First—The price of ore will depend upon its quality and on local conditions and is not, therefore, a fixed figure.

Second—As stated previously, many water-powers in Ontario and Quebec can be developed to furnish an electirc horse-power year at from $4.00 to $5.00. This lower cost will reduce the electric energy required per ton of pig, as stated in the estimated cost.

Third—A better class of charcoal than was available for the experiments and proper protection against its consumption on top of the furnace will materially decrease the quantity of charcoal required per ton of pig, as stated in the cost sheet, and consequently lower the cost of production below the figures stated.

DEPARTMENT OF MINES,
OTTAWA, CANADA.

FORMALDEHYDE DISINFECTION. DETERMINATION OF THE YIELD OF FORMALDEHYDE IN VARIOUS METHODS OF LIBERATING THE GAS FOR THE DISINFECTION OF ROOMS.[1]

BY DANIEL BASE.

Received June 9, 1906.

IN the multitude of experiments on disinfection by formaldehyde gas very few of the experimenters have made any attempt to determine the exact amount of formaldehyde gas that entered the room from the charging apparatus. Several writers make reference to the percentage of the gas present in the air of the room, but they either do not state how the determinations were made or they obtain the percentage indirectly;[2] M. von Brunn,[3]

[1] These experiments were performed in the Division of Pharmacology, Hygienic Laboratory, U. S. Public Health and Marine Hospital Service, and are published by the permission of Surgeon-General Wyman; the results are incorporated in Bulletin 27, of the Hygienic Laboratory, where they are used by Dr. T. B. McClintic to illustrate his bacteriological results.

[2] Kinyoun: "Formaldehyde as a Disinfecting Agent and its Practical Application," Pub. Health Rep., U. S. P. H. & M. H. S., Jan. 29, 1897; Sprague: "Rapid Disinfection with High Percentages of Formaldehyde," Medical News, Dec. 11, 1897 (work done in the Hyg. Lab., U. S. P. H. & M. H. S.); Hill and Rickards: "Notes on Formaldehyde," Proc. 13th Ann. Meeting, Am. Pub. Health Assn., Dec. 9–12, 1902 (work done in Boston Board of Health Bacteriological Laboratory).

[3] v. Brunn: "Formaldehyddesinfection durch Verdampfung verdünnten Formalins" (Breslauer Methode), Z. Hygiene und Infectionskrankheiten, 30, 201 (1899).

however, made determinations directly on the charged air of a room by drawing 20 liter volumes of the air through water and titrating the formaldehyde absorbed by the iodine method. In those cases where the percentage of formaldehyde in the air of the room has been referred to, it was in connection with the particular method of charging with which the experimenter happened to be working. In my experiments the attempt has been made to determine the amount of formaldehyde gas given off into a room from a definite volume of formalin by five different methods, and from the results, to fix the relative standing of these methods as to the yield of formaldehyde gas.

These experiments were suggested by the publication of a new method of liberating formaldehyde gas from formalin, proposed in 1904 by Henry D. Evans, chemist, and Dr. J. P. Russell, bacteriologist, of the Laboratory of Hygiene, Augusta, Me.[1] The method consists in pouring the formalin quickly upon fine crystals of potassium permanganate, contained in a suitable metallic vessel. It was tested by Russell on over fifteen hundred cultures of bacteria exposed in different parts of rooms of various locations and dimensions. The results indicate this method of liberating the gas to be an efficient one, and if the same results be found by others, this method no doubt will supplant some of the older and more cumbersome methods, because of its ideal simplicity, the rapidity with which a room can be charged, and the inexpensive apparatus required. The Evans-Russell method seems an anomalous one as the formaldehyde gas is obtained by a process which destroys a part of the substance, and it was thought to be desirable to determine how much of the gas is given off in a room from a definite volume of formalin. For the sake of making a comparative study, other methods of charging a room were tried and determinations of the yield of formaldehyde made. The following methods were tried: the autoclave, Trenner-Lee retort, Kühn lamp, and the "sheet-spraying method."

Evans, in the article cited above, states that "all determinations of the amounts of formaldehyde were made by Romijn's potassium cyanide method,[2] as experience showed that this method is capable of yielding better results than the iodine

[1] "Formaldehyde Disinfection," 13th Ann. Rep., State Board of Health of Maine.

[2] Z. anal. Chem. 36, 18 (1897); Smith: This Journal, 25, 1028 (1903).

methods." The method of experimenting is not described. In a letter received after my experiments were under way, Evans states that he "is at present engaged with the analysis of the gas in closed rooms, drawing measured portions of the air through cyanide and iodine solutions." It would seem from this that he had not obtained the percentage yield which he claimed for his method of liberating formaldehyde gas from formalin by examination of the air in a room. In my experiments the high yield which Evans gives in his article, namely, about 80 per cent., was by no means obtained.

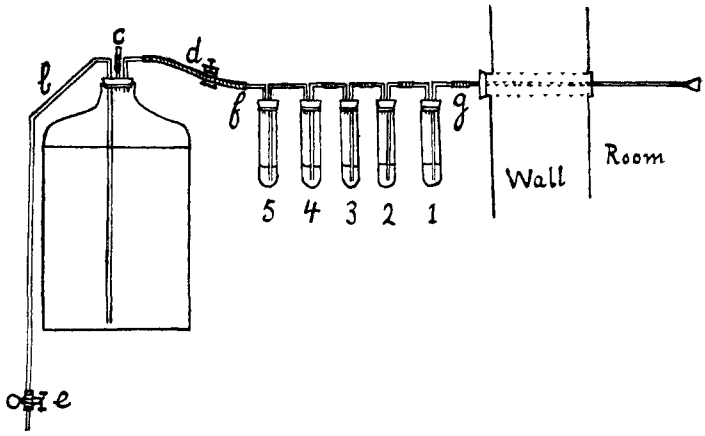
DESCRIPTION OF APPARATUS AND METHOD OF PROCEDURE.

The room into which the gas was liberated contained 2,000 cubic feet of space and was lined on the sides and ceiling as well as on the floor with sheet zinc, which overlapped the frames of the windows and doors. There were two well-fitting windows on opposite sides and two doors on the other two opposite sides. One of the doors had a small pane of glass inserted into it through which a view into the room was possible at all times. The wall containing this door was pierced by three parallel rows of zinc tubes about two inches in diameter and closed by rubber stoppers. The joints between the inner ends of the tubes and the wall of the room were made air-tight. The tubes of the middle row, which were about midway between the floor and ceiling and about six feet from the former, were used for drawing air from the room. For this purpose an ordinary glass tube about three feet long, to the end of which a small funnel was fitted, was passed through the rubber stopper and allowed to project outside the room about three inches. This end was joined by a rubber connection with a series of five thick-walled test-tubes about $7 \times {}^{3}/_{4}$ inches, fitted with alternating long and short connecting glass tubes. The lower end of each long tube was tapered to a small orifice. For purposes of reference we may call these tubes 1, 2, 3, 4 and 5, tube 1 being next to the room.

The tubes contained the absorbing medium through which the air of the room was drawn by means of a partial vacuum. A large graduated bottle holding 20 liters of water, fitted with an inlet tube, a siphon tube, and an air tube was used for this purpose. The whole arrangement is shown in the figure below.

