The average correction to be made then on the Liebig titration is 2 cc. of the mercuric solution, but as readily seen this can be applied to fresh urine only since in old urine the effect of the ammonia of decomposition becomes too great to be easily corrected. In the clinical examination of fresh urine the correction may be applied with only a small margin of error, while in fuller analyses, where the disturbing factors are also estimated, it may be used with considerable accuracy. My thanks are due to Mr. Grulee, who made many of the experiments above.

NORTHWESTERN UNIVERSITY, CHICAGO,
July 20, 1901.

ON THE DETERMINATION OF FORMALDEHYDE.

BY A. G. CRAIG.

Received July 10, 1901.

THE methods for the determination of formaldehyde may be classed, by their reactions, in three groups, as follows :

Group 1.—Depending on a specific reaction.

Group 2.—Formation of addition products with elimination of the elements of water.

Group 3.—Oxidation and reduction.

Group 1 contains :

(*a*) The ammonia method.[1]

$$6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O.$$

(*b*) The potassium cyanide method.[2]

$$KCN + CH_2O = N{\equiv}C{-}\overset{\overset{H_2}{\|}}{C}{-}O{-}O{-}K.$$

(*c*) The fixed alkali method.[3]

$$NaOH + 2CH_2O = NaOOCH + CH_2OH.$$

Group 2 contains :

(*a*) The hydroxylamine method.[4]

$$NH_2OH.HCl + CH_2O = CH_2NOH + HCl + H_2O.$$

(*b*) The aniline method.[5]

$$C_6H_5NH_2 + CH_2O = C_6H_5NCH_2 + H_2O.$$

The precipitate is weighed.

[1] L. Legler: *Ber. d. chem. Ges.*, **16**, 1333.
[2] G. Romijn: *Ztschr. anal. Chem.*, **36**, 18.
[3] Legler: *Ber. d chem. Ges.*, **16**, 1333.
[4] Brochet and Cambier: *Compt. rend.*, **120**, 449.
[5] Trillat: *Bull. Soc. Chim.*, [3], **9**, 305.

(*c*) Same as above except that the excess is titrated.[1]

Group 3 contains most of the methods which have been proposed.

(*a*) The ammoniacal silver nitrate method[2] depends on the reduction of metallic silver when silver nitrate is boiled with ammonia and formaldehyde.

(*b*) The acid silver nitrate method.[3]

$$KClO_3 + AgNO_3 + 3CH_2O = 3CHOOH + AgCl + KNO_3.$$

(*c*) The iodine method.[4]

$$CH_2O + 2I + 2NaOH = 2NaI + CHOOH + H_2O.$$

(*d*) The alkaline permanganate method.[5]

(*e*) Another potassium permanganate method.[6]

(*f*) The bichromate method.[7]

(*g*) The hydrogen peroxide method.[8]

$$CH_2O + H_2O_2 + NaOH = NaOOCH + 2H_2O.$$

A careful study of the various methods and the comments on them brought out the fact that no fixed standard had been used to test the accuracy of the methods, but that the highest or the average results were taken to be the best.

A sample of trioxymethylene was prepared by evaporation. Trials were made of titration with potassium permanganate and oxalic acid. The end-point was sharp, and tests showed that the formaldehyde was completely destroyed.

The most successful scheme was as follows: 280 cc. bottles, having glass stoppers closed with graphite and tied down; trioxymethylene, about 0.5 gram.; 25 cc. 1 : 1 sulphuric acid; 40 cc. 1 per cent. potassium permanganate. The bottle is closed and heated to 80° C. for fifteen minutes. The solution is then cleared up with standard oxalic acid and titrated to pink. The results obtained were 96.4 per cent. and 96.0 per cent.

