Halphen test, was unable to detect phytosterol, although the presence of phytosterol was easily recognized when only 2 to 3 per cent. of cottonseed oil was added. The crystals from these lards were all true cholesterol forms, and gave the correct melting-point when treated with acetic anhydride and purified.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, NO. 104.]

A STUDY OF METHODS FOR THE DETERMINATION OF FORMALDEHYDE.

BY R. H. WILLIAMS.

Received March 9, 1905.

THE work herein described consists of a comparison and criticism of the four methods most generally recommended for the determination of formaldehyde—Legler method,[1] hydrogen peroxide method,[2] iodimetric method,[3] and potassium cyanide method.[4] Having no means of obtaining formaldehyde in a pure, anhydrous state it became necessary to study the accuracy of these methods by indirect and comparative, rather than by direct and absolute tests. First, the conditions usually given for these methods were followed, and then such modifications tried as were believed to give increased accuracy or greater rapidity, the ultimate object being to determine, if possible, the best conditions for each method, and then to form a judgment as to their comparative merit.

Legler Method.—The conditions maintained were essentially those given by Smith.[5] Thirty determinations of formaldehyde were made under these conditions variously modified, and the results obtained established the following facts: That the best end point is obtained when a rather dilute solution of formaldehyde is taken, and N/5 reagents are used. That it is best to carry on the reaction in small flasks or bottles, thus minimizing the free space over the reacting liquids. That, after standing twenty-four hours, the maximum absorption takes place when the excess of ammonia is 1 cc. or more, and when the concentration of the

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[1] Legler: *Ber. chem. Ges.*, **16**, 1333.

[2] Blank and Finkenbeiner: *Ibid.*, **31**, 2979.

[3] Romijn: *Z. anal. Chem.*, **36**, 18-24.

[4] *Ibid.*

[5] This Journal, **25**, 1028.

same is not less than N/8. The results from six additional determinations, made in a solution of formaldehyde of approximately 2 per cent., and calculated on the original solution, are as follows:

	Per cent.	Per cent.	Per cent.
After standing 24 hours	34.76	34.84	34.88
" " 48 "	34.96	34.82	.....
" " 9 days	34.95	.....	.....

Six determinations were made, using 2 to 3 grams of the original solution (Kahlbaum's formaldehyde) in each case. The results are: 34.75, 35.06, 34.99, 35.02, 34.90, 34.63 per cent.

While the results are in accord with those previously obtained, the end-point was not as satisfactory as when the more dliute solution was used, which accounts for the greater variation in the results.

The best conditions for this method, are as follows: Weigh into a 250 cc. glass stoppered flask, 15 grams of the commercial formalin, and dilute to the mark. This solution will contain approximately 2 per cent. of formaldehyde. After determining its acidity in terms of the standard ammonia, place 10 cc. in a small bottle or flask, provided with a well-fitting stopper, and add 40 to 50 cc. of N/5 ammonia solution. Allow to stand for twenty-four hours, then titrate the excess of ammonia with N/5 acid, sulphuric or hydrochloric, using not more than 2 drops of 0.1 per cent. rosolic acid solution as indicator.

Hydrogen Peroxide Method.—The first determinations were made under the conditions given by Smith[1] with these modifications,—about 2 grams of Kahlbaum's formaldehyde were taken, while the concentrations of the acid and alkaline solutions were respectively normal and 1½ normal. Low results were obtained, due, no doubt, to the rather unusual temperature conditions, and the less concentrated alkaline reagent. The temperature of the room in which this work was done rarely exceeded 15° C., and under these conditions, the time usually allowed the reaction, (ten to fifteen minutes), was not sufficient to insure complete oxidation.

Four additional determinations were made, and in each case, the flasks were well shaken several times, and allowed to stand until the escape of gas practically ceased. The time required was

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[1] *Loc. cit.*

about one hour. The results are: 35.82, 35.92, 35.74, 35.78 per cent.

The best conditions for this method are as follows: Weigh portions of 2 grams each of formalin in 250 cc. Erlenmeyer glass-stoppered flasks, and add to each 30-40 cc. standard sodium hydroxide, 1 to 2 normal, preferably normal. Add cautiously from a pipette, 50 cc. of hydrogen peroxide solution. Shake at intervals of three to five mintues for fifteen minutes to one hour, depending upon temperature and concentration of reagents, then titrate the excess of sodium hydroxide with sulphuric acid, using 8 to 12 drops of litmus as indicator. The acidity of the hydrogen peroxide and formalin must be determined, and the figures obtained enter into the calculation.

Iodimetric Method.—The conditions as given by Smith were followed. The results of six determinations are: 35.57, 35.44, 35.71, 35.70, 35.64, 35.70 per cent.

Six additional determinations were made to test the influence on the results of different amounts of iodine in excess. The results are:

5 cc. I in excess. Per cent.	25 cc. I in excess. Per cent.	35 cc. I in excess. Per cent.
35.49	35.51	35.53
35.67	35.69	35.77

Potassium Cyanide Method.—The conditions followed were essentially those given by Romijn. The only modifications were such as affected the volume and concentration of some of the reagents.