When everything was ready connection was made at *g* and *f*,

the screw-cock *d* was closed, the siphon *b* started by opening the pinch-cock *e*, and water allowed to flow until the level in the bottle was exactly on the upper line of the graduation, at which moment the cock *e* was closed; then the glass plug *c* was inserted.



The apparatus was now ready for starting the experiment. It is needless to say that the bottle, with all its tubes, up to the point *d* was tested for leaks. All rubber joints were tied before the experiment was started and tight-fitting rubber stoppers were used in tubes 1, 2, 3, 4 and 5.

To begin the experiment cock *e* was opened, whereby water flowed out until a certain partial vacuum was reached in the bottle, when it ceased. Then *d* was opened cautiously and the rate of bubbling of the air from the room through the tubes 1, 2, 3, 4, and 5 was so regulated that 10 liters of air required about one hour and fifteen minutes; this rate is easily secured after a few trials. As soon as the air began to bubble, the water started to run again from the siphon tube *e*. The flow was continued until the level in the bottle had reached the desired mark of the graduation, when cock *e* was closed. Air continued to bubble until the partial vacuum in the bottle was reduced.

In order to make the conditions of pressure as nearly as possible like those in the apparatus at the beginning, the long tubes in 1, 2, 3, 4, and 5 were drawn up until the orifices were just below the surface of the liquid. This caused more air to bubble through the tubes. The volume of air drawn from the room is measured by

the volume of water that flowed from the bottle between the two marks of graduation. Finally tube 1 was disconnected at *g* and tube 5 at *f*. The series of tubes was then removed for titration.

SOLUTIONS AND TITRATION.

As the quantity of formaldehyde in a relatively small proportion of the air (say 10 liters) of the room was small, it was decided to use the potassium cyanide method of titration and also to use a solution of potassium cyanide as absorbing medium. The cyanide method is admitted to be accurate for small quantities of the aldehyde.

Potassium Cyanide Solution.—This was made by dissolving 3.3 grams of the salt (purity of 96 per cent. or over) in water; the volume was made up to 500 cc. The solution was standardized in the usual way against an excess of a decinormal solution of silver nitrate acidified with 4 or 5 drops of concentrated nitric acid, the excess of silver solution in the filtrate being determined by a standard sulphocyanate solution with iron alum as indicator.

In the titration of a dilute formaldehyde solution a definite volume or weight (known not to be in excess) is added to 10 cc., or more if necessary, of the standard potassium cyanide solution. The latter, after stirring, is added to an acidified excess of decinormal silver nitrate solution, the whole made up to 100 cc. or 200 cc., and the excess of silver in 50 or 100 cc. of the clear filtrate titrated with sulphocyanate. From the amount of sulphocyanate required the volume of silver nitrate precipitated by potassium cyanide is calculated, and the difference between this and the volume of silver nitrate equivalent to the amount of cyanide solution originally taken is the number of cubic centimeters of silver solution that represents the formaldehyde present; this number of cubic centimeters multiplied by 0.003 (more correctly 0.00298) gives the weight of absolute formaldehyde, HCOH.

The silver cyanide precipitate must be removed before titrating an excess of silver by sulphocyanate, because it interferes with the sharpness of the end-point and causes error.

As stated in the foregoing, potassium cyanide solution was chosen as the medium for absorbing the formaldehyde gas in the air of the charged room. It was soon discovered that the air bubbling through the solution carried away a little hydrocyanic acid. To avoid loss of the latter the last tube containing the

cyanide solution was followed by one containing silver nitrate solution, which effectually precipitated all the hydrocyanic acid carried over into it. The silver nitrate tube was followed by one containing distilled water. This tube showed no trace of hydrocyanic acid when tested by the ferric ferrocyanide reaction, and no formaldehyde when tested by Schiff's fuchsin-bisulphite reagent,[1] or ammonio-silver nitrate solution.

In preliminary experiments the contents of the silver nitrate tube, after formaldehyde-laden air had been drawn through the series, was tested for formaldehyde to determine if any had escaped absorption in the cyanide tubes. To some of the liquid, about 2 cc. of Schiff's reagent were added; a precipitate of silver chloride was produced, but no pink or purple color, thus indicating the absence of formaldehyde. For comparison the reagent was also added to a few cubic centimeters of silver nitrate solution to which had been added a trace of formaldehyde; the contents of the tube soon acquired a pink color. It seemed evident that formaldehyde is wholly absorbed from air passing through a series of tubes containing cyanide solution. This conclusion was further strengthened by experiments on the absorption of formaldehyde from air by water alone.

After nearly all the results given further on had been obtained by the cyanide method, there came to my notice an article by Trillat[2] in which the author states that formaldehyde can be completely absorbed from air by passing it through a sufficient number of absorption tubes containing water alone. This suggestion was put to the test and it was found that three water tubes absorbed all of the formaldehyde, the last tube containing only a trace. My reason for not having chosen water at the start as an absorbing medium was that I supposed a solution containing a substance, as cyanide, which combines chemically with formaldehyde would be better suited than pure water as an absorbing agent. Owing to circumstances, it was not possible for me to repeat all of the experiments and use water tubes to absorb the formaldehyde, but in several instances the absorption

[1] Schiff's reagent: This is prepared by adding 20 cc. of a solution of sodium bisulphite (sp. gr. 1.27) to 1000 cc. of aqueous fuchsin solution (1:1000), and, after one hour, adding 10 cc. of pure concentrated hydrochloric acid. It should be preserved in a well stoppered bottle.

[2] Trillat, A.: "Présence normal de la formaldéhyde dans les produits de la combustion incomplete," Rev. Hyg., Vol. 27, No. 2, Feb. 20, 1905.

from the same charged air of the room was carried out in cyanide tubes and in water tubes, side by side. Although three tubes are sufficient, five tubes of water were used for greater certainty. In these parallel experiments the percentage results in the case of absorption by water were practically the same as those in the case of absorption by cyanide. On examining the literature before putting my results together, I found von Brunn's article, in which he determined formaldehyde by drawing the charged air through water. von Brunn used in his determinations 3 Drechsel gas wash-bottles, each containing 100 cc. of water and aspirated 20 liters of air in twenty to thirty minutes. This would have been a too rapid rate for the volumes of liquid used in the absorbing tubes in my experiments, in which the rate of aspiration was from one-fourth to one-fifth as fast as in von Brunn's experiments. He found that nearly all of the formaldehyde was absorbed in the first bottle, the third one containing practically none.

DETAILS AS TO QUANTITY AND MANIPULATION IN THE DETERMINATION OF FORMALDEHYDE IN THE AIR OF THE CHARGED ROOM.

To give the figures involved in obtaining each result tabulated below would needlessly increase the length of this paper, but to give an idea of quantities of reagents used and method of carrying out the titration one experiment will be described in full.

Tube 1 contained about 8 cc. KCN solution.

Tube 2 contained about 5 cc. KCN solution.

Tube 3 contained 2 cc. KCN solution.

Tube 4 contained about 8 cc. N/10 $AgNO_3$ solution.

Tube 5 contained about 10 cc. distilled water.

Only the total quantity of cyanide need be measured, which, in this case, was exactly 15 cc., distributed about as stated. There should be not less than 8 or 9 cc. of cyanide solution in the first tube, lest there be an excess of uncombined formaldehyde in the liquid at the end of the absorption. Distilled water was added to the three cyanide tubes to make the column of liquid about 1.5 inches high, and to the silver nitrate tube to make a column about 1 inch high. The tubes were connected and air drawn through them as described above.

Volume of air drawn from room was 10 liters.

Time required to draw air was one hour, four minutes.

The five tubes were disconnected. Seven cc. of N/10 $AgNO_3$ solution were introduced into a 250 cc. flask and 8 or 10 drops of strong nitric acid added, then through a funnel, the silver nitrate solution in tube 4 and its connecting tubes was carefully rinsed into the flask, followed in like manner by tubes 1, 2 and 3. The flask was then filled to the graduation mark with water and the contents thoroughly shaken. One hundred cc. of the clear filtrate were titrated for excess of silver nitrate; 1.4 cc. of potassium sulphocyanate solution were required.

Ten cc. KCNS solution = 10.21 cc. N/10 $AgNO_3$.

Ten cc. KCN solution = 9.64 cc. N/10 $AgNO_3$.

By calculation the formaldehyde absorbed from the 10 liters of air corresponded to 3.03 cc. N/10 silver nitrate solution, which represents $3.03 \times 0.003 = 0.00909$ gram of formaldehyde. One cubic foot of the air (28.315 liters) contained 0.0257 gram of formaldehyde.

The quantity of formalin used to charge the room in nearly all the experiments, tabulated further on, was 600 cc. of 35.66 per cent. by volume; *i. e.*, 100 cc. of the formalin contained 35.66 grams of absolute formaldehyde. The strength was determined by the Blank and Finkenbeiner method of titration with hydrogen dioxide and caustic soda solutions.[1] The formalin was taken from the same supply in all the experiments.

In the experiment just described 600 cc. of formalin were used to charge the room. The results may be expressed in percentage, based on the amount of absolute formaldehyde taken per cubic foot of space in charging the room. The weight per cubic foot is $\frac{600 \text{ cc.} \times 0.3566}{2000} = 0.107$ gram HCOH.

The percentage would be $\frac{0.0257 \times 100}{0.107} = 24.01$.

From von Brunn's determinations, the question would seem to arise whether in my experiments the amount of formaldehyde found in the air of the room really represented all the formaldehyde in the room. To make this clear, it will be necessary to state the results of von Brunn's experiments. He first showed that when diluted solutions of formaldehyde are distilled from flasks, no paraformaldehyde is formed in the distillate or the

[1] For description, see original article in Ber. 31, 2979, or the U. S. Pharmacopoeia, 8th decennial revision, or Sutton's "Volumetric Analysis."

residue, as far as could be judged by the absence of cloudiness in the liquids when cooled, and that the sum of the amounts of formaldehyde found in the distillate and residue was practically equal to the amount of formaldehyde present before distillation. The concentrations of the solutions distilled ranged from 21.5 to 4.35 per cent. He states that paraformaldehyde is formed only when the concentration of a solution rises above 40 per cent. during distillation, but that with diluted solutions, for example 20 per cent. or less, there is little tendency for the per cent. to rise in the residue in the flask during distillation.

von Brunn next proceeded to make distillations from the "Breslau still" devised by C. Flügge,[1] of Breslau. This still has a large heating surface and relatively small outlet so that the pressure rises to 29 cm. of water (about 2.1 cm. of mercury). In two distillations of diluted formalin and determination of the formaldehyde in the distillate and residue, there was a loss of about 2 per cent., which was accounted for by the collection of some paraformaldehyde in the tube of the condenser. When this was titrated, it made up the difference. von Brunn attributed the formation of the small quantity of paraformaldehyde to the increase of pressure in the Breslau still as compared with that in the case of distillation from glass flasks.

Having thus a means of knowing pretty closely how much formaldehyde entered a room by determining how much remained in the residue in the still, von Brunn determined the amount of formaldehyde in the air of a charged room, in the manner already stated. He made three determinations, and the highest amount obtained was 16.94 per cent. of the total weight of formaldehyde introduced into the room. He worked with approximately 8 per cent. solutions, and in the experiment just mentioned, 2990 cc. of liquid, containing 255.6 grams of formaldehyde, were evaporated into a room of 2824 cubic feet. A piece of filter-paper hung up in the room and removed half an hour after the charging was finished, was found to have absorbed formaldehyde at the rate of 1.236 grams per square meter of surface. The conclusions at which von Brunn arrived may be interesting to some who are concerned with disinfection by formaldehyde and they are therefore given here. "It can be said

[1] Flügge: "Die Wohnungsdesinfection durch Formaldehyd," Z. Hyg. und Infectionskrankheiten, 29, 276 (1898).

that the greatest portion of the liberated formaldehyde is condensed at once on the surface of the walls and on the objects in the room. Accordingly the idea that in disinfection the formaldehyde acts as a gas needs correction. The more experiments have been made with formaldehyde, the more has it been observed that its maximum germicidal effect can only be attained in the presence of an abundance of water vapor. Therefore it appears that, by vaporizing formaldehyde, we only accomplish a uniform distribution of the disinfectant in space, but that the real efficacy lies not in the formaldehyde gas, but in the solution which condenses everywhere on surfaces."

von Brunn and all others who used the Breslau method of Flügge to charge rooms made it a point to bring the moisture up to or very nearly to the saturation point, under which conditions formaldehyde will no doubt be condensed upon objects ordinarily present in rooms much more readily than when the moisture is short of saturation. In my experiments the air of the room became saturated with moisture in only one case, namely, in charging with the Kühn alcohol lamp; moreover, there were no objects in the room and the only surfaces exposed to the formaldehyde gas that were not zinc-lined, were those of the glass windows and their frames. It is not probable that any considerable amount of formaldehyde was condensed on the zinc walls of the room. In fact there is good reason for believing that there was practically no condensation, because determinations made on the total amount of formaldehyde charged into a large glass bottle (24 liters) by the permanganate-formalin method on a reduced scale, agreed fairly well with those made on the air of the large room charged by the same method. Had there been such loss of formaldehyde from the air of the room by condensation upon the walls as von Brunn states, the results just referred to would never have approximated as closely as they did. The results of the determinations of the formaldehyde charged into the glass bottle are given in Tables 6 and 7.

Von Brunn did not state what the conditions were in the room which he charged, but it is probable that it was an ordinary one and contained the objects usually present, such as chairs, table, clothing, etc. In fact most experimenters have purposely left such objects in rooms in order to have conditions very nearly like those in living rooms when about to be disinfected.

Axel Jörgensen[1] found that paper, cloth, etc., condense formaldehyde from moist air laden with it, and that a room with wooden walls, having been charged and then ventilated for several days until the odor had vanished and closed again for more than a month, had developed such an odor of formaldehyde when opened that one could not endure remaining in it. He concludes that the total surface of walls in rooms is important, and that proportionately more formaldehyde should be introduced when there is a large wall-surface to compensate for the greater condensation and thus leave the same amount of gas in the air as would be present in a smaller room with less condensation. This point has also been brought out by Peerenboom, Walter and Schlossmann, and Werner. Jörgensen recommends for disinfection purposes rooms with walls of stone, glass, or metal.