A trial was made of sealing some of the sample in a test-tube with water and heating. Solution was complete in one-half hour at 100° C. The results by titration were unsatisfactory. Fear-

[1] Klar: *Pharm. Ztg.*, **40**, 611.
[2] Orchard: *Analyst*, **22**, 4.
[3] Grützner: *Arch. Pharm.*, **234**, 634.
[4] G. Romijn: *Ztschr. anal. Chem.*, **36**, 18.
[5] Smith: *Analyst*, **21**, 148.
[6] Jones: *Am. Chem. J.*, **17**, 539.
[7] Nicloux: *Bull. Soc. Chim.*, [3], **17**, 839.
[8] Blank and Finkenbeiner: *Ber. d. chem. Ges.*, **31**, 2979.

ing that the sample might be impure, some of it was sublimed in a combustion tube tightly closed, with a cannon tube at one end and a condenser at the other. The pressure did not rise very high. The sublimate collected in and beyond the condenser, partly as a fine white powder, and partly as a solid mass. A brown tarry substance remained unvolatilized. A portion of the sublimate was sealed up with water and boiled. The boiling was continued every day for a week, but the sublimate did not dissolve.

An attempt was made to titrate the sublimate as above, but it required one hour at 95° to dissolve it, and results of 108.6 per cent. and 106.2 per cent. were obtained, showing that the permanganate was reduced by the heat.

The Grützner method was next tried: "Into a glass stoppered flask put 5 cc. of solution containing about 0.15 gram of formaldehyde, about 1 gram potassium chlorate, 50 cc. decinormal silver nitrate, and 1 cc. nitric acid. The closed flask is gradually warmed in the water-bath with frequent shaking. The reaction is complete in one-half hour. The end of the reaction is easily seen when the solution becomes clear above the silver chloride. The excess of silver nitrate may be titrated or the silver chloride may be weighed."

A sample of trioxymethylene was obtained from E. Merck, and portions were dried in the steam oven. Various experiments were made as to the best form of bottle, time, temperature, light, etc. By heating in blackened water to 80° C. and then one-half hour between 80° and 90°, filtering rapidly, and drying at 200° to constant weight, a pure white silver chloride was obtained, but the results in twenty determinations varied from 91 per cent. to 120 per cent. No reason could be found for this variation except in the inconstancy of the reaction. The Grützner method, then, seems to be altogether unreliable.

The Blank and Finkenbeiner method is as follows: "1 gram trioxymethylene or 2 cc. formaldehyde is placed in a flask and 25 cc. of double normal soda solution added. Then 50 cc. of hydrogen dioxide, of strength 2.5 per cent. or 3 per cent. is added cautiously, the addition lasting three minutes. Allow stand two to three minutes and titrate with sulphuric acid, using litmus."

The commercial hydrogen dioxide contained acid, which was either neutralized or titrated, usually the former. The trioxy-

methylene was found to dissolve easily in the solution on the addition of the hydrogen dioxide. It was found that it is necessary to allow the flask to stand ten minutes before titrating. Results were as follows:

	Per cent.
Allowed to stand ten minutes cold	92.2
Heated slowly ten minutes	91.9
Sample dried by heating in flask to 85° for fifteen minutes with slow stream of natural gas	95.8
Sample heated to 85° for one hour, then a slow stream of natural gas passed for ten minutes	96.9
Gas passed for seven hours cold	96.4
Heated one hour at 85°, gas passed fifteen minutes, and then allowed to stand over calcium chloride five days	97.5

These results showed that the trioxymethylene contained water, and that, in the limited time allowed, it was practically impossible to dry it. The substance is almost as volatile as water, especially when warmed, and long standing in desiccators seemed the only way of drying it thoroughly. It was impossible to tell when the substance was dry, as when it apparently contained as much as 8 per cent. of water it was powdery, not sticking to glass, nor showing the slightest dampness. This explains the variable results of the earlier experiments and will prove of value in interpreting the results.

The Legler method is as follows: "To a sample of formaldehyde in a flask a sufficient excess of normal ammonia is added, allowed to stand tightly corked, and titrated back, using litmus, to which hexamethylene tetramine is neutral."

According to G. Lösekann,[1] the amine is monobasic to methyl orange, and must be titrated to a full red. It was decided to use methyl orange in order to avoid error from the presence of carbon dioxide.

W. Eschweiler[2] states that accurate results can be obtained only by allowing to stand five days or by boiling for one hour. Carl E. Smith[3] states that it is necessary to allow to stand only fifteen minutes.