Place 15 cc. N/10 silver nitrate in a 100 cc. flask and acidify with 8 to 10 drops of 50 per cent. nitric acid. Add 10 cc. of a solution of potassium cyanide approximately N/10, dilute to the mark, mix thoroughly, and filter. Titrate 50 cc. of the filtrate with N/40 ammonium sulphocyanate for excess of silver nitrate, using 5 cc. of a saturated solution of ferric alum as indicator. From the data thus obtained, the ratio between the potassium cyanide and silver nitrate solutions can be calculated. Another portion of the N/10 silver solution, 10 to 20 cc., is acidified as before, and then added to 30 to 40 cc. of the potassium cyanide solution, which has previously been treated with 10 cc. of the formaldehyde solution (about 1 per cent.). After shaking thoroughly, the excess of the silver nitrate solution is determined in an aliquot part of the filtrate, as before. The percentage of formaldehyde may be found from the following formula:

$$\frac{\text{cc. } AgNO_3 \text{ [Equiv. to cc. of KCN absorbed]} \times 0.003 \times 100}{\text{weight of } CH_2O \text{ taken}} = \%$$

Six determinations were made, yielding the following percentages: 35.15, 35.06, 35.20, 35.01, 35.21, 35.07.

Discussion of Results.—From a review of the percentages thus far obtained, it was observed that the two oxidation methods gave closely agreeing results, and the same was true of the condensation methods, yet the former gave results a per cent. higher than the latter. It was thought that the variation might be due either to the presence of some impurity capable of oxidation, or to a polymerized form of formaldehyde, which affected unequally the two types of methods. As Kahlbaum's formaldehyde had been used exclusively in these determinations, it was thought that a set of estimations of formaldehyde made in commercial formalin, and another in paraformaldehyde, would clear up the point in question. A sample, largely paraformaldehyde, was obtained from commercial formalin, being the residual liquid after distilling off two-thirds of the original volume.

The averages of from two to ten determinations are given below.

	Methods.			
Formaldehyde used.	Legler.	H_2O_2.	Iodimetric.	KCN.
Kahlbaum's	34.87	35.82	35.66	35.12
Commercial formalin	35.06	36.14	36.15	35.24
Largely paraformaldehyde	49.45	51.00	51.24	49.76

The discrepancies between the results obtained from the oxidation and condensation methods are the same in character, whatever the nature of the sample taken. The extent of the discrepancy is greatest in the case of the largely polymerized form, which is easily explained by the increased concentration. Since the variation cannot be explained by the presence of either impurities or paraformaldehyde, it was thought that in the case of the Legler method, the low results might be due to the instability of hexamethylenetetramine in the presence of a strong acid. Should compounds of an alkaline nature arise in this way, low results would be inevitable.

Eight determinations were made, acetic acid being used to determine the excess of ammonia in four of these, and sulphuric acid in the others. The results are:

With acetic acid.		With sulphuric acid.	
34.99	34.89	34.79	34.86
34.78	34.95	34.72	34.91

It should be stated that, in all this work where the excess of ammonia was titrated with acid, the neutral point was taken to be that at which the last trace of pink disappeared. When such small quantities of rosolic acid are used, the liquid is practically colorless at this point. Had the first color change been taken as the end-point, results more nearly in accord with those of the oxidation methods would have been obtained.

The applicability of these methods to the determination of formaldehyde in the presence of other substances was studied. Tests were made with ethyl alcohol, paraldehyde, acetaldehyde, acetone and methyl alcohol, and carried out in the following manner.[1] Three drops of the substance, whose influence was to be tested, were added, with the prescribed amount of formaldehyde in each case, and the latter determined according to the conditions given. Where the substance added had no influence, the result is given as "normal," otherwise the actual percentage is given.

		Substance added.				
Method.	Formaldehyde. Per cent.	Ethyl alcohol.	Paraldehyde.	Acetaldehyde.	Acetone.	Methyl alcohol.
Legler	34.87	Normal	Normal	47.8	Normal	Normal
H_2O_2	35.82	"	"	38.6	"	"
Iodimetric	35.66	36.4	36.5	39.6	50+	36.49
KCN	35.12	Normal	Normal	35.30	Normal	Normal

CONCLUSIONS.

(1) The iodimetric method is rapid and accurate; and preferable for pure, dilute solutions.

(2) The hydrogen peroxide method is the most satisfactory for strong, impure solutions. The time necessary for a complete oxidation is widely variable, depending upon concentration and temperature.

(3) The potassium cyanide method is recommended for dilute, impure solutions. The results are lower than those obtained by the oxidation methods.

(4) The end-point in the Legler method is not satisfactory,

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[1] For previous experiments on the influence of some of these substances, see Romijn: *Z. anal. Chem.*, **36**, 18-24. Blank and Finkenbeiner: *Ber. chem. Ges.*, **31**, 2979. L. Peska: *Chem. Ztg.*, **25**, 743.

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.

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

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