If von Brunn's experiments were made in an ordinary room with objects in it and walls of absorbing material, the small percentage of the total formaldehyde introduced that he found in the air of the room can readily be accounted for. In my experiments it seems quite certain for the reasons given above that the amount of formaldehyde found in the air actually represented the whole amount of formaldehyde in the room at the time, or in other words condensation of formaldehyde upon the zinc walls did not occur.

As already stated, the windows and doors of the room into which the charges of formaldehyde were introduced, were tight-fitting, more so than those of the average living room, yet the room was not perfectly air-tight. Therefore the results recorded further on do not represent the total amount of formaldehyde that left the charging apparatus, but rather the average amount present in the room during the time of the determination and after a certain interval from the time the charging was finished. On a quiet day the rate of leakage was relatively small as is shown by the results, so that the amount of formaldehyde found on such a day soon after the charge was introduced must be fairly close to what would have been found if the room had been perfectly air-tight. In a few experiments, the window-frames and cracks of the doors

[1] Jörgensen: "Untersuchungen über Formaldehyddesinfection nach der Breslauer Methode,—speciell Desinfection von Uniformen betreffend," Z. Hygiene und Infectionskrankheiten, 45, 237 (1903).

were covered by pasting on heavy smooth paper, but the amount of formaldehyde found was only a little larger than when the paper was omitted; this would seem to show that the rate of leakage from the room was small.

PERMANGANATE-FORMALIN METHOD OF CHARGING THE ROOM, PROPOSED BY EVANS AND RUSSELL.

When formalin is poured upon crystals of potassium permanganate a vigorous action takes place after a few seconds, accompanied by a strong ebullition of the liquid and sufficient heat to produce a large quantity of steam. The reaction is apparently over in a comparatively short time (about five minutes) and with proper proportion of substances, the residue in the vessel is almost dry. The heat produced by the action of the permanganate on a portion of the formaldehyde is sufficient to evaporate nearly all the remainder.

The exact nature of the chemical reaction that takes place was not investigated as for the purposes of the experiments the fact of main interest was that an abundance of formaldehyde is given off in gaseous form. According to Evans and Russell, "analysis of the gas thrown out into a room by this reaction showed it to consist of formaldehyde, water vapor, carbon dioxide, and a very small amount of formic acid. In the generator were found a lower oxide of manganese, a little formaldehyde, carbon dioxide, potassium hydroxide, and, I think, a little potassium formate resulting from the neutralization of the potassium hydroxide by formic acid." It seems highly probable that the decomposition takes place essentially according to the following reaction:

$$4KMnO_4 + 3HCOH + H_2O = 4MnO(OH)_2 + 2K_2CO_3 + CO_2.$$

In accordance with this reaction about one-fifth of the formaldehyde is destroyed. The reaction is of value, of course, only because it furnishes the heat necessary to vaporize the rest of the formaldehyde.

Evans and Russell used the ratio of 100 cc. of formalin to 37.5 grams of permanganate, but it was found in the present experiments that with this proportion considerable formalin remained in the residue in the generator, as was evidenced by its wet condition and powerful odor of formaldehyde. After some experimenting the ratio of 100 cc. of formalin to 50 grams of permanganate was adopted; this gave a residue fairly free from liquid.

The quantity used to charge the room of 2,000 cubic feet was in nearly all cases 600 cc. formalin (35.66 per cent. by volume). The generator was a galvanized iron pail 10 inches wide and 10 inches high holding 12 liters (3 gallons). The ebullition was so vigorous that the frothy mass often reached nearly to the top of the pail. The pail was placed in the center of the room, the permanganate dropped into it, the formalin poured quickly upon it, and a hasty exit made from the room.

The action is more rapid, the more finely powdered are the permanganate crystals; in the experiments to follow, the small needle crystals of commerce were used without further powdering.

Many variations of conditions might have been tried, such as covering the pail with sheet asbestos to retain the heat, or heating the pail before the experiment, or placing it in hot water, or powdering the permanganate crystals, etc., but as time was a factor it was thought best to adopt those conditions which would be least cumbersome to execute by public officers or others in disinfecting rooms.

In the experiments (Table I) the ratio of the quantities used was 100 parts by volume of formalin to 50 parts by weight of permanganate, and approximately fifteen minutes were allowed to elapse between the time of mixing these and the beginning of drawing the air through the absorption tubes. This seemed sufficient time for the action to cease and for the formaldehyde gas to diffuse through the air of the room. The relative humidity in the room before and after charging was determined by means of a dry and wet bulb thermometer, which was so arranged that it could be swung around in the room and the results observed by the operator through a pane of glass in the door. By means of tables the grains of moisture per cubic foot were calculated. Before a new charge was put into the room all formaldehyde of the previous one was gotten rid of by opening the door and windows until no odor was perceptible.

Comments.—Although the room in which the experiments were made was zinc-lined and the doors and windows were fairly close-fitting, yet it was not air-tight, so that the conditions were not of that exact quantitative character which obtains in an operation like the precipitation of sulphuric acid by barium chloride. In view of this fact, although the percentages vary by several units, they can be considered as agreeing fairly well. In III, where the

TABLE I.—EXPERIMENTS WITH PERMANGANATE AND UNDILUTED FORMALIN.

Date and temperature of room before experiment	Formalin (35.66 per cent. by volume). cc.	$KMnO_4$. Grams.	Time between mixing and drawing air.	Time required to draw air.	Volume of air drawn in liters.	Relative humidity before experiment.	Relative humidity ten minutes after mixing.	Increase in grains of moisture per cubic foot.	Absolute formaldehyde taken per cubic foot. Gram.	Absolute formaldehyde found per cubic foot.	Yield. Per cent.	Condition of wind, etc.
I. 6/27, '05, 71° F.	600	300	*a.* 14 min.	1 hr. 10 min.	10	72	86	1.47	0.107	0.0403	37.70	Moderate wind.
			b. 3 hrs. 38 min.	1 hr. 21 min.	10				0.107	0.0243	22.70	Moderate wind.
II. 6/28, '05. 69° F.	800	400	*a.* 12 min.	1 hr. 32 min.	10	63	86	2.0	0.1426	0.0505	35.41	Slight breeze.
			b. 22 hrs. 17 min.	1 hr. 10 min.	11				0.1426	0.0172	12.07	Very slight breeze.
III. 6/30, '05. 77° F.	400	200	15 min.	1 hr. 12 min.	10	79	85	0.58	0.0713	0.025	35 06	Moderate wind.
IV. 7/24, '05. 79° F.	600	300	17 min.	1 hr. 21 min.	10	79	94	1.72	0.107	0.0419	39.15	Practically no wind. Windows and doors of room pasted up.

room was made more nearly air-tight by pasting paper over the cracks of the door and covering the window frames, the per cent. is a little higher. These experiments also indicate that the relation between the formalin and permanganate in the ratio taken is fairly quantitative and that the percentage yield of formaldehyde gas is approximately the same whether 400, 600 or 800 cc. be taken for a charge. Experiments I *b* and II *b* give an idea of the rate of leakage of formaldehyde from the room. In I *b*, the loss after an interval of about three and one-half hours was 2/5 of the formaldehyde, in II *b* it was about 3/5 after an interval of twenty-two hours.

It is probable that on a very quiet day after fifteen or twenty minutes with a charge of 600 cc. formalin (35.66 per cent. by volume) the weight of the gas in the room would be at least between 38 and 39 per cent. of the weight in the 600 cc. of formalin taken, and in a room with fairly tight windows and doors.

EXPERIMENTS WITH PERMANGANATE AND DILUTED FORMALIN.

A number of experiments were made with formalin diluted with various quantities of water, and with different weights of permanganate.

A fixed volume of formalin was taken (600 cc.) and the interval between setting off the charge and beginning to draw air, the volume of air drawn (10 liters), and the time required to draw it were about the same as in Table I. In several instances two experiments were made simultaneously with 5 and 10 liters of air respectively.

Comments.—Of the various proportions used that of 600 cc. formalin, 300 cc. water and 375 grams of permanganate gives the highest yield of formaldehyde gas.

In Experiment I the determinations *a* and *b*, made simultaneously and on the same volume of air, gave the same results, which would seem to indicate that the method of analysis, under the same conditions, gives constant results. In Experiment III, 5 liters of air in *a* were drawn in the same time as 10 liters in *b* with practically the same result, which seems to point to the conclusion that 5 liters of air is a large enough quantity for a determination.

In Experiments IV, V, VI and VII the same proportion of materials were used to charge the room, but the results in IV are

TABLE II.—EXPERIMENTS WITH PERMANGANATE AND DILUTED FORMALIN.

	Date and temperature of room before experiment.	Formalin (35.66 per cent. by volume). cc.	Water. cc.	$KMnO_4$. Grams.	Time between mixing and drawing air.	Time required to draw air.	Volume air drawn in liters.	Relative humidity before experiment.	Relative humidity ten minutes after mixing.	Increase in grains of moisture per cubic foot.	Absoluteformaldehyde taken per cubic foot. Gram.	Absoluteformaldehyde found per cubic foot.	Yield. Per cent.	Condition of wind, etc.
I.	7/3, '05.	600	600	450	17 min.	*a.* 1 hr. 20 min.	10	81	94	1.79	0.107	0.0272	25.4	Slight breeze.
	81° F.					*b.* 1 hr. 20 min.	10				0.107	0.0272	25.4	Slight breeze.
II.	7/10, '05.	600	300	450	16 min.	1 hr. 5 min.	10	83	98	2.06	0.107	0.03081	28.8	Moderate wind.
	81° F.													
III.	7/11, '05.	600	300	300	16 min.	*a.* 1 hr. 9 min.	5	74	94	2.28	0.107	0.0242	22.6	Moderate wind.
	81.5° F.					*b.* 1 hr. 8 min.	10				0.107	0.02336	21.8	Moderate wind.
IV.	7/12, '05.	600	300	375	14 min.	*a.* 45 min.	5	77	96	2.14	0.107	0.0289	27.0	Brisk wind.
	81° F.					*b.* 1 hr. 14 min.	10				0.107	0.02965	27.7	Brisk wind.
V.	7/17, '05.	600	300	375	15 min.	*a.* 34 min.	5	70	90	2.55	0.107	0.03755	35.1	Gentle breeze.
	85° F.					*b.* 1 hr. 5 min.	10				0.107	0.0356	33.27	Gentle breeze.
VI.	7/18, '05.	600	300	375	*a.* 17 min.	42 min.	5	70	88	2.3	0.107	0.0341	31.84	Gentle breeze.
	85° F.				*b.* 17 min.	1 hr. 20 min.	10				0.107	0.03296	30.80	Gentle breeze.
					c. 2 hrs. 27 min.	1 hr. 18 min.	10				0.107	0.02548	23.81	Gentle breeze.
	Cont'd				*d.* 4 hrs. 24 min.	1 hr.	10				0.107	0.02276	21.27	Gentle breeze.
	7/19, '05.				*e.* 24 hrs. 33 min.	1 hr. 23 min.	10				0.107	0.01028	9.6	Gentle breeze.
VII.	7/21, '05.	600	300	375	*a.* 21 min.	47 min.	5	79	94	1.72	0.107	0.03517	32.87	Practically no wind;
	79° F.				*b.* 21 min.	1 hr. 17 min.	10				0.107	0.03517	32.87	windows and doors
	Cont'd				*c.* 4 hrs. 7 min.	1 hr. 18 min.	10				0.107	0.02658	24.84	pasted up with
	7/22, '05.				*d.* 23 hrs. 46 min.	1 hr. 13 min.	10				0.107	0.01546	14.44	stout smooth paper.

low on account of the brisk wind blowing at the time, and should not be compared with those of V, VI and VII. The three determinations of V, VI and VII which are comparable show a fairly close agreement. VI and VII show the rate of leakage from the room, the loss of formaldehyde in VI in two, four and twenty-four hours after the first determination being about 2/10, 3/10 and 7/10 respectively, in VII after four and twenty-three and one-half hours being about 25/100 and 56/100 respectively, *d* and *e* of VI and *c* and *d* of VII, which are comparable, show that when there is very little wind the leakage from the room when pasted up with paper is not much less than when it is not pasted. V *a* seems to be abnormally high when compared with VI *a* and VII *a*.

With the proportions of 600 cc. formalin (35.66 per cent.), 300 cc. water and 375 grams potassium permanganate, it is probable from the results that after fifteen or twenty minutes on a quiet day in a tight room the amount of formaldehyde gas obtained would be approximately 32 per cent.

The addition of water to the formalin has the effect of increasing the amount of moisture sent out into the room which probably would offset in disinfection the lower per cent. of formaldehyde obtained than in the case of undiluted formalin, since it is claimed by many that high relative humidity is an important factor in the action of formaldehyde gas upon bacteria.

CHARGING THE ROOM BY THE AUTOCLAVE.

Six hundred cc. of formalin, 60 cc. of glycerol, 120 grams of calcium chloride, and water sufficient to make a volume of 1000 cc. constituted the charge for each experiment. The pressure was raised to between 50 and 60 pounds, when the cock was opened and injection continued till the pressure had fallen to about 20 pounds. Then the pressure was raised and vapor again injected.

This process was repeated until the pressure rose very slowly and vapor almost ceased to escape from the nozzle of the autoclave, which was inserted through a suitable hole in the door. After each experiment there was little liquid left in the autoclave.

Comments.—From the result of III *a* it seems probable that on a calm day in a fairly tight room the amount of formaldehyde by the autoclave from 600 cc. of formalin would be approximately 42 per cent. after an interval of about thirty minutes from the time of removing the nozzle from the room.

TABLE III.—EXPERIMENTS WITH THE AUTOCLAVE.

Date and temperature of room before experiment.	Time required to exhaust autoclave.	Time between beginning of discharge to drawing of air.	Time required to draw air.	Volume of air drawn in liters.	Relative humidity before experiment.	Relative humidity five minutes after removing autoclave.	Increase in grains of moisture per cubic foot.	Absolute formaldehyde taken per cubic foot. Gram.	Absolute formaldehyde found per cubic foot.	Yield. Per cent.	Condition of wind.
I. 6/23, '05. 80° F.	25 min.	3 hrs. 32 min.	1 hr. 18 min.	10	75	96	2.96	0.107	0.0406	37.94	Almost no wind.
II. 6/26, '05. 81.5° F.	25 min.	*a.* 35 min.	1 hr. 17 min.	10	81	94	2.00	0.107	0.04213	39.37	Good breeze.
		b. 3 hrs. 33 min.	1 hr. 4 min.	10				0.107	0.0216	20.18	Storm.
III. 7/15, '05. 80° F.	22 min.	*a.* 40 min.	1 hr. 10 min.	11	75	94	2.23	0.107	0.04448	41.57	Almost no wind.
		b. 1 hr. 41 min.	1 hr. 20 min.	11				0.107	0.04116	38.46	Almost no wind.

II *a* is lower than III *a*, which was to be expected because of the stronger wind blowing.

II *b* shows the rapid loss of formaldehyde gas during a strong wind or storm. During the time the air was drawn in this experiment a severe thunderstorm was in progress, with the result that during the interval of three hours between *a* and *b* nearly half the formaldehyde escaped from the room.

Apparently over half the formaldehyde gas in the 600 cc. of formalin used to charge the air was lost. It is altogether improbable that the most of this escaped from the room during the twenty-five minutes required to exhaust the autoclave, as is evident from the slow rate of loss on a calm day shown in I and III *a* and *b*. It is more probable that under the high temperature and pressure in the autoclave the formaldehyde undergoes change. It would be an interesting problem to work out the fate of the lost formaldehyde. The mixture of formalin, glycerol and calcium chloride was devised by A. Trillat to prevent, as he asserted, the formation of paraformaldehyde. If the results in my experiments represent the amount of formaldehyde injected into the room, and there seems to be no strong reason to think the contrary, then there is a loss of formaldehyde somehow in the autoclave. There are two plausible views, either that the formaldehyde is partly decomposed, or polymerized, or perhaps both.

CHARGING THE ROOM BY THE TRENNER-LEE RETORT.

The formalin in this method is simply heated to the boiling-point under atmospheric pressure in a retort and the issuing water vapor and formaldehyde gas are passed into the room through a suitable tube.

In the following experiments 600 cc. of formalin to which were added 6 cc. of glycerol were taken for the charge, and the heat was continued under the retort until vapor practically ceased to issue from the outlet tube. When the retort was removed there was little liquid left in it.

Comments.—The yield of formaldehyde gas by this method was appreciably higher than by the autoclave method, although the time required to exhaust the apparatus was more than twice as long in the former as in the latter. Because of this longer time there was naturally more loss by leakage in this method before beginning to draw air. The higher percentage would be ex-

TABLE IV.—EXPERIMENTS WITH TRENNER-LEE RETORT.

Date and temperature of room before experiment.	Time required to exhaust retort.		Time between removal of retort and drawing air.	Time required to draw air.	Volume of air drawn in liters.	Relative humidity before experiment.	Relative humidity at end of injection.	Increase in grains of moisture per cubic foot.	Absolute formaldehyde taken per cubic foot. Gram.	Absolute formaldehyde found per cubic foot. Gram.	Yield. Per cent.	Condition of wind.
I. 7/27, '05. 73° F.	1 hr.		22 min.	1 hr. 6 min.	10	73	86	1.5	0.107	0.05037	47.07	Very slight breeze.
II. 7/28, '05. 76° F.	1 hr.	*a.*	21 min.	1 hr. 10 min.	10	82	89	0.96	0.107	0.04935	46.12	Very slight breeze.
Cont'd 7/31.		*b.*	3 hrs. 40 min.	1 hr. 4 min.	8				0.107	0.04183	39.1	Very slight breeze.
		c.	72 hrs.	1 hr. 7 min.	10				0.107	0.00637	5.95	Strong wind, July 29, 30, 31.

pected, since in the retort the formaldehyde is not subjected to as high a temperature and pressure as in the autoclave. Although the yield was greater in the retort method than in any other tried, there arises the question as to what becomes of the rest of the formaldehyde. In view of von Brunn's experiments, it seems probable that some of the formaldehyde was polymerized to paraformaldehyde the greater part of which perhaps remained in the retort. It is also likely that some paraformaldehyde entered the room, although there was nothing in the appearance of the room atmosphere to indicate this. The atmosphere was clear.

Experiments II *a* and *b* show the slow rate of leakage from the room on a quiet day, the loss in an interval of three hours and twenty minutes being about 3/20 of the amount found in *a*. I and II agree very closely, the difference being only about 1 per cent. From I and II, it seems probable that on a quiet day in a tight room the amount of formaldehyde gas present by this method after an interval of twenty minutes from removal of the retort would be approximately 47 per cent.

In regard to the question of the formation of paraformaldehyde when formalin is heated, most contradictory statements are found in the literature. Novy and Waite[1] assert the following: "The fear of polymerization of formalin on boiling is not well grounded. Certain it is that formalin can be distilled from its aqueous solution without polymerization, and that the results obtained are in every way equal to those obtained from paraform and decidedly superior to the so-called formalin lamps." "The statement is freely made that formaldehyde solutions cannot be heated without polymerization and thus interfering with further evaporation. Formalin, if heated slowly in an open dish, may possibly polymerize, especially when concentrated to about 25 cc., but we have never found this to take place when the formalin solution was rapidly heated in a glass flask or copper container." On the other hand von Brunn in the article cited, which was published a year later, stated that when formalin of about 32 per cent. or more was distilled from a glass flask, the residue in the flask upon cooling became cloudy or opaque, indicating paraformaldehyde. Only when diluted solutions, 20 per cent. or less, were distilled, was there no paraformaldehyde formed. Novy and Waite had used

[1] "The Disinfection of Rooms," Med. News, 72, 641 (1898).

an approximately 40 per cent. solution. The loss of formaldehyde as indicated in my determinations seems to point to the formation of paraformaldehyde in the retort and to the correctness of von Brunn's statements.

SHEET-SPRAYING METHOD.

Two sheets, about 8 x 5 feet were hung up in the room in a slanting position at an angle of about 45°. It was found advantageous to have them just damp to the touch when hung up, as the formalin was absorbed by the fibers more quickly and had very little tendency to run off the sheet. Six hundred cc. of formalin were sprayed uniformly and the door closed. About one and one-half hours were allowed for the formaldehyde to diffuse before beginning to draw air. The sheets were washed before the next spraying.

Comments.—Compared with the previous methods this one produces a fairly good quantity of formaldehyde gas in the air of the room. The results show that the quantity increases during a relatively long period of time. In Experiment II *c* the quantity of formaldehyde gas found after an interval of twenty-two hours was only 2.75 per cent. less than that found in II *a*, ninety minutes after closing the room.

Evidently, an advantage of this method is the fact that formaldehyde continues to be supplied to the air of the room for a long time, whereas, in the other methods, the per cent. of the gas begins to diminish by leakage from the moment the charging is finished.[1]

It is impossible to indicate the yield of gas in this method, as the gas is given off continuously for a long period. Moreover it is probable that on a dry day the amount of gas given off after a definite interval would be greater than on a very humid day, on account of slower evaporation in the latter case, and no doubt low temperatures would also have a retarding effect on the evaporation.

EXPERIMENT WITH THE KUHN LAMP.

This is one of the various lamps devised for the purpose of generating formaldehyde by the partial oxidation of methyl

[1] The high degree of efficiency of this method, from the bacteriological side, has recently been emphasized by Ravenel and Gilliland, Univ. of Penn. Med. Bull. Vol. 16, p. 77.

TABLE V. - EXPERIMENTS WITH SHEET-SPRAYING METHOD.

Date and temperature of room before experiment.		Time between closing room and drawing air.	Time required to draw air.	Volume of air drawn in liters.	Relative humidity before experiment.	Relative humidity after closing room.	Gain in grains of moisture per cubic foot.	Absolute formaldehyde taken per cubic foot. Gram.	Absolute formaldehyde found per cubic foot.	Per cent.	Condition of wind.
I. 8/3, '05. 76.5° F.	*a.*	1 hr. 26 min.	1 hr. 13 min.	10	72	83	1.6	0.107	0.02576	24.07	No wind.
	b.	3 hrs. 47 min.	1 hr. 8 min.	10		(after 5 hrs.)		0.107	0.03262	30.48	No wind.
II. 8/4, '05. 78° F.	*a.*	1 hr. 40 min.	1 hr. 15 min.	10	83	85	0.49	0.107	0.0252	23.55	Gentle breeze.
	b.	4 hrs. 5 min.	1 hr. 7 min.	10		(after 3 hrs.)		0.107	0.0305	28.50	Gentle breeze.
Cont'd 8/5.	*c.*	23 hrs. 30 min.	1 hr. 17 min.	10				0.107	0.02225	20.80	No wind.

alcohol. In the Kühn lamp this is brought about by means of hot platinized asbestos, which has the power of causing the oxygen of the air and methyl alcohol vapor to combine according to the following reaction:

$$\underset{\text{methyl alcohol.}}{CH_4O} + O = \underset{\text{formaldehyde.}}{CH_2O} + H_2O.$$

The platinized asbestos is heated by first burning some of the alcohol, after which the flame is extinguished. Alcohol continues to vaporize and the heat produced in the oxidation keeps up the temperature of the apparatus. The time usually allowed for the exhaustion of the lamp is about two hours.

One thousand cc. of common methyl alcohol were placed in the reservoir of the lamp and 1500 cc. of water in the basin around the reservoir. During the action of the lamp an abundance of moisture was formed, which condensed on the small glass pane in the door of the room.

In a previous experiment it was found necessary to have two silver nitrate tubes to absorb the hydrocyanic acid which was carried over from the cyanide absorption tubes by the air bubbling through them. This was no doubt due to the presence of a great excess of carbonic acid and perhaps a small quantity of formic acid.

While formaldehyde is formed by the action of the platinized asbestos in the Kühn lamp it is not the only product of oxidation, for the oxidation extends as far as the formation of carbon dioxide. It is known that formic acid is oxidized to carbon dioxide by platinized asbestos. Engels condemns the methyl alcohol lamps and states that about 90 per cent. of the alcohol is oxidized to carbon dioxide and water and that the vapors from the lamps contain from 3 to 5 per cent. of carbon monoxide.[1]

The presence of either carbon dioxide or formic acid in the air bubbling through the cyanide absorption tubes would cause the liberation of some hydrocyanic acid, which would be carried over. The precipitate in the first silver nitrate tube was somewhat larger than in the case of the other methods. The precipitate in the second silver nitrate tube did not appear until towards the end of the experiment.

[1] Engels: "Experimentelle Beiträge zur Wohnungsdesinfection mit Formaldehyd," Archiv. Hygiene, 49, 129–199 (1904).

Result: Began to draw air two hours after the lamp was started. Volume of air drawn, 10 liters. Time required, one hour, thirteen minutes. Condition of wind, gentle breeze.

Temperature of room before experiment, 79; relative humidity, 87.

Temperature of room two hours after starting lamp, 85; relative humidity, 98.

If the quantity of formaldehyde found be referred for comparison to the amount of absolute formaldehyde allowed per cubic foot in the other methods, where 600 cc. of formalin were taken to charge the room, it is equivalent to $\frac{0.01096 \times 100}{0.107} = 10.24$ per cent.

Comments.—The quantity of absolute formaldehyde obtained from 1000 cc. of methyl alcohol is considerably less than that obtained from 600 cc. of formalin by any of the other methods. Because of this relatively small quantity and the cumbersomeness and unreliability of the lamp as a means of producing the gas it was not thought worth while to make further determinations. One merit which the Kühn lamp has is that it produces more moisture in the air of the room than the other methods described.

Conclusions.—The results obtained must be interpreted as representing the quantities of formaldehyde gas that may be expected to be present in a room made not absolutely but fairly air-tight when charged with formalin by the various methods described, on a day of little wind and after a certain interval of time which varies with the method used. According to the quantity of formaldehyde yielded it seems fair to arrange the methods in the following order:

(1) Trenner-Lee retort.

(2) Autoclave.

(3) Permanganate-formalin, 300 grams to 600 cc.

(4) Sheet spraying.

(5) Permanganate-diluted formalin in the proportions of 600 cc. formalin, 300 cc. water and 375 grams permanganate.

(6) Kühn lamp, using 1000 cc. methyl alcohol as against 600 cc. formalin in the other methods.

For simplicity and expedition, the permanganate-formalin method is preferable to all the others. Moreover, the quantity of formaldehyde gas can easily be increased by using more formalin, which only requires a larger pail, a piece of apparatus not very

difficult to obtain, and correspondingly more permanganate. If it is desirable or necessary to have a greater degree of humidity in the air than results from this method, that could easily be supplied from a simple tin or copper still.

Although the sheet spraying-method may not give at any time so high a percentage of the gas as the permanganate-diluted formalin method, it is placed before the latter, because in the spraying method the amount of gas is kept up for a long time, while in the diluted formalin method it is constantly diminishing and after five or six hours would be less than in the spraying method.

The experiments described were carried out at summer temperature, between 69° and 85° F. No attempt was made to determine if any solid paraformaldehyde was present along with the gaseous formaldehyde in the air of the room, but it is quite likely that none or very little was present, since the air of the room after charging was free from haziness.[1] Paraformaldehyde as such has no value as a disinfectant, but it has the same effect on potassium cyanide in titrations as the gaseous product.

It may not be out of place to add here the conclusions of a recent experimenter as to the "practical requirements for an effective formaldehyde disinfection."[2] (1) In all cases, an average of 5 grams of formaldehyde (absolute) per cubic meter of space (0.1416 gram per cubic foot) should be present, with seven hours' action. (2) In exceptional cases, where loss of formaldehyde can not be avoided, or where numerous objects or a good deal of matter of an organic nature which can not be

[1] M. B. Porch (assistant in Pharmacology, Hygienic Laboratory, Washington), using the same apparatus and methods that I did, but working at lower temperatures, found that polymerization of formaldehyde gas begins at about 62° F., and becomes more marked as the temperature decreases, which is evidenced by the persistent hazy condition of the air of the room, the low percentage yield of formaldehyde, and the deposition of paraformaldehyde in the room. He obtained in the permanganate-formalin method a yield of 25.1 per cent. at 62° F. and 11.1 per cent. at 52° F., as against 38.39 per cent. obtained by me at the higher temperatures of my experiments, namely, 71° and 79° F. He found similar results in the case of the autoclave method and that in the sheet-spraying method little formaldehyde is evaporated in cold weather and that polymerization takes place on the sheet.

[2] G. Werner: "Zur Kritik der Formaldehyddesinfektion," Archiv. Hygiene, 50, 305 (1904).

conveniently removed, are present in the room, the quantity of formaldehyde should be doubled. (3) In all cases, when the room temperature is below 50° F., it should be raised. 68–77° F. is an efficient temperature. (4) The strength of the formalin used should be known. Werner used the Breslau still in his experiments and saturated the air with moisture, using a hair hygrometer to determine the latter.

