

The author wishes to add some tests made upon the correctness of Herzfeld's formula for the temperature correction for raffinose:

AS APPLIED TO HYDROLYZED HALF-NORMAL CANE-SUGAR IN 100 CC.

Temperature. °C.	DILUTION.	
	Original reading.	Calculated to 20° C. normal inversion.
17.2	-17.06	-32.59
20.0	-16.32	-32.64
20.9	-16.07	-32.59
21.6	-15.93	-32.66

AS APPLIED TO MIXTURE OF 12.367 GRAMS CANE-SUGAR AND 0.657 GRAM RAFFINOSE IN 100 CC. DILUTION.

Temperature. °C.	DILUTION.	
	Original reading.	Calculated to 20° C. normal inversion.
16.4	-14.40	-27.00
20.0	-13.50	-27.00
23.0	-12.78	-26.97

It is not advisable to make the polarization at any temperature without the use of the jacketed tube.

CARO, MICHIGAN,  
April 22, 1903.

---

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, LABORATORY OF INSECTICIDES AND AGRICULTURAL WATERS, U. S. DEPT. OF AGRICULTURE, No. 52.—SENT BY H. W. WILEY.]

## A COMPARATIVE STUDY OF METHODS OF DETERMINING FORMALDEHYDE.

BY BERNARD H. SMITH.

Received June 26, 1903.

THE uses of formaldehyde have widely increased during the past few years. As a disinfectant it has come to be used in enormous quantities by health inspectors, its vapor or a dilute solution destroying many kinds of pathogenic bacteria; as a preservative it is one of the most effective and one of the most convenient to use; it is an important fungicide, the agriculturist finding it a valuable aid in combatting certain plant diseases, while as an insecticide it rids man of those insects, often more plentiful than appreciated, that choose to live in the crevices close to his food or his bed.

With the increasing use of formaldehyde, many new methods have been suggested for its quantitative determination. While some of these are rather difficult of manipulation or have other

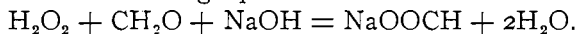
drawbacks, others are of great value. With the view of determining, if possible, which of the commonly used methods was the most accurate and which could be applied to strong and which to weak solutions with the greatest convenience, this study was undertaken.

The solutions were made up in large quantities and kept closely stoppered, the same solutions being employed in all the methods tested. The strongest of these was the commercial formalin advertised to contain 40 per cent. formaldehyde. The others contained approximately 15 per cent., 10 per cent., 5 per cent., 1 per cent.,  $\frac{1}{10}$  per cent., and  $\frac{1}{100}$  per cent. It should be stated that the last three were made up quite accurately, while the others contained somewhat less than the percentages given. The methods worked with up to the present time are as follows: The Blank and Finkenbeiner, the Legler, the gravimetric hexamethylenetetramine, the iodimetric, the potassium cyanide and the volumetric aniline method. In the following tables, Roman numerals are used to indicate the solutions, the strongest being I, the second strongest II, and so on to VII.

#### THE BLANK AND FINKENBEINER METHOD.<sup>1</sup>

This method is as follows:

About 3 grams of the formaldehyde solution are weighed into a flask containing 25 cc. of double normal sodium hydroxide. Then 50 cc. of hydrogen peroxide of approximately 3 per cent. strength is added cautiously, the addition lasting three minutes. The hydrogen peroxide oxidizes the formaldehyde to formic acid, which in turn is neutralized by the sodium hydroxide present, as shown in the following equation:



The excess of alkali is titrated with twice normal sulphuric acid, using litmus as indicator.

The following results were obtained:

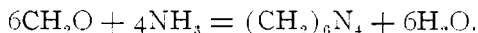
I. Per cent.	II. Per cent.	III. Per cent.	IV. Per cent.	V. Per cent.	VI. Per cent.	VII. Per cent.
37.28	14.43	9.74	4.86	1.02	...	...
37.27	14.45	9.80	4.81	1.01	...	...
37.33	14.48	9.67	4.75	1.05	...	...

It is important that a few minutes should elapse after the addition of the hydrogen peroxide for the titration.

<sup>1</sup> *Ber. d. chem. Ges.*, 31, 17, 2979 (1898).

