the factors which could affect the results would be necessary before any satisfactory procedure could be devised. The investigation of these factors has resulted in the development of a quick and very sensitive method for the determination of acetylene. The application of this method to the determination of water, especially the determination of very small amounts in materials of high purity which was the primary object of the investigation, has been much less successful; some of the difficulties encountered will be described in the latter part of the paper (p. 359).

The formation and properties of a colloidal solution are influenced by so many factors that more than five hundred experiments were required to determine the effect of each factor and to devise a method which will give uniform results.

Lack of space prevents the publication, here, of more than an outline of the experimental work; but a more complete account will soon be published as a Scientific Paper of the Bureau of Standards.

2. Development of Method.

The method was developed by the preparation of colloidal solutions from known amounts of acetylene, secured by measuring from any ordinary buret into a distilling flask a standard solution of acetylene in ether.

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[1] Published by permission of the Director of the Bureau of Standards.

[2] This Journal, 36, 2462–8 (1914).

[3] *Z. anorg. Chem.*, 34, 453–4 (1903).

The use of such a solution seemed especially desirable since it eliminated the variables affecting the amount of acetylene evolved from a constant weight of water when reacting with calcium carbide, and at the same time permitted an exact duplication of the conditions which appeared to be most favorable for the quantitative evolution and determination of acetylene from small amounts of water, *i. e.*, solution in ether with subsequent distillation, in a stream of hydrogen, into the absorbing solution. This made the results applicable in the investigation of the water method itself.

The standard solution of acetylene in ether was prepared by passing into 500 cc. of ether, for several minutes, a stream of acetylene which was generated from specially prepared calcium carbide and washed with water. The solution was then diluted with ether sufficiently for use. The carbide used was prepared for this purpose by Dr. C. W. Kanolt, of this Bureau from pure precipitated calcium carbonate and a considerable excess of sugar charcoal. The solution of acetylene in ether was standardized gravimetrically by precipitation with ammoniacal cuprous chloride and subsequent determination of copper in the precipitate. In making this determination, it was found absolutely necessary to exclude air fron the apparatus in which the precipitate is produced and washed. Otherwise part of the copper goes into solution. This precaution is ignored in most, if not all, of the published methods for making this determination.

The influence of the variable factors affecting the formation of the colloidal solution was investigated by absorbing definite amounts of acetylene, from measured volumes of the standard solution, in 30 cc. of absorbing solution. After the absorption was completed this solution was diluted to 100 cc. before comparing with a color standard in a colorimeter of simple construction From a consideration of the results of these experiments the following method was chosen. The necessary directions are given in italics. Comments are given in the ordinary type.

3. Procedure for the Determination of Acetylene.

(*a*) **Preparation of Absorbing Solution.**—*Dissolve 0.25 g. of gelatin in hot water, dilute to 500 cc., and add 500 cc. of 95% alcohol and 1.25 g. of hydroxylamine hydrochloride. To 20 cc. of this solution add 10 cc. of concentrated ammonium hydroxide and a small amount of curpous chloride.* One- or two-hundredths of a gram of cuprous chloride is all that is required although as much as half a gram is not objectionable. If a greater amount of solution is required to fill the absorption apparatus it should be made up in the same proportions.

Several substances have been tried as protective colloids besides gelatin, but all have been found unsuitable. More than the above amount of gelatin is not required and much more is objectionable, since it may be precipitated by the alcohol and the various salts in solution. A large amount of alcohol in the solution favors completeness of absorption and uniformity of results, but too large an amount precipitates the gelatin from solution. The amount of ammonia in solution must be regulated rather carefully. Either too little or too much ammonia results in the formation of a precipitate and in incomplete absorption. The presence of ammonium chloride or other strong electrolyte causes coagulation and erroneous results; an excess of hydroxylamine salts should be avoided for the same reason, but more than the amount given in the above directions may be used if required to completely discharge the blue color of cupric-ammonium salts. It is best, however, to add any excess of hydroxylamine necessary to decolorize, when diluting with water after absorption, rather than before; the presence of a small amount of cupric salts during the absorption does not affect the results.

