acid salts of orthotelluric acid. No selenate or sulphate of silver is known that is isomorphous with either of these salts.

(4) $HgHTeO_4.3H_2O$ crystallizes in the triclinic system. It is the only crystalline mercurous tellurate that has been prepared.

(5) Two crystalline salts of divalent mercury have been prepared, *viz.*: Hg_3TeO_6 and $HgTeO_4.2H_2O$. The former appears in the form of amber-colored crystals belonging to the isometric system; the latter is white and crystallizes in the orthorhombic system.

(6) The crystalline compound described by Oppenheim as a double salt of silver nitrate and tellurate is normal silver tellurate ($Ag_2TeO_4.2H_2O$).

(7) It has not been found possible to prepare the acid tellurates of silver described by Berzelius.

(8) Potassium tellurate may be prepared in crystalline form by slow evaporation of its solution, provided care is exercised to prevent supersaturation of the solution.

(9) Telluric acid does not completely replace the carbonic acid in an equivalent quantity of potassium carbonate. Crystalline normal potassium tellurate cannot be obtained from potassium carbonate and telluric acid as described by Berzelius.

(10) Although telluric acid is a weak acid, hot concentrated solutions of it attack mercury, silver, lead, tin, arsenic, antimony, bismuth, nickel, zinc, aluminum, and cadmium.

(11) There are no well authenticated cases of isomorphism between sulphates and tellurates or between selenates and tellurates.

[CONTRIBUTION FROM THE INSECTICIDE AND WATER LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

A STUDY OF THE HYDROGEN PEROXIDE METHOD OF DETERMINING FORMALDEHYDE.

BY J. K. HAYWOOD AND B. H. SMITH.

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DURING the last year or two the authors have made use of the Blank and Finkenbeiner hydrogen peroxide method of determining formaldehyde, and have in the vast majority of cases obtained results which agreed with one another very satisfactorily and with the results obtained by other methods. However, a result would occasionally be obtained which was manifestly incorrect, although the details of the method were followed closely. Besides this, other chemists who tested the same method were not always able to get closely agreeing results. It appeared, therefore, that there must be present certain disturbing factors which should be discovered before the method was adopted as a safe and correct one. With the above points in view the authors determined to make a comparative study of the various methods that have been proposed for determining formaldehyde by means of oxidation with peroxide, and, if possible, determine which was the best and on what factors was the error dependent.

The first method tested was the one usually followed by the authors which in detail corresponds closely to the original Blank and Finkenbeiner procedure.

Method.—Measure out 3 cc. of the formaldehyde (the specific gravity of which has been previously determined) into a flask containing 25 cc. of double normal sodium hydroxide, then add 50 cc. of pure 2.5 to 3 per cent. hydrogen peroxide with occasional shakings, in six to ten portions during three minutes, through a funnel placed in the neck of the flask to prevent spurting. Let stand three to five minutes (usually the latter), *shaking about every thirty seconds*, and finally titrate the excess of hydroxide with normal sulphuric acid, using litmus as indicator. Besides the above, seven- and fifteen-minute periods of allowing the hydrogen peroxide to act on the formaldehyde were also tried since it was possible that three minutes was not long enough to complete the reaction. On two samples, A and B, secured from the different manufacturers, the following results were obtained.

BY AUTHORS' PROCEDURE.

Time of action of total quantity of H_2O_2.	Per cent. of formaldehyde.	
	A.	B.
3 minutes	36.90	36.92
7 minutes	36.99	37.02
15 minutes	36.90	37.11

It appears from the above that in one case at least a longer period than three minutes is necessary for complete oxidation of the formaldehyde; however, the difference between a three- and fifteen-minute period of action is small.

The next procedure tested was one recently suggested by Fresenius and Grünhut.[1] These authors discovered the following interesting facts in regard to the hydrogen peroxide method.

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[1] *Z. anal. Chem.*, **44**, 16 (1905).

(1). That when the formaldehyde is added to the double normal sodium hydroxide solution there is danger of part of the formaldehyde acting on the hydroxide according to the equation $2HCHO + NaOH = HCOONa + CH_3OH$, before the peroxide is added, so that two equivalents of formaldehyde correspond to one equivalent of sodium hydroxide instead of the ratio being 1 : 1 as required by the Blank and Finkenbeiner method. (The equation followed in this method is either

$$HCHO + NaOH + H_2O_2 = HCOONa + 2H_2O$$

or

$$2HCHO + 2NaOH + H_2O_2 = 2HCOONa + 2H_2O + H_2.)$$

(2) That low and varying results are obtained if the flask is cooled during the time that the peroxide is acting on the formaldehyde.

Based on these observations they have suggested the following method of procedure which leaves the formaldehyde in contact with the sodium hydroxide a minimum length of time.

Method.—Weigh out about 3 grams of formaldehyde in a weighing-tube with a ground glass stopper. Place the tube in a flask containing 25 cc. of double normal sodium hydroxide, tip the tube over and immediately commence the addition of 50 cc. of 3 per cent. hydrogen peroxide. This addition is so regulated by dropping from a burette that three minutes is required for the entire addition, the flask being constantly shaken throughout this time. After standing two or three minutes with occasional shaking the excess of alkali is titrated just as before.

The following results were obtained by this method on A and B, one titration of the excess of alkalinity being made *immediately* after the addition of peroxide and the other four minutes after the addition.

PROCEDURE OF FRESENIUS AND GRÜNHUT.

Time of action of total quantity of H_2O_2.	Percentage of formaldehyde.	
	A.	B.
0 minutes	37.04	36.92
4 minutes	37.04	37.02

It is evident from the above that one sample (A) was entirely oxidized as soon as the addition of peroxide was completed, while in the other case (B) a few minutes more were required for complete oxidation.