THE LEGLER METHOD.<sup>1</sup>

A definite quantity of the formaldehyde solution is placed in a flask containing more normal ammonia than is required for the formation of the corresponding hexamethylenetetramine, which is formed as follows:



After standing, the excess of ammonia is titrated back, using rosolic acid as indicator.

Results were obtained with this method as follows:

I.	II.	III.	IV.	V.	VI.	VII.
Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
36.99	14.44	9.62	4.55	...	...	...
37.08	14.50	9.72	4.42	...	...	...
37.14	14.40	9.82	4.33	...	...	...

Concordant results were hard to obtain with solutions of less than 5 per cent. in strength, though with the stronger solutions the results were very good. Care must be exercised to prevent loss of ammonia and the end-point is rather unsatisfactory. In this work, the determinations were allowed to stand twenty-four hours, which gives practically identical results with the one-hour boiling modification used by Craig.<sup>2</sup> The boiling and cooling scheme suggested by the latter largely offsets the strongest advantage of the method, that of ease of manipulation. In the comparison of this method with that of Blank and Finkenbeiner's in the same article, the Legler method is shown to give slightly higher results. Though the two methods are in "practical accord" as he suggests, in the writer's comparisons the hydrogen peroxide method almost invariably gave higher results.

THE GRAVIMETRIC HEXAMETHYLENETETRAMINE METHOD.<sup>3</sup>

"Ten grams of the formaldehyde solution are weighed into a flask and treated with an excess of standard ammonium hydroxide solution. The corked flask is shaken at intervals for several days. By this means the whole of the formaldehyde is converted into hexamethylenetetramine. The solution is then transferred to a weighed platinum dish, evaporated at a low heat—below 100° C., nearly to dryness, and the drying finished in a desiccator."

<sup>1</sup> *Ber. d. chem. Ges.*, 16, 1333 (1883).

<sup>2</sup> *This Journal*, 23, 638 (1901).

<sup>3</sup> Annual Report, Conn. Expt. Station, 1899, p. 145.

Haywood<sup>1</sup> has recently shown that this method is unsatisfactory, owing to the fact that there is a continual loss of weight of the hexamethylenetetramine when left in the desiccator. The following determination, made on Solution I, is typical of the results obtained by the author. After evaporating nearly to dryness, the dish was placed in a desiccator and weighed at intervals of forty-eight hours, the weights obtained giving the following percentages of formaldehyde:

Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
41.83	40.34	39.46	38.70	38.02	37.40	36.87
36.35	35.91	35.60	35.24	34.90	....	....

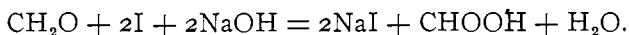
The weighing was here discontinued, as the last figures are obviously below the percentage of formaldehyde contained in the solution.

#### IODIMETRIC METHOD.<sup>2</sup>

The method used is a slight modification of the one originally proposed by Romijn,<sup>3</sup> and is as follows:

"Thirty cc. normal sodium hydroxide and 5 cc. of the dilute formaldehyde solution are placed in a well-stoppered bottle and N/5 iodine (40 to 70 cc.) added until the liquid becomes yellow. After shaking for a minute, the liquid is acidified with 40 cc. of normal acid and the residual iodine titrated with N/10 thiosulphate. A blank titration should be made."

In the presence of an alkali, iodine acts indirectly as an oxidizing agent, giving, when formaldehyde is present, the iodide of the base and formic acid. The following equation illustrates the reaction:



A solution containing as much as 5 per cent. formaldehyde may be determined without dilution by this method, provided that not more than 2 grams of the solution are used. In the following table, weighed portions of the three strongest solutions were diluted to contain approximately 1 per cent. of formaldehyde and the diluted solutions were used for the analysis.

<sup>1</sup> Bulletin No. 73, Bureau of Chemistry, Department of Agriculture, "Report of Referee on Insecticides and Fungicides before Official Association of Agricultural Chemists," 1902.

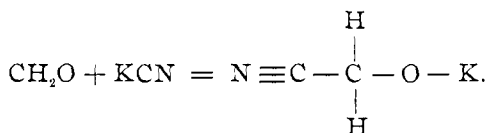
<sup>2</sup> *Ztschr. anal. Chem.*, 39, 60-63 (1900).

