The thymol fraction was collected in a weighed receiver and the weight of thymol determined. The preceding table shows the results obtained.

It is to be noted from the table that potassium hydroxide is far superior to sodium hydroxide with respect to the yield of thymol. The best yield was obtained using 3 parts of potassium hydroxide to 1 part of sulfonate at 350° with a fusion period of 1/2 hour. However, considering the experimental error, practically the same yield was obtained using only 2 parts of potassium hydroxide. By using mixtures of the two hydroxides better yields were obtained than with sodium hydroxide alone, the yield increasing with the proportion of potassium hydroxide in the mixture.

The synthetic thymol obtained when seeded with a small crystal of natural thymol solidified completely. It was identified by its phenylurethane derivative (m. p., 107°) and its formation of trinitrothymol (m. p., 109°).

Summary

An improved method is described for the synthesis of thymol from *p*-cymene. The yields obtained in the various steps of the process indicate the possibility of utilizing *p*-cymene, the main constituent of so-called sulfite turpentine, as a source for synthetic thymol.

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THE DETERMINATION OF FORMALDEHYDE IN PARAFORMALDEHYDE[1]

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The object of this paper is to present the results of a study of certain methods for the determination of formaldehyde in paraformaldehyde. Of the many methods available[2] for the determination of formaldehyde the following will be considered: (1) fixed alkali, (2) iodimetric, (3) peroxide, (4) neutral sulfite, (5) oxidation with permanganate or dichromate in an acid solution and weighing the carbon dioxide produced.

Delepine[3] gives the formula of paraformaldehyde as $(CH_2O)n.H_2O$ showing water as the only impurity. To obtain a standard of composition, a sample of paraformaldehyde was analyzed in the Liebig combustion furnace. In two determinations the carbon dioxide absorbed gave by calculation 96.80 and 96.73 (mean, 96.77%). The water absorbed was very close to 3.23%.

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[1] This work was financed by the National Electrolytic Company and is published with their kind permission.

[2] Lockeman and Corner, *Z. anal. Chem.*, **54**, 11 (1915).

[3] Delepine, *Bull. soc. chim.*, [3] **17**, 849 (1897).

The results obtained,[4] given in Table I, show that the "fixed alkali" method alone yields results which depart seriously from the analysis (96.77) as made in the combustion furnace. The choice of a method will then be influenced by the other substances that may be present and the time available for an analysis.

"Fixed Alkali" Method.—The "fixed alkali" method[5] is based on the following reaction: $2CH_2O + NaOH = CH_3OH + HCOONa$. The procedure as carried out is primarily that described by C. E. Smith.[6]

Simply stated, it consists in heating in boiling water for 30 minutes a small flask containing 0.35–0.60 g. of paraformaldehyde and 25 to 30 cc. of *N* sodium hydroxide. After cooling the mixture, the excess base is titrated with *N* acid using phenolphthalein as an indicator. Fresenius and Grunhut[7] state that this method is "valuable only when the solution remains colorless."

Seven trials were made with this method, and in all attempts the solution became yellow. The values found were 96.02, 95.97, 95.91, 95.89, 96.27, 95.61, 96.19% with corresponding time of heating 31, 30, 33, 30, 30, 52, 43 minutes; average value, 95.98 with an average deviation of 0.15.

TABLE I

DETERMINATION OF FORMALDEHYDE IN PARAFORMALDEHYDE BY DIFFERENT METHODS

Method	No. of detns.	Mean % CH_2O	Av. dev.
"Fixed Alkali"	7	96.0	0.15
Iodimetric	15	96.7	0.13
Peroxide	8	96.8	0.16
Neutral sulfite	20	96.7	0.3
Oxidation and absorption of CO_2	4	96.9	0.2

When in the peroxide and iodimetric methods the time between the addition of alkali and hydrogen peroxide or iodine is appreciable, a reaction occurs just as in the fixed alkali method. H. and A. Euler[8] take up the rate of this reaction with sodium, barium and calcium hydroxide but the base used was dilute (0.02 *N* to 0.05 *N*) while that used in these methods is about *N* or even of greater concentration.

To determine the effect of concentration of alkali, about 0.43 g. of paraformaldehyde was treated with alkali of various concentrations in a tightly stoppered flask. The excess of alkali was titrated using litmus as an in-

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[4] The method of oxidation by dichromate and titration of the excess [M. Nicloux, *Bull. soc. chim.*, [3] **17,** 839 (1897)] was tested with an excess of about 4 cc. of 0.5 *N* dichromate. The results obtained were 96.17, 96.33, 96.20 and 96.29 with an average value of 96.25 and an av. diff. of 0.06. The reason that these results are lower than the others may be an insufficient excess of dichromate or not sufficient acid. No attempt was made to investigate this method further.