(*b*) **Absorption of Acetylene.**—*The gas to be tested for acetylene should be bubbled at a moderate rate into a rather small volume of the absorbing solution through a glass tip with a small opening.* The effect of changing the volume of the absorbing solution is shown in Table I. In each case the composition of the absorbing solution was the same and the solution was diluted to 100 cc. before making the colorimetric comparison. Since these experiments were very carefully made after the effect of all other variables had been investigated, the tendency to obtain higher results when using the smaller volume of absorbing solution is probably not due to experimental error. It is believed that this effect is due to equilibrium within the solution, the significance of which will appear later.

TABLE I.—EFFECT OF VOLUME OF ABSORBING SOLUTION.

Volume of absorbing solution. cc.	Acetylene.		Difference.
	Present. Mg.	Found. Mg.	
30	0.68	0.71	+0.03
30	0.41	0.41	±0.0
30	0.54	0.55	+0.01
30	0.27	0.26	—0.01
60	0.41	0.38	—0.03
60	0.54	0.53	—0.01
60	0.27	0.24	—0.03
90	0.41	0.38	—0.03

It is important that a small tip be used for introducing the gas into the solution. In the experimental work two tips were used for this purpose, one having an internal diameter of about 2 mm. and the other a diameter of about 0.2 mm. It was found that 30 to 50% of the acetylene escaped when using the larger tip at rates of from 30 cc. to 75 cc. per minute. There was no indication of loss of acetylene when using the small tips at rates up to 50 cc. per minute, and loss of acetylene did not exceed 10% even when the rate was 100 cc. per minute.

(*c*) **Dilution and Comparison with Color Standard.**—*After the absorption of the acetylene, the colloidal solution is diluted with water to a convenient volume and compared in a colorimeter with a color standard of fixed value, which may be a fixed depth of a solution of a red dye or a piece of ruby glass. The value of the standard must be determined by previous calibration with known amounts of acetylene.* A large number of experiments have shown that, within the limit of accuracy of the colorimeter readings, it is immaterial how much the colloidal solution is diluted before the readings are taken, provided the volume of solution is taken into account in calculating the amount of acetylene. For example, if a sample of acetylene is absorbed in 30 cc. of solution and the resulting liquid successively diluted with water to 60, 90, 120 cc. and comparisons with the same color standard are made at each dilution, it will be found that the depths of colloidal solution required to match the standard are in the ratios 1 : 2 : 3 : 4.

4. Preparation and Standardization of a Color Standard.

The most satisfactory standard for use in colorimetric work is of course a solution having a known value and of the same character as the solution whose value is to be determined. Unfortunately, however, a colloidal solution of copper carbide cannot be preserved for any considerable length of time and it is quite difficult to prepare one of known value. The color of colloidal solutions prepared under different conditions varies widely, and those produced by the action of an excess of acetylene on small amounts of a copper salt cannot be compared accurately with the colloids prepared from small amounts of acetylene and an excess of the copper salt.

It is possible, however, to match the colloidal solution with a solution of red dye or a piece of ruby glass. The standard solution used for comparison in the experimental work had the following composition:

Chromanilbraun R	0.21 mg.
Carmoisine B	0.04 mg.
Gum arabic	2.5 g.
Water	100 cc.

This solution was designated on an arbitrary color scale as standard "H 25" and will, for the sake of brevity, be so designated in this discussion.

Although it is possible to match very closely any depth of a given colloidal copper carbide solution with a dye solution, such as solution "H 25," the ratio between the depths of the two solutions is not constant but varies with the depth. When comparing small depths, the color, *i. e.*, the relative amount of light of the longer and shorter wave lengths transmitted, is the determining factor in making the comparison. When a greater depth is used, practically all light except red is excluded and the point of agreement is no longer determined by the color of the two fields in the colorimeter, but by whether one field is lighter or darker than the other.

Upon plotting the results of any series of comparisons of the colloidal solutions produced by known amounts of acetylene with a fixed color standard it appears that, within the limits of experimental error, the results obtained with all lie on a straight line represented by the equation

$$x = ay + b,$$

in which x = amount of acetylene, $y = \frac{1}{\text{depth of colloidal solution}}$, and a and b are constants. In this equation b represents, of course, the point at which the curve cuts the horizontal axis and its value is that of the smallest amount of acetylene which will produce a color in the absorbing solution. The value of a is dependent upon the color standard used. Both constants must be experimentally determined.

When a variable depth of a standard solution is used for the comparison, the ratio $\frac{\text{depth of standard solution}}{\text{depth of colloidal solution}}$ may be used as the value for y and the equation $x = ay + b$ still holds, provided the ratio between the depths of the two solutions is the same for all depths. As pointed out in the preceding section, this is not the case with any of the solutions used as standards, but it may be assumed without appreciable error for amounts of acetylene not greater than 0.1–0.2 mg. For larger amounts a constant depth of standard solution should be used in order to provide a color standard of fixed value.

The value of b was at first thought to represent the minimum concentration of acetylene in the gas mixture which would be absorbed by the solution. If the existence of such a minimum were the true explanation of the fact that the curve does not pass through the origin, it is evident that a given amount of acetylene diluted with a large volume of hydrogen would give lower results than the same amount of acetylene diluted with a small volume of hydrogen. That such is not the case was clearly shown by experiments. The only other probable explanation seemed to be that there is an equilibrium in the absorbing solution and that b represents the minimum concentration of dissolved acetylene which will produce a colored colloid. If this is true the value of b should be proportional to the volume of absorbing solution. The experiments given in Table I and plotted in Fig. 1 show that this relation is at least approximately correct.

Fig. 2 shows the results of one series of comparisons of "standard solution H 25" with known amounts of acetylene from a carefully analyzed solution in ether. The equation of the straight line averaging these values is $x = 1.43\, y + 0.03$, where x is expressed in tenths of a milligram of acetylene and y is the ratio $\frac{\text{depth of standard solution}}{\text{depth of colloidal solution}}$.

Calibration of any Color Standard.—Since the value of b depends upon the volume of the absorbing solution and is independent of the color standard used, its value may be experimentally fixed once for all. This value has been carefully determined several times under different conditions and has always been found to be between 0.02 and 0.05 mg. It seems probable that, in any operations in which there is fairly complete absorption, the value of b may be assumed to be 0.03 mg. for 30 cc. of absorbing solution without causing any error in excess of 0.01 mg. In order to calibrate any color standard it is then only necessary to make one accurate comparison of the standard with a colloidal solution prepared from a known amount of acetylene. This comparison gives simultaneous values for x and y in the equation $x = ay + 0.03$, and the value of a may be easily calculated. Unknown amounts of acetylene may then be determined for the same equation, using the values already found for a and b, or, for convenience, a curve may be plotted and values taken from that.

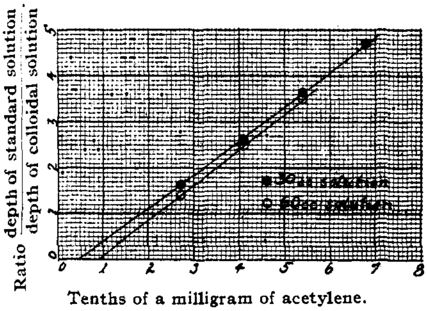

Fig. 1.—Effect of volume of absorbing solution.

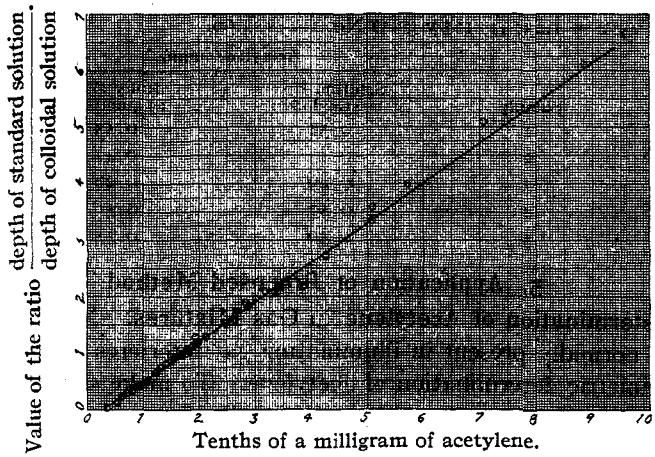

Fig. 2.—Result of one series of comparisons using "standard H 25" and known amounts of acetylene. Equation of straight line is $x = 1.43\, y + 0.3$.

Chemists who desire to make only an approximate determination without the labor of previously calibrating a standard, may do so by using as a standard a depth of 10 cm. of a solution of 0.04 g. of azolitmin in 100 cc. of water. The value of *a* for a solution of this strength made from a sample of the dye of Kahlbaum grade was found to be 0.13 mg. It is not known how much variation will be found among different samples of azolitmin; but it is apparent from the slope of a curve for azolitmin given in the complete paper, that any variation in the strength of the azolitmin or the quality of the dye will cause much less than a proportional error in the amount of acetylene found.

As a color standard, a piece of ruby glass or a glass plate covered with a film of gelatine and stained with oxamine red or other suitable dye may be used instead of a solution. Once having calibrated the standard as described above, the same results are obtained no matter what standard is used, provided the two colors are enough alike to permit an accurate comparison and the standard does not change. A ruby glass is, of course, permanent, but the author is unable to say how much reliance may be placed in the permanence of color of a stained film.

Table II gives the results of a series of determinations of unknown amounts of acetylene using two different standards for comparison. The results are in substantial agreement.

TABLE II.

Determination of unknown amounts of acetylene, using as standards: (1) 10 cm. solution H 25 $a = 1.43$; (2) ruby glass No. 1 $a = 3.69$.

	Acetylene found.	
Sample.	Solution H_{25} as standard.	Ruby glass as standard.
1	0.51	0.55
2	0.43	0.41
3	0.29	0.28
4	0.57	0.56
5	0.56	0.55

5. Application of Proposed Method.

(*a*) **Determination of Acetylene in Gas Mixtures.**—None of the constituents normally present in illuminating gas interferes in any way with the colorimetric determination of acetylene. To make such a determination it is only necessary to pass a measured volume (0.5–2 liters) of the gas into the absorbing solution and make the colorimetric comparison. The whole determination can be made in about ten minutes. Four successive determinations of the acetylene in illuminating gas taken directly from the house piping gave 0.30, 0.30, 0.32 and 0.33 cc. per liter. The method was applied by Mr. J. D. Edwards in this laboratory to the testing of hydrogen of high purity. One part of the acetylene was readily determined in 250,000 parts of the hydrogen from one source. Hydrogen from another source, believed to contain only a small fraction of this amount of acetylene, produced a red stain on the tip of the inlet tube in the absorbing solution, but no coloration in the liquid.

In order to ascertain whether acetylene could be determined in air by this method, a sample of the acetylene solution in ether was first run in the usual manner with a stream of hydrogen to carry it into the absorber; then the determination was repeated with the same amount of acetylene and a stream of air instead of hydrogen. The acetylene-air mixture was passed through a strongly alkaline solution of pyrogallol and thence into the absorber; and the pyrogallol solution was heated to boiling before the stream of air was stopped. When hydrogen was used the test showed 0.56 mg. of acetylene; with air 0.53 mg. of acetylene was found.

The experiment also proved that a solution of potassium hydroxide could be used if necessary to remove hydrogen sulfide, carbon dioxide, or similar interfering gases. It was found by several experiments that small amounts of carbon dioxide did not affect the determination, but that larger amounts had the same effect as the introduction of a small amount of a strong electrolyte into the solution. The color of the colloid produced by acetylene carried over in a stream of pure carbon dioxide was too brown to admit of any accurate comparison.

(*b*) **Determination of Water.**—The determination of small amounts of water by the colorimetric method, which was the primary object of this investigation, presents several difficulties which are nearly insurmountable.

Efforts were made to determine water in a variety of materials by the use of the apparatus described below. The sample to be tested was brought into contact with calcium carbide, in a small glass apparatus, either with or without anhydrous ether to act as a solvent. The flask in which the reaction took place was connected to a condenser and thence to a tube filled with carbide to prevent the escape of water vapor. Ether dried over sodium could be introduced directly or could be distilled through a phosphorus pentoxide tube into the reaction flask. The whole apparatus could be swept out with hydrogen dried over phosphorus pentoxide.

The greatest difficulty encountered is due to the fact that calcium carbide itself, or the calcium hydroxide which it always contains, appears to occlude acetylene, which it holds with great tenacity but gives off slowly for long periods. It may be that the source of trouble is a small amount of water which is held by the calcium hydroxide and which reacts with the carbide very slowly. Whatever the exact cause, there is no question that with any carbide obtainable commercially all efforts to remove this acetylene by ignition or evacuation have proven unsuccessful. The acetylene which causes the trouble may be removed by boiling the carbide two or three times with an anhydrous liquid such as ether. After such treatment the carbide must not be exposed to the air even for an instant. After the reaction between the carbide and the sample being tested for water is finished, it is necessary to remove the acetylene produced in the same way as before the test. It is apparent that a considerable amount of ether is required for the two purposes and that a large volume of hydrogen is required to sweep out the apparatus completely. It has been found almost impossible to dry ether so thoroughly that the amount required by this test will produce no acetylene which can be detected. Even the ether from a bottle entirely filled with a loose mass of sodium wire which remains apparently perfectly bright may produce a surprising amount of acetylene, and phosphorus pentoxide appears to lose very quickly its power to remove the water completely from ether vapor. It is consequently very difficult to secure consistent blanks.

A second source of difficulty, which has been recognized by every chemist who has used the carbide method for the determination of water, is the fact that the theoretical amount of acetylene is never produced from a known quantity of water. This is particularly true when dealing with very small amounts of water. In the author's experiments the amount of acetylene produced has varied from 50–80% of the theoretical, generally approaching the latter figure.

In consequence of these sources of difficulty and error, tests made with the colorimeter have little more significance than the much simpler qualitative tests described in an earlier paper.[1] A negative test is quite conclusive, but the detection of an amount of acetylene less than 0.1 mg. has little more than qualitative significance.

Negative tests have shown that the standard samples of benzoic acid, naphthalene and sugar issued by this Bureau are almost absolutely anhydrous. As an example of the kind of results which may be expected when water is present, the following tests are given of a sample of alcohol in which Mr. E. C. McKelvy, of this Bureau, had determined the amount of water by the method of critical solution temperature.[2]

TABLE III.—DETERMINATION OF WATER IN ALCOHOL.

Found by critical solution temperatures. Water = A. Mg.	Found by colorimetric method.		
	Acetylene. Mg.	Water = B. Mg.	B × 100/A.
1.0	0.48	0.62	62
1.0	0.58	0.80	80
6.0	3.5	4.8	80
6.0	3.6	5.0	82
50	21.2[3]	29.2	59

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[1] THIS JOURNAL, 36, 2462–8 (1914).

[2] *Bull. Bur. Standards*, 9, p. 344.

[3] Acetylene determined gravimetrically.

6. Summary.

A colorimetric method for the detection of small amounts of acetylene has been developed in the course of an investigation upon the determination of small amounts of water by the use of calcium carbide. The results upon the determination of water have not been satisfactory, but the method for acetylene has been worked out successfully.

The determination is carried out by conducting the gas to be investigated into an ammoniacal solution of cuprous chloride containing gelatin and alcohol, and comparing the red colloidal solution so obtained with a suitable standard, which may be either a solution of red dye or a piece of ruby glass.

After a careful investigation of the effect of varying the composition of the absorbing solution, the following procedure was adopted in making up the solution: Dissolve 0.25 g. of gelatin in hot water, dilute to 500 cc., and add 500 cc. of 95% alcohol and 1.25 g. of hydroxylamine hydrochloride. To 20 cc. of this solution add 10 cc. of concentrated ammonium hydroxide and a small amount of cuprous chloride. After the absorption of the acetylene, the solution is diluted to 100 cc. and compared in a colorimeter with the standard which has been chosen. The standard used in the experimental work was a solution containing chromanilbraun R, carmoisine B and gum arabic. A more convenient, though less accurate, standard is a fixed depth of a solution of azolitmin. If 10 cm. of a solution of azolitmin containing 1 part of the dye to 2500 parts of water is used as standard, the amount of acetylene in 100 cc. of colloidal solution may be calculated from the equation $x = 0.13\,y + 0.03$, where x = no. of milligrams of acetylene and $y = 1 \div$ no. of centimeters of colloidal solution required to match the standard.

The method is very sensitive. Amounts of acetylene as small as 0.03 mg. may be detected and amounts up to 2 mg. determined with an accuracy of better than 0.05 mg. Several applications of the method are described.

Hydrogen sulfide, and large amounts of oxygen and carbon dioxide interfere with the test, but all of these may be removed by passing the gas to be tested through a hot alkaline solution of pyrogallol without loss of acetylene.

The investigation required some experiments upon the determination of larger amounts of acetylene by precipitation with cuprous chloride and subsequent determinations of the copper. It was found that in order to obtain accurate results by this method it is absolutely necessary to carry out the filtration and washing of the precipitate in the absence of air.

WASHINGTON, D. C.