In the article just mentioned by Fresenius and Grünhut it was suggested that an addition of 5 cc. of hydrogen peroxide to the sodium hydroxide before the addition of formaldehyde might prove of advantage. This was tried and the results obtained were as follows: for A, 37.03 per cent. formaldehyde and for B, 36.79 per cent. formaldehyde. When the formaldehyde was allowed to stand in contact with the 5 cc. of hydrogen peroxide +25 cc. of 2N soda before the extra 45 cc. of hydrogen peroxide were added, the percentage of formaldehyde was reduced in proportion to the time that this action was continued, thus showing that there is undoubtedly some action between the sodium hydroxide and formaldehyde according to the equation $2HCHO + NaOH = HCOONa + CH_3OH$.

Since there is this danger of the formaldehyde acting on the sodium hydroxide before the peroxide is added, it occurred to the authors that the simplest way to avoid any chance of such error is to add the total 50 cc. of peroxide to the soda before the addition of the formaldehyde and allow the mixture to stand long enough (with shaking about every thirty seconds) for the reaction to take place. This scheme was tried and the following results obtained:

	Per cent. of formaldehyde.	
Time of action of H_2O_2.	A.	B.
5 minutes	33.89	30.39
10 minutes	37.22	34.44
15 minutes	37.28	37.17
20 minutes	37.28	37.17

It will be noted that constant results were obtained at the end of about fifteen minutes and that *these results are slightly higher than the results obtained by any of the other methods.* It was at first thought that this increase in the formaldehyde figure might be due to experimental errors, but the determinations were repeated a number of times with the same results. The explanation of this is, that in all the other methods there is some action directly between the formaldehyde and sodium hydroxide, either at the time when the formaldehyde is first added to the sodium hydroxide solution or more probably, later on in the reaction when the temperature has been raised and yet an excess of peroxide is not present (it being used up about as fast as it is added).

Since an error of 0.1 cc. in the reading of the double normal soda originally added corresponds to an error of about 0.19 per cent. formaldehyde, an attempt was next made to carry out the method as just described but to use 50 cc. of normal instead of 25 cc. of double normal soda. The following results were obtained:

	Per cent. of formaldehyde.	
Time of action of H_2O_2.	A.	B.
10 minutes	29.00	...
15 minutes	31.24	32.39
20 minutes	34.07	37.07
30 minutes	37.28	37.17

It is evident from this that normal soda can be used but the time necessary to complete the reaction is much increased. Several samples were tested by this method and it was found that it was not sure, *i. e.*, at one time the reaction would be completed in thirty minutes while at another time it would take forty-five minutes to complete it, another time forty minutes, etc. A probable explanation of this marked slowing of the reaction was sought in the statement made by Fresenius and Grünhut that low, varying results are obtained if the flask is cooler during the time that the peroxide is acting on the formaldehyde. In this case, to be sure, the flask was not cooled, but it was more dilute, which practically amounted to cooling in that the heat of reaction had to raise the temperautre of a much larger body of liquid. Observations were made of the temperatures attained in all of the methods described above, and it was found that the time necessary to complete the reaction was a direct function of the temperature reached, so that in the procedures where a maximum temperature was attained the reaction took place in the shortest length of time. This being so, an attempt was made to hurry the reaction between the peroxide and formaldehyde in the presence of normal soda by keeping on the steam-bath. The following results were obtained:

	Pei cent. of formaldehyde.	
Time of action of H_2O_2.	A.	B.
5 minutes	37.22	37.21
10 minutes	37.22	37.21

It is evident from this that the greatest factor in decreasing the time necessary for the completion of the reaction is a sufficiently high temperature. If the temperature is raised to 100° C., the reaction will take place very quickly.

Based on the above experiments the following procedure for carrying out the Blank and Finkenbeiner method has been adopted by the authors. It has been tested on a number of samples and has been found to always lead to safe, accurate results with the expenditure of a minimum amount of time and attention.

Method.—Measure out 50 cc. of normal sodium hydroxide in a small Erlenmeyer flask (say of 500 cc. capacity) and add 50 cc. of pure 3 per cent. hydrogen peroxide. Now add from a pipette 3 cc. of the formaldehyde solution under examination (the specific gravity of which has been previously determined), allowing the point of the pipette to almost reach the liquid in the flask. Place a funnel in the neck of the flask and put on the steam-bath for five minutes, shaking occasionally during this time. Remove from the steam-bath, wash the funnel with distilled water, cool the flask down to about room temperature and titrate the excess of sodium hydroxide with normal acid, using litmus as indicator. This cooling of the flask before titration with acid was found necessary so as to get a sharp end-reaction with the litmus. From the volume of formaldehyde used and the specific gravity, the percentage by weight of formaldehyde can be determined.

INNER CRUCIBLE METHOD FOR DETERMINING SULPHUR AND HALOGENS IN ORGANIC SUBSTANCES.

BY S. S. SADTLER.

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TO ALL workers in organic chemistry who have to make determinations of sulphur and halogens in research or commercial work, the use of the Carius furnace is almost always found troublesome. It has always been so to the writer, and after many plans to avoid its use, he devised the way to be here described.

The general idea does not seem to be a new one, as Dr. Edgar F. Smith said in discussion upon an unpublished paper read by the writer before the Philadelphia Section of this Society, that he had used an inverted inner crucible with caustic lime as a reagent to determine chlorine in organic substances when a student. More recently Shimer[1] described an inner crucible method for determining carbon in steel, etc. The writer tried inverting small platinum and porcelain crucibles in large platinum crucibles, but with sulphur compounds containing volatile constituents the oil

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[1] *Chem. Eng.*, November, 1904.