<sup>3</sup> *Ibid.*, 36, 18-24 (1897).

I.	II.	III.	IV.	V.	VI.	VII.
Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
36.94	14.36	9.60	4.53	0.98	0.095	...
37.06	14.46	9.58	4.60	0.96	0.089	...
...	...	9.64	4.62	...	0.094	...

THE POTASSIUM CYANIDE METHOD.<sup>1</sup>

This is another method which is applicable to solutions containing but small quantities of formaldehyde. According to the originator of the method it depends upon the fact that formaldehyde combines with potassium cyanide to form an additional product, represented by the following:



In the determination, the formaldehyde is mixed with a known quantity of potassium cyanide, the latter being in excess. If this mixture is added to an excess of silver nitrate the uncombined cyanide is precipitated as silver cyanide. By using a standard silver nitrate solution and titrating the excess, we can easily calculate the amount of potassium cyanide used by the formaldehyde, and accordingly can determine the amount of formaldehyde present. The method is as follows: Ten cc. of N/10 silver nitrate are treated with six drops of 50 per cent. nitric acid in a 50 cc. flask. Ten cc. of a solution of potassium cyanide (containing 3.1 grams of KCN in 500 cc. of water) are then added and well shaken. An aliquot portion of the filtrate, say 25 cc., is titrated according to the method of Volhard with an N/10 solution of ammonium sulphocyanate for excess of silver. Another 10 cc. portion of N/10 silver nitrate is acidified with nitric acid and treated with 10 cc. of the potassium cyanide solution to which has been added a measured quantity of the dilute formaldehyde solution. The whole is made to 50 cc. and a 25 cc. filtrate from it titrated with N/10 ammonium sulphocyanate for the excess of silver, as before. The difference between these two results multiplied by 2 gives the amount of potassium cyanide that has been used by the formaldehyde in terms of N/10 ammonium sulphocyanate.

<sup>1</sup> *Ztschr. anal Chem.*, **36**, 18-24 (1897).

In obtaining the following results, all solutions containing more than 1 per cent. were diluted.

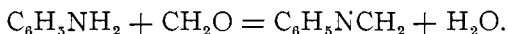
I.	II.	III.	IV.	V.	VI.	VII.
Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
37.12	14.40	9.61	4.60	1.002	0.102	0.0099
37.07	14.55	9.63	4.54	0.972	0.102	0.0099
37.18	14.48	9.59	4.64	0.99	...	...

With solutions of 1 per cent. strength it was found necessary to use 15 cc. of silver nitrate. It is preferable to add six or eight drops of nitric acid instead of two as used by Romijn, as the titration is sharper when the solution is more strongly acid. In working with Solution VII, a 200 cc. flask was used instead of the 50 cc. flask, and 100 cc. of the filtrate titrated.

Attention should be called to the fact that the directions for using this method, as given in Allen's "Commercial Organic Analysis,"<sup>1</sup> which were taken from a review that appeared in the *Analyst*,<sup>2</sup> are not explicit. The essential feature of the method being that formaldehyde forms an additional product with potassium cyanide, the formaldehyde solution must be mixed with the cyanide solution and the mixture added to the silver nitrate. This is not made clear in the article referred to. In the same translation another error is introduced in that the operator is told to dilute to 500 cc. instead of 50 cc., as in the original article.

#### THE ANILINE VOLUMETRIC METHOD.<sup>3</sup>

If formaldehyde be treated with an aqueous solution of aniline, methylene aniline is precipitated, as illustrated by the following:



Following is the method of procedure:

"Four hundred cc. of aniline solution, containing 3 grams of aniline per liter, are placed in a flask and 1 cc. of formaldehyde solution added, by drops, with shaking. The mixture is made up to 500 cc. and after some time filtered. The excess of aniline is then estimated in 50 cc., taking as the end-point that at which the red color acquires a strong bluish tone, remaining unaltered on further addition of acid."

The end-point in this titration is quite indefinite, the "bluish

<sup>1</sup> Third edition, p. 221.

<sup>2</sup> *Analyst*, 22, 221 (1897).

<sup>3</sup> *Pharm. Ztg.*, 40, 611 (1895).

tone" developing very gradually. After repeated unsuccessful trials, the attempt to use the method was abandoned.