G. L. Taylor directs to allow to stand twelve hours, and L. F. Kebler[5] says: "It is undesirable to report results on a reaction

[1] *Ber. d. chem. Ges.*, **22**, 1565.
[2] *Ibid.*, **22**, 1929.
[3] *Am. J. Pharm.*, Feb., 1898.
[4] *Ibid.*, April, 1898.
[5] *Ibid.*, Sept., 1898.

of less than six hours' duration. * * * Neither were the results constant for duplicate of the same sample. * * * In my opinion, the only reason that Professor Smith arrived at the results he did was because the number of samples worked on was too limited."

It was decided to boil one hour. Trials on the same sample showed that practically the same result was obtained by allowing to stand eighteen hours at 16°, and one hour at 100°,—93.1 per cent. for the former and 93.5 per cent. for the latter. The work was done with prescription bottles holding from 2 to 4 ounces, with soft rubber stoppers. Several attempts were made to dry the trioxymethylene, but as no 100 per cent. results could be obtained it was concluded that it was impossible to dry it in the limited time allowed for the first series of experiments.

A sample of commercial formaldehyde was tested, boiling in 2-ounce bottles for one hour, and titrating to full redness with methyl orange. The results were 37.34 per cent., 37.44 per cent. and 37.35 per cent. The Blank and Finkenbeiner method gives for this sample 37.30 per cent. These two methods are therefore in practical accord.

The chief difficulty in using the Legler method is the volatility of the normal ammonia. Carl E. Smith[1] proposes a way of getting rid of the standard ammonia by liberating ammonia from ammonium chloride by means of normal soda. In these experiments, the principal difficulty from the ammonia has been, not the loss of strength in the standard solution but the loss during the determination. This is not remedied by Professor Smith's modification.

By the following scheme both these sources of error are removed: Prepare a normal solution of sulphuric acid. Make up an approximately normal solution of ammonia, the exact strength being immaterial. Procure several 3-ounce prescription bottles with smooth sides and close-fitting soft rubber stoppers. Prepare a methyl orange solution. Procure a boiler in which the bottles may be immersed to the neck without upsetting (a large beaker will do). Take as much of the sample as will contain 0.5 gram of formaldehyde. Measure with the pipette, 25 cc. of the ammonia solution into each of the bottles, and to half of them add a sample of formaldehyde; stopper tightly. If the necks of the bottles are

[1] *Am. J. Pharm.*, Feb., 1898.

small, the stoppers need not be tied down. Place the bottles in the boiler, add cold water to the necks, and heat to boiling. Boil for one hour, and cool by running in cold water slowly, being careful not to allow the cold water to touch the hot bottles. Titrate with sulphuric acid and methyl orange, *to the first indication of a color change*. Take the difference between the readings for the blanks and those for the samples, as the ammonia consumed, in normal cubic centimeters. Of this difference, 1 cc. equals 0.0601 gram of formaldehyde.

Trials were made on the sample of trioxymethylene which was previously used, but which had been standing for one year. Results were obtained as follows: 99.8, 98.5, 100.0. and 100.1 per cent. On a sample of commercial formaldehyde, these results were obtained: 38.0, 37.7, 37.6, 37.8, 37.8, 38.1 per cent. As this work was done at night, probably better results could be obtained under better conditions.

These experiments indicate that Lösekann obtained good results by titrating to a full red, because the loss during the titration about equals the amount of acid added between the first color change and the full red; that is, about 0.25 cc. By following Lösekann's directions, fairly good results may be obtained with normal ammonia solution, without the use of a blank. The rubber stopper changes its shape during the heating, and probably a glass-stopper would be better if convenient, and if a secure fit could be made. From the results of these experiments it is observed that the reaction of the Legler method is quantitative, and that the results are as accurate as the means will allow. The same may be said of the Blank and Finkenbeiner method.

The Legler method has the advantage that it is cheaper, more convenient, and less subject to error from impurities than the sample. In using the Legler method, the maximum results can be obtained by boiling for one hour.

It must be remembered that the errors in the Legler method do not balance each other. The tendency is toward low results. Therefore, in any series of results, the higher results are likely to be the better. A blank determination is necessary. In the titration a correct end-point is very important. In both the Legler and the Blank and Finkenbeiner methods, any acid present must be accounted for.

LABORATORY OF THE WESTERN UNIVERSITY
OF PENNSYLVANIA.