[5] Legler, *Ber.*, **16,** 1333 (1883).

[6] Smith, *Am. J. Pharm.*, **70,** 86 (1898).

[7] Fresenius and Grunhut, *Z. anal. Chem.*, **44,** 15 (1905).

[8] H. and A. Euler, *Ber.*, **38,** 2551 (1905).

dicator because in some of the experiments the unchanged formaldehyde was determined by the peroxide method. The results are given in Table II.

TABLE II

EFFECT OF CONCENTRATION OF ALKALI ON CONVERSION OF FORMALDEHYDE

Run	Wt. of sample G.	Age of soln. Hours	Alkali N	CH_2O found Fixed alkali %	Peroxide %	Total %
1	0.4309	2	0.5	15.21	...	...
2	.4308	2	.5	15.69	...	...
3	.4272	6	.25	11.00	...	...
4	.4360	6	.5	28.82	68.26	97.08
5	.4291	6	.5	29.28	...	...
6	.4321	6	.5	29.35	...	...
7	.4310	6	.75	46.03	...	...
8	.4271	6	1.0	57.14	...	...
9	.4297	15	0.5	50.09	47.15	97.22
10	.4314	24	.5	61.87	35.05	96.92
11	.4324	24	.5	61.31	...	...
12	.4302	30	.5	67.22	30.59	97.81
13	.4331	39	.5	72.20	25.12	97.32
14	.4275	48	.5	76.92	21.37	98.39

Table II shows that the speed of this reaction is dependent upon the concentration of the alkali, for Runs 3, 4, 7 and 8 show that with the change of alkali from 0.25 *N* to *N* the conversion increased from 11% to 57%. This reaction is also independent of the area exposed to the air, for the conversion in Run 5 with a surface of 38.5 sq. cm. was 29.28%, while in Run 6 with a surface of 2.4 sq. cm. the conversion was 29.35% or within the experimental error. The solutions in Runs 12, 13 and 14 of 30 to 48 hours' duration showed a yellow tinge and, therefore, the results are probably not very dependable.

Iodimetric Method.—This method, which originated with Romijn,[9] is based on the following reaction. $CH_2O + I_2 + 3OH^- = HCOO^- + 2I^- + 2H_2O$.

About 0.1 g. of paraformaldehyde is weighed into a flask of about 200 cc. capacity; 20 cc. of 0.8 *N* sodium hydroxide solution is then added, and immediately thereafter at least 10 cc. in excess of the theoretical amount of 0.2 *N* iodine solution, and the flask stoppered. The solution in the flask is allowed to stand for about 5 minutes and shaken occasionally, after which 20 cc. of *N* hydrochloric acid is added and the excess of iodine thus liberated titrated with 0.2 *N* sodium thiosulfate solution, using starch as indicator.

The values found were 96.60, 96.54, 96.57, 96.42, 96.80, 96.69, 97.03, 96.66, 96.70, 96.81, 96.60, 96.95, 96.79, 96.76 and 96.80% with an average of 96.71% and an average deviation of 0.13%.

When the solution containing the alkali and dissolved paraformaldehyde is allowed to stand for any considerable length of time before the addition

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[9] Romijn, *Z. anal. Chem.*, **36**, 18 (1897).

of the iodine solution the results are low, in agreement with results given under the fixed alkali method. With the time intervals of 1, 3, 6, 9 and 11 minutes, 96.79, 96.44, 96.36, 96.35 and 95.49% were obtained, the method otherwise being the same.

Using the procedure which gave consistent results but with excess iodine of 10.16, 6.65, 5.23 and 3.31 cc., 96.79, 95.79, 96.00 and 95.68% were obtained. This shows that 10 cc. of iodine solution in excess is necessary.

The lowering of the formaldehyde content was very marked when iodine and base were mixed before the addition of paraformaldehyde. The values found were 23.66, 23.94, 24.87, 20.35% with excess iodine of 39.60, 41.62, 42.96, 42.03 cc. and time of contact before neutralizing the base 20, 171, 220, and 11684 minutes, respectively. This mixing of the base and iodine before the addition of paraformaldehyde allows the reaction, $3IO^- = 2I^- + IO_3^-$, to occur and the iodate when once formed does not seem to be an active oxidizing agent in an alkaline solution.

Hydrogen Peroxide Method.—The "peroxide" method, as given first by O. Blank and H. Finkenbeiner,[10] consists in the oxidation of formaldehyde in an alkaline solution with hydrogen peroxide to formic acid and titration of the excess alkali.

About 0.4 g. of paraformaldehyde is weighed into a 200cc. flask: 30 cc. of *N* alkali is run in and 30 cc. of 3% hydrogen peroxide, previously neutralized to litmus,[11] is added slowly from a pipet. Addition of the peroxide usually takes about 3 minutes and the flask is gently shaken during this time to relieve the rapid evolution of gas. The flask is heated in water (temperature, 85°) for 5 minutes and then *rapidly* cooled. The excess alkali is titrated with *N* acid.

The values thus determined were 96.87, 96.53, 96.85, 97.23, 96.91, 96.78, 96.48, 96.90% with average of 96.82%, and average deviation of 0.16%, with a time of heating 5, 5, 5, 17, 6, 5, 9 and 7 minutes, respectively.

Neutral Sulfite Methods.—The neutral sulfite[12] is based on the following reaction: $H_2O + CH_2O + Na_2SO_3 = CH_2OHSO_3Na + NaOH$.

One drop of indicator is added to 25 cc. of the sulfite solution and then just enough acid to destroy the pink color, followed by the sample to be analyzed, which should contain 0.5 to 1.0 g. of formaldehyde, depending upon the acid used. The approximate amount of acid is run in to give an end-point in a few seconds; after 30 seconds the solution is again titrated if the pink color reappears.

Addition of water during titration is to be avoided. Auerbach and Barschall[13] working with formaldehyde solutions, corrected for the hydrolysis of the sodium sulfite during titration. In the present work this correction was not made nor attempted, as it was desired to check the accuracy of the analysis on paraformaldehyde without it.

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[10] Blank and Finkenbeiner, *Ber.*, **31**, 2979 (1898).

[11] The litmus solution used was prepared according to directions of the U. S. Pharmacopeia, IX, p. 581.

[12] Lemme, *Chem.-Ztg.*, **27**, 896 (1903), modified and improved by J. Doby, *Z. angew. Chem.*, **20**, 353 (1907).

[13] Auerbach and Barschall, "Arbeiten aus dem Kaiserlichen Gesundheitsamte," **22**, 592 (1904–1905).

The results obtained, as given in Table III, show good agreement when 4 N sulfite solution is used. It is advisable to use rosalic acid as indicator in place of phenolphthalein in view of the consistently lower average deviation thereby obtained.

TABLE III

EXPERIMENTS WITH NEUTRAL SULFITE METHOD

Conc. N	Acid	Na_2SO_3 N	No. of observations	Av. dev.	CH_2O in paraformaldehyde %
0.306	H_2SO_4	2	12[a]	0.64	94.56
0.498	H_2SO_4	2	10[b]	.22	96.37
1.187	HCl	2	10[b]	.35	96.54
0.498	H_2SO_4	4	6[a]	.49	96.60
1.187	HCl	4	10[a]	.40	96.74
0.498	H_2SO_4	4	13[b]	.32	96.70
1.187	HCl	4	7[b]	.20	96.69

[a] Phenolphthalein indicator. [b] Rosalic acid indicator.

Oxidation with Potassium Dichromate or Potassium Permanganate and Absorption of Carbon Dioxide.—The procedure used in oxidizing paraformaldehyde with an excess of potassium dichromate or permanganate in hot sulfuric solution with quantitative evolution of carbon dioxide was that of Messinger.[14] The apparatus in all its essential details corresponds to that described by Olsen.[15] Three runs with potassium permanganate gave 96.69, 96.89 and 97.26%, respectively, while with potassium dichromate a single run gave 96.96%.

In this oxidation a slow stream of air is used to sweep out the carbon dioxide formed. To detect any formaldehyde vapors that might have been carried over, a water trap was inserted in the line before the absorbers and an analysis made, following the usual procedure. At the close of the run the water in the trap gave a negative resorcinol-sulfuric acid test for formaldehyde.

In conclusion, it may be stated that when the procedures outlined are followed, the analyses by all except the "fixed alkali" method are in substantial agreement with the result obtained by use of the Liebig combustion furnace.

Summary

It has been shown that of the five recognized methods for the determination of formaldehyde in paraformaldehyde, all except the "fixed alkali" method give results in substantial agreement with those obtained in the Liebig combustion furnace.

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[14] Messinger, *Ber.*, **21**, 2914 (1888).

[15] Olsen, "Quantitative Analysis," D. Van Nostrand Co., **1908**, p. 308.