ON THE SEPARATION AND ESTIMATION OF FORMIC ALDEHYDE.

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SOME months ago one of us (ANALYST, xxi., 148) described a process for the estimation of formic aldehyde, depending upon the oxidation of that substance into formic and carbonic acids by potassium permanganate in alkaline solution. This process we have endeavoured, according to an intention stated in the paper referred to, to apply to the estimation of formic aldehyde in milk, and in doing so we have obtained certain results which seem worthy of notice.

It was of course necessary, in the first place, to ascertain whether pure milk yielded, when distilled, any substance capable of reducing alkaline permanganate. Examination of four different samples showed that the distillate from fresh milk exerts practically no such reducing action. The distillate from 100 c.c. of milk required, in fact, scarcely more permanganate than is necessary to give the colour indicating the end-point of the titration. Milks which had been kept several days, still more sour and decomposed milks, yielded appreciable amounts of organic matter on distillation. The process is therefore only applicable to fresh milk.

Several experiments were made on the distillation in a current of steam of milk and aqueous solutions, to which a known amount of formic aldehyde had been added. The recovery of the aldehyde was, however, slow and unsatisfactory. We found, for example, