NOTE ON THE DETECTION OF FORMALIN.

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A SOLUTION of formaldehyde, called "formalin," having come into use as a food preservative, it becomes of importance to be able to detect and estimate it.

The literature of formaldehyde is very voluminous, and numerous tests for it have been proposed. As is well known, aldehydes reduce Fehling's solution and ammoniacal silver nitrate, and give Schiff's reaction. These reactions, however, are by no means characteristic of the aldehyde.

Legler's method for the estimation of formaldehyde (*Ber.*, xvi., 1333) by titration with ammonia is to a certain extent characteristic of formaldehyde, but is not applicable to dilute solutions. Legler states that 3 molecules of ammonia are equal to 4 of formaldehyde, while Lösekan (*ibid.*, 22, 1565) maintains that 3 molecules are equal to 6 of formaldehyde. This discrepancy is explained by Eschweiler (*ibid.*, 22, 1929), who shows that with methyl-orange, cochineal, tropæolin, and congo-red 6 molecules are indicated, while with litmus and phenolphthalein only 4. This is due to the acid reaction of the hexa-methylene-tetramine formed.

Plöchl (*ibid.*, 21, 2117) states that when a neutral solution of formaldehyde is mixed with ammonium chloride it becomes acid; on heating CO_2 is evolved, and trimethylamine is formed.

Kleeberg (*Annalen*, 263, 283) shows that formaldehyde combines with phenols in the presence of HCl , but he did not succeed in purifying the compounds formed.

Pulvermacher, in a series of papers, describes many condensation products with substituted ammonias; and also shows (*Ber.*, 26, 2360) that the very insoluble formalazine is produced by mixing formaldehyde and hydrazine hydrate; this yields a platino-chloride $(\text{C}_2\text{H}_4\text{N}_2)_6\text{H}_2\text{PtCl}_6$.

Trillat (*Compt. Rend.*, 116, 891) gives the following tests for formaldehyde: The solution is to be mixed with dimethylaniline acidified with sulphuric acid and agitated. After heating for thirty minutes on the water-bath, it is made alkaline, boiled until the smell of dimethylaniline has disappeared, then filtered. If the filter-paper be

moistened with acetic acid, and powdered lead oxide be sprinkled on it, a blue colour, due to the formation of tetra-methyl-diamido-diphenylmethane is produced if formaldehyde is present. Or the formaldehyde solution may be mixed with a solution of aniline (3 grammes to 1 litre), when a white precipitate of anhydro-formaldehyde aniline appears, which may be weighed. A precipitate is also given by acetaldehyde. Trillat says that, as formaldehyde easily forms condensation products, it is not always detected in food after a lapse of time.

Three years ago one of us worked with formaldehyde as a preservative for milk, and used as a method for its detection the reduction of Fehling's solution, or of ammoniacal silver nitrate solution. Quite recently Thomson (*Chem. News*, lxxi., 247) has proposed the use of the latter, and, although he modifies the test by working in the cold, he does not succeed in obtaining a reaction which is characteristic of formaldehyde.

Schiff's reagent has been used as a test for formaldehyde. It is, however, very unsatisfactory unless care be taken, for if an excess of sulphurous acid is used, no reaction is obtained with traces of formaldehyde, and any alkali combined with an acid weaker than SO_2 also gives a red coloration. The red coloration appears on warming Schiff's reagent, on blowing air through it, or even on placing it in an uncorked bottle, so that unless great precautions are taken the test is unreliable. Still, it is useful as a confirmatory test. In applying it as such to milk, we precipitate the casein with a little sulphuric acid, filter, and then add a little Schiff's reagent to the filtrate; any red colour which may appear roughly indicates the amount of formaldehyde present.

Another test which we believe to be well known, though it has not actually appeared in print, was pointed out by Mr. Hehner. It is the formation of a blue colour when milk, formaldehyde, and sulphuric acid are mixed together. This was first brought to our notice by Mr. Bevan, who had obtained a blue colour in a Leffmann-Beam experiment, which he could not account for. We suggested that it might be due to formaldehyde, but we were unable to obtain the reaction with other milks, owing to our having used an excess of formaldehyde. We find that when formaldehyde is in large quantity, say 0.5 per cent., no blue colour is obtainable.

We have since found that the above reaction is due to the albuminoids of milk. We have also obtained it from egg albumen and peptone, but not from gelatin. To obtain the reaction it is only necessary to add sulphuric acid (94 per cent. H_2SO_4 gives the best results) to the milk, when a blue ring is formed at the junction of the two fluids. The food suspected may be distilled and the formaldehyde obtained in plain aqueous solution; but we prefer the use of peptone for testing, as the blue colour is not then obscured by the charring of the organic matter by the acid.

Bearing in mind Pulvermacher's researches, we have found a reaction between formalin and diphenylamine. A solution of diphenylamine in water is made, just sufficient sulphuric acid being added as will effect solution. The liquid to be tested (or the distillate) is added to this solution and boiled. In the presence of formaldehyde a white flocculent precipitate is deposited, which is often coloured green if the acid used contained nitrates.

We find it most convenient to distil into the diphenylamine solution and then boil. This simple test we believe to be characteristic of formaldehyde.

We are engaged in determining the composition of the precipitate, and in working out the quantitative estimation of formaldehyde in this manner.

We are able to confirm Trillat's observation that after a certain time formaldehyde cannot be detected. We can obtain the reaction in milk which has not curdled.

We think from the list of methods enumerated that there is not the slightest difficulty in definitely proving the presence of formaldehyde in foods when present. Hehner's reaction, confirmed by the diphenylamine test, Schiff's test, and those proposed by Trillat, Pulvermacher and Plöchl, should be amply sufficient.

DISCUSSION.

Mr. M. A. ADAMS said he could confirm Mr. Bevan's observations as to the preservative power of formalin, having used it successfully for several years. His practice was to add it immediately on receipt of the sample before the analysis was started; four drops to a third of a pint was quite sufficient to preserve samples for a length of time.

He had found that the growth of moulds, unlike bacterial growth, was not inhibited by formalin.

Mr. RICHMOND remarked that he noticed that Mr. Bevan had found it necessary to add the formalin while the milk was still fresh, and if it was allowed to turn, formalin failed to keep it without decomposition; this fact he had also observed in connection with the use of hydrofluoric acid as a preservative some years ago. With regard to the increase in the total solids, an immense number of compounds had been prepared from formaldehyde by condensation in the presence of various bodies, and he thought it not improbable that such an action might occur when formalin was added to milk, the resulting compounds accounting for some, at any rate, of the increase. It had been found, for instance, that formaldehyde condensed very easily in the presence of lime, giving formose, and in view of the alkaline salts present in milk, it was not difficult to imagine the formaldehyde becoming converted into formose, or some other compound, the weight of which would be added to that of the total solids.

Mr. W. W. FISHER said he had made the experiment of boiling milk containing formalin with hydrochloric acid, and had obtained a blue reaction, developing into purple, the colour disappearing on more prolonged boiling. He had not worked it out, but thought that if it could be really established it might prove useful as a test.

Mr. C. A. SEYLER said that he had obtained in using Schmid's process a yellow colour, when formalin was present. In its absence he had noticed a pale violet colour at first, soon masked, however, by the yellow of caramel. On dissolving cheese in hydrochloric acid a distinct pale violet was produced, but in the presence of formaldehyde the casein was coloured a strong yellow, and became much less soluble. There was no doubt that formaldehyde had a considerable action on albuminoids. Albumin seemed to be rendered insoluble (although not precipitated at once), and, when once precipitated, it could not be got back into solution again. He had found that milk to which formalin had been added after curdling could not be brought to a thin liquid state by shaking up with ammonia.

Dr. DYER inquired whether formalin had any influence on the proportion of fat as determined by any method, or whether it was simply the non-fatty solids that were affected.

Mr. BEVAN said he had not made any direct experiments on the action of formalin on fat; all he could say was that the total percentage of fat in the milk was not affected, as far as was indicated by ordinary methods of estimation.

He could exactly confirm what Mr. Seyler had said as to the casein being rendered insoluble after precipitation. The action of formalin on gelatin was tolerably well known, and numerous patents had been taken out in connection with it for the purpose of rendering gelatin insoluble.

Like Mr. Adams, he had sometimes found moulds on the top of milk samples that had been kept for some time.

Mr. BODMER said he wished to again raise the question as to whether it would not be well, in face of the growing use of formalin in the trade, that some understanding should be come to by the Society as to the action of its members in the event of their detecting the presence of formalin in samples passing through their hands officially.

Dr. SYKES called attention to the recent investigations of Weigle and Merkel, who had found that the addition of formalin to milk rendered the casein indigestible.*

The CHAIRMAN (Mr. Otto Hehner) said that although he was fully aware of the importance of the point (especially as formalin was being used for other articles besides milk), the subject which it opened was so very wide that the Society could not deal with it on the present occasion, and he therefore hoped that Mr. Bodmer would not press his suggestion.