Four of the methods are summarized in the following table, which gives the average percentages of formaldehyde found in the solutions used, and also shows the working range of each when no dilutions are made.

Method.	I. Per cent.	II. Per cent.	III. Per cent.	IV. Per cent.	V. Per cent.	VI. Per cent.	VII. Per cent.
H <sub>2</sub> O <sub>2</sub> .....	37.33	14.45	9.74	4.81	..	...	...
Legler .....	37.07	14.45	9.65	4.43	...	...	...
Iodimetric.....	...	...	...	4.5	0.97	0.093	...
Potassium cyanide .	...	...	...	...	0.988	0.102	0.0099

The following conclusions may be drawn from the comparisons made:

First, the Blank and Finkenbeiner method is very satisfactory for strong solutions.

Second, the Legler method, while not giving quite as high results as the former, is fairly satisfactory.

Third, the gravimetric hexamethylenetetramine method is practically worthless.

Fourth, the iodimetric and the potassium cyanide methods give good results on dilute solutions. It should be remembered that in diluting strong solutions to the range of these methods, a small error in weighing may be considerably multiplied. The potassium cyanide method is best adapted to the estimation of very small quantities of formaldehyde, it being possible to determine with accuracy 1 part in 100,000.

Fifth, in the hands of the writer, the end-point of the aniline volumetric method was impossible to read.

Since preparing the foregoing paper there has come to my attention an article reviewed in the *Zeitschrift für angewandte Chemie*, April 7, 1903, the original article having appeared in the *Deutsche Gerber Zeitung*, 1-4, 6, 8, 12. The author, C. Wallnitz, has compared seven commonly used methods of determining formaldehyde and has arrived at the following conclusions: That the hydrogen peroxide and the iodine methods are superior to the others tested when the reagents are freshly prepared; that the ammonium chloride<sup>1</sup> method, the Legler ammonium method,

<sup>1</sup> Hugo Schiff: *Chem. Ztg.*, 27, 14, Jan. 7, 1903.

and the aniline volumetric method all lack distinctness in the end-point readings; and further, that the gravimetric silver nitrate method of L. Vanino is practically useless, not being exact in its results.

The potassium cyanide method, which is one of the most accurate, was not included in this investigation.

## BIBLIOGRAPHY.

- Ber. d. chem. Ges.*, 16, 1335 (1883).  
*Compt. Rend.*, 120, 449 (1887).  
*Ber. d. chem. Ges.*, 22, 1565-1929 (1889).  
*Ibid.*, 24, 576 (1891).  
*Ztschr. anal. Chem.*, 31, 348 (1892).  
*Ber. d. chem. Ges.*, 26, 415 (1893).  
*Pharm. Ztg.*, 40, 611 (1895).  
*Ztschr. anal. Chem.*, 34, 623 (1895).  
*Ibid.*, 35, 116, (1896).  
*Archiv. Pharm.*, 234, 634 (1896).  
*Analyst*, 21, 94, 148 (1896).  
*Ztschr. anal. Chem.*, 36, 18, 527, 717 (1897).  
*Analyst*, 22, 4, 5, 221 (1897).  
*Bull. Soc. Chim.*, 17, 839 (1897).  
*Ber. d. chem. Ges.*, 31, 2979 (1898).  
*Am. J. Pharm.*, 70, 86, 432 (1898).  
Annual Report Conn. Expt. Sta., 1899, p. 143.  
*Ber. d. chem. Ges.*, 32, 1961 (1899).  
*Ztschr. anal. Chem.*, 39, 60, 329 (1900).  
*Chem. Centrbl.*, 71, 692 (1900).  
*J. Chem. Soc.*, June, 1900, p. 373.  
*Ibid.*, May, 1900, p. 326.  
*Ztschr. anal. Chem.*, 40, 50, 92, 587, 720 (1901).  
*Monatsh. Chem.*, 21, 1079 (1901).  
This Journal, 23, 638 (1901).  
*Chem. Ztg.*, 25, 743 (1901).  
Bull. No. 73, Bureau of Chem., 1902, p. 164.  
*Deutsche Gerber Ztg.*, 1903, No. 1-4; 6, 8, 12.