DETERMINATION OF FORMALDEHYDE CHARGED INTO A LARGE GLASS BOTTLE BY THE FORMALIN-PERMANGANATE METHOD, AND ALSO THE AMOUNT LEFT IN THE RESIDUE IN THE GENERATOR.

These experiments were carried out in two large bottles, one holding a trifle over 24 liters (0.85 cu. ft.), the other very nearly 18 liters (0.63 cu. ft.). The mouths of the bottles were 2.75 inches wide and were closed with tight-fitting corks, the pores of which were closed with melted paraffin.

A porcelain crucible holding 24 cc. was fitted into an excavated flat cork, which was suspended in a stirrup of thin twine.

The formalin was practically 40 per cent. by volume, as determined by the Blank and Finkenbeiner hydrogen dioxide method. In most of the experiments 0.7 cc. of this was used to charge the bottles; it was measured from a long slender pipette, in which 0.1 cc. made a column 1.7 cm. long. The method of procedure was as follows:

About 40 cc. of approximately decinormal potassium cyanide solution was measured from a burette into the bottle and about 50 cc. of water added. The liquid was then rolled over the side of the bottle to produce a greater absorbing surface. Then the crucible containing the formaldehyde was suspended in the mouth of the bottle, the permanganate dropped in from a piece of glazed paper, and the whole let down quickly into the bottle by a string and the cork securely placed. After a few seconds a vigorous action began, which seemed to be finished in about five minutes. About fifteen minutes, however, were allowed to elapse before the crucible was removed. This was done by slightly loosening the stopper, drawing up the crucible as near as possible to the stopper, removing the stopper for an instant, taking the crucible out, and then replacing the stopper. By repeatedly rolling the cyanide solution over the side of the bottle the formaldehyde was soon

absorbed (in about half an hour). When the odor of formaldehyde could no longer be detected, the contents of the bottle were transferred by thorough washing into a 500 cc. flask containing an excess of decinormal silver nitrate (about 10 cc.) acidified with nitric acid. The volume was made up to the graduation mark, the flask thoroughly shaken, and 250 cc. of the filtrate titrated with sulphocyanate solution, and calculation made as already described.

Method of procedure for the residue in the crucible. After the crucible was removed the contents were thoroughly extracted with water and filtered into a 250 cc. flask. The volume was made up to the graduation mark, and 50 cc. of the solution were added to about 15 cc. of the cyanide solution. After stirring, this was poured into an excess of acidified silver nitrate solution, which was stirred until the precipitate collected into a clot. The clear filtrate from the precipitate was then titrated with sulphocyanate solution for excess of silver.

Comments.—In all the experiments but the last two the ratio used was 1 part by volume of formalin to 0.5 part by weight of permanganate, the same as was used in the experiments of Table I. With this proportion the total amount of formaldehyde found in the air of the bottle and in the residue was fairly constant, considering the conditions of the experiments.

Evidently there is an advantage in using permanganate in powdered form, as is shown by comparing the results of IV, V, VI, VII and VIII with those of I, II and III. No doubt the reason for this is that action takes place more quickly with production of a higher temperature, so that more formalin evaporates from the crucible and less remains with the residue.

The results in Experiments I, II and III (average 33 per cent.) are lower than the results in Table I, which refer to experiments in charging the room of 2,000 cu. ft. This would be expected considering the small quantities used, whereby the quantity of heat produced is not so large, and the cooling of the generator is more rapid. In the experiments where powdered permanganate was used, the percentage yield is higher and in line with the results in Table I.

In Experiment IX, where only 0.5 cc. of formalin was used, the result is low; but this is probably due to the fact that the

TABLE VI.—RESULTS OF EXPERIMENTS IN GLASS BOTTLES.

	Date.	Size of bottle in liters	Formalin (40 per cent. by volume). cc.	$KMnO_4$. Gram.	Formaldehyde found in bottle. Per cent.	Formaldehyde found in residue. Per cent.	Total of formaldehyde found in bottle and residue. Per cent.	Remarks.
I.	8/15, '05.	24	1	0.5	33.03	.....	.....	$KMnO_4$ in small needle crystals.
II.	8/16	24	1	0.5	33.52	38.25	71.77	$KMnO_4$ in small needle crystals.
III.	8/18	18	1	0.5	32.47	40.35	72.82	$KMnO_4$ in small needle crystals.
IV.	8/17	18	0.7	0.35	35.48	33.86	69.34	$KMnO_4$ ground to moderately fine powder.
V.	8/18	18	0.7	0.35	36.53	35.20	71.73	$KMnO_4$ ground to moderately fine powder.
VI.	8/18	24	1	0.5	.....	35.11	.....	$KMnO_4$ ground to moderately fine powder.
VII.	8/21	18	0.7	0.35	37.00	32.20	69.20	$KMnO_4$ ground to moderately fine powder.
VIII.	8/22	18	0.7	0.35	37.83	32.76	70.59	$KMnO_4$ ground to moderately fine powder.
IX.	8/19	18	0.5	0.25	33.28	38.10	71.38	$KMnO_4$ ground to moderately fine powder.
X.	8/25	18	0.7	0.4	34.37	25.16	59.53	$KMnO_4$ ground to moderately fine powder.
XI.	8/28	18	1	0.39	25.20	42.79	67.99	$KMnO_4$ ground to moderately fine powder.

quantity of formalin is too small to produce as vigorous an action as in the other cases.

In Experiment X the proportion of permanganate was increased, with the result that the amount of formaldehyde sent out into the bottle was not affected much, but considerably less remained with the residue.

In Experiment XI the permanganate was decreased to the ratio used by Evans (Maine Board of Health) in the report on his method. The result shows a considerable decrease in the formaldehyde sent out into the bottle and large increase in the amount remaining in the residue.

EXPERIMENTS WITH DILUTED FORMALIN AND PERMANGANATE.

Two experiments were made with 0.6 cc. formalin diluted with 0.3 cc. water and 0.375 gram of powdered permanganate, which are the same proportions as used in most of the experiments in Table II. The procedure was the same as described above.

TABLE VII.

	Date.	Formaldehyde found in bottle. Per cent.	Formaldehyde found in residue. Per cent.	Total found. Per cent.
I.	8/23, 1905.....	31.00	34.23	65.23
II.	8/23, 1905.....	32.16	34.04	66.20

The percentage yield was about the same as that given in Table II, but less than that in the previous experiments (Table VI) with undiluted formalin. The formaldehyde remaining with the residue was about the same as in the previous experiments where powdered permanganate was used. The total formaldehyde found was less than in the experiments with undiluted formalin, indicating a greater destruction of formaldehyde.

UNIVERSITY OF MARYLAND,
BALTIMORE.

THE AMOUNT OF SODIUM SULPHITE RECOVERABLE FROM FOOD PRODUCTS AS A BASIS FOR THE ESTIMATION OF THE AMOUNT ORIGINALLY PRESENT.

BY CLIFFORD D. HOLLEY.

Received April 4, 1906.

AT A time when so many misleading statements are being made concerning sodium sulphite and sulphurous acid as food pre-