which fact, as well as the low results, must be attributed to causes other than the influence of strong acids on hexamethylenetetramine.

(5) Paraformaldehyde, when present, counts as formaldehyde.

(6) The discrepancy in the results obtained by the two different types of methods is due to conditions inherent in the methods themselves—not to the presence of impurities or to a polymerized form of formaldehyde. Apparently, either the condensation reactions are not complete, or a small part of the formic acid, produced by the oxidation reactions is oxidized farther, giving high results.

QUANTITATIVE LABORATORY,
March 1, 1905.

## A COLORIMETRIC METHOD FOR THE DETECTION AND ESTIMATION OF FORMALDEHYDE.

BY FREDERIC BONNET, JR.

Received February 23, 1905.

IT HAS been pointed out[1] that certain alkaloids give very characteristic color reactions with formaldehyde. A closer investigation of this subject has shown that these reactions can be applied not only to the qualitative detection, but also, in some cases, to the quantitative estimation of formaldehyde.

If a substance containing formaldehyde is placed in an evaporating dish and 1 cc. of a freshly prepared sulphuric acid solution of morphine in a watch-glass is floated or placed upon it, the morphine solution becomes more or less colored, varying from pink to dark blue, according to the amount of formaldehyde present. The coloration is due to the vapor of the formaldehyde, which reacts with the morphine. By this method so small an amount as 4 parts of formaldehyde in 1,000,000 can be detected.

The morphine sulphate solution is made by dissolving 0.35 gram of white crystalline morphine sulphate in 100 cc. of cold, strong, chemically pure sulphuric acid (sp. gr. 1.84). Unfortunately, this solution does not keep any great length of time, as the sulphuric acid slowly decomposes the morphine, even at ordinary temperatures.[2] The following tests were made, therefore, with fresh solutions.

[1] Grünhut: *Z. anal. Chem.*, **39**, 329 (1900).

[2] Allen's "Commercial Organic Analysis," **8**, 314 (1892).

MILK.

About 60 cc. of milk, containing a known amount of formaldehyde, were placed in a 3-inch evaporating dish; and 1 cc. of the morphine solution was floated upon the surface by means of a 1 inch watch-glass. The dish was then immediately covered with a 4 x 5 inch glass plate. The results are given below.

TABLE I.—TEMPERATURE 20° C.

| No. | Containing $CH_2O$. | Remarks. |
|---|---|---|
| 1 | Pure milk | No coloration after 3 hours. |
| 2 | 4 : 100 | Coloration appeared in a few minutes, which soon turned black. |
| 3 | 4 : 1,000 | Coloration appeared in a few minutes. Upon standing it also turned black. |
| 4 | 8 : 10,000 | Good ring colorating after about 8 minutes. |
| 5 | 4 : 10,000 | " " " " " 15 " |
| 6 | 8 : 100,000 | Fairly good ring coloration in about 45 minutes. |
| 7 | 4 : 100,000 | " " " " " " 1 hour. |
| 8 | 8 : 1,000,000 | Slight coloration throughout, in about $1\frac{3}{4}$ hours. |
| 9 | 4 : 1,000,000 | " " " " " $2\frac{1}{2}$ " |

In the following experiment an attempt was made to determine the time of formation of the first definite ring or color:

TABLE II.—TEMPERATURE 12° C.

| No. | Containing $CH_2O$. | Remarks. | |
|---|---|---|---|
| 1 | Pure milk | No coloration after 9 hours. | |
| 2 | 4 : 100 | Definite ring in about 4 min. | Black in 15 min. |
| 3 | 8 : 1,000 | " " " " 5 " | |
| 4 | 4 : 1,000 | " " " " $6\frac{1}{2}$ " | Blue black in 30 minutes. |
| 5 | 8 : 10,000 | " " " " 10 " | |
| 6 | 4 : 10,000 | " " " " 16 " | Pink then brown. |
| 7 | 8 : 100,000 | " " " " 50 " | |
| 8 | 4 : 100,000 | " color in about 2 hours. | |
| 9 | 8 : 1,000,000 | Slight " " " 4 " | |
| 10 | 4 : 1,000,000 | Practically no color after 9 hours. | |

Comparison of the two tables shows that the temperature is an important factor when testing for very small amounts of formaldehyde. About 20° was found to be the most convenient and serviceable temperature for making the test.

To determine whether formaldehyde could still be detected by the morphine reaction, in milk which had undergone decomposition, the solutions of Table I were allowed to stand one week at

room temperature (± 18° C.) in tightly stoppered bottles. At the end of this time they were again tested.

TABLE III.—TEMPERATURE 20° C.

| No. | Containing $CH_2O$. | Condition of milk. | Remarks. |
|---|---|---|---|
| 1 | None | Spoiled after about 12 hrs. | No coloration after 4 hrs |
| 2 | 4 : 100 | Good | Coloration in a few min. |
| 3 | 4 : 1,000 | Good | Coloration in a few min. |
| 4 | 8 : 10,000 | Good | Good ring coloration. |
| 5 | 4 : 10,000 | Good | " " " |
| 6 | 8 : 100,000 | Spoiled on 6th day. | Fairly good ring coloration. |
| 7 | 4 : 100,000 | Spoiled on 3rd day. | Fairly good ring coloration. |
| 8 | 8 : 1,000,000 | Spoiled on 2nd day | Slight coloration |
| 9 | 4 : 1,000,000 | Spoiled after about 12 hrs. | Practically no coloration. |

The results in Table III show that the morphine test is applicable even when the milk has undergone decomposition.

BUTTER.

The morphine test was also tried with butter. Fresh butter, free from preservatives, was worked up for fifteen minutes in an aqueous solution containing 4 parts of formaldehyde to 100 of water. After pouring off the solution the butter was rolled into a ball. Similar sized lumps of butter were treated in the same way with solutions containing 4 : 1,000 and 4 : 10,000. The balls, allowed to air-dry uncovered for eighteen hours, were flattened on the bottoms of 3-inch evaporating dishes and the tests made as with the milk. In this case small porcelain crucibles were used for the morphine solution.

TABLE IV.—TEMPERATURE 18° C.

| No. | Solutions containing $CH_2O$. | Remarks. |
|---|---|---|
| 1 | Pure Butter | No coloration. |
| 2 | 4 : 100 | Coloration in a few min. |
| 3 | 4 : 1,000 | " " " " |
| 4 | 4 : 10,000 | " " 15 min. |

The above butter, after standing in a warm place for one week, gave the following results:

TABLE V.—TEMPERATURE 18°.

| No. | Solutions containing $CH_2O$. | Condition of butter. | Remarks. |
|---|---|---|---|
| 1 | None | Decomposed | No color |
| 2 | 4 : 100 | Good | Coloration in few min. |
| 3 | 4 : 1,000 | Good | Coloration strong |
| 4 | 4 : 10,000 | Slightly decomposed | Coloration |

Since the test depends solely upon the composition of the vapor above a liquid or moist surface, only those substances can interfere which have appreciable vapor pressures and which react with the morphine solution.

Salicylic acid, benzoic acid and hydrogen peroxide, the common preservatives of this nature were tested and gave no reaction. Various other substances were tested in this connection from time to time and very few gave any color reactions whatever. Thus, acetone, ethyl ether, ethyl alcohol, chloralhydrate, chloroform, formic acid, furfural, carbon bisulphide, gave no reaction, while methyl alcohol, acetaldehyde and acrolein, in strong pungent solutions, gave pale brownish and benzaldehyde, and fusel oil light yellow colorations, all of which are very different from the characteristic formaldehyde test.

## QUANTITATIVE ESTIMATION.

Experiments to determine whether the foregoing test could be applied quantitatively were made as follows:

A standard solution of milk was made by dissolving 11 cc. of a Kahlbaum solution containing 34 per cent. by weight[1] of formaldehyde in 100 cc. of milk, giving a solution of 4 : 100. From this, solutions containing 8 : 1,000, 4 : 1,000, 8 : 10,000, 4 : 10,000, 8 : 100,000, 4 : 100,000, 8 : 1,000,000, and 4 : 1,000,000 were made by adding the required amount of milk.

Samples of milk containing varying amounts of formaldehyde were then prepared, the amount in each being unknown, for the the time being, to the experimenter. Sixty cc. of each of these samples were placed in evaporating dishes and tested as in the qualitative trials. The approximate time of the first ring or color formation gave an idea (as is shown by Table II) of the amount of formaldehyde present. Knowing approximately the amount of formaldehyde in solution, fresh portions of the unknown milk were compared with the corresponding standard solutions, care being taken that the tests were started at the same time and were made under like conditions.

In each of the above prepared unknown samples the amount of formaldehyde found was essentially the same as that which had been put into the solution. Over a range extending from 8 : 1,000 to 8 : 1,000,000, solutions containing the same amounts of formal-

[1] *Z. anal. Chem.*, **44**, 13 (1905); also. This Journal, **25**, 1028 (1903).

dehyde gave the same characteristic coloration in the same period of time. It is necessary for accurate work that equal amounts of the unknown and known solutions be taken, and that the amounts of the morphine solution used should be the same; also the evaporating dishes and the watch-glasses should be alike both in size and shape.

SUMMARY.

This method gives not only a simple means of detecting formaldehyde, but in the case of liquids allows of its estimation. It is applicable when the formaldehyde is present with a great variety of substances and can be adapted with almost equal facility to both liquid and solid products.

In conclusion I wish to thank Dr. L. W. Andrews for his kind suggestions.

WORCESTER POLYTECHNIC INSTITUTE,
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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 105.]

# THE INFLUENCE OF ATMOSPHERIC OXIDATION UPON THE ANALYTICAL CONSTANTS OF FATTY OILS.

(SECOND PAPER.)

BY H. C. SHERMAN AND M. J. FALK.

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IT HAS been shown[1] that non-drying and semi-drying oils, on exposure to air, undergo changes similar to those which take place when the corresponding fatty acids are treated with potassium permanganate in alkaline solution, oleic acid being apparently converted into dioxystearic, and linoleic into sativic acid. The "oxidation," therefore, appears to result mainly in the addition of hydroxyl groups, two of these groups taking the place which, in the determination of the iodine number, would have been taken by two halogen atoms. If, as stated by Ballantyne,[2] atmospheric oxidation causes no change in the volume of the oil, the increase in specific gravity and the decrease in iodine absorbing power are to each other as the weight of the hydroxyl group is to that

[1] This Journal, **25**, 711 (1903).
[2] *J. Soc. Chem. Ind.*, **10**, 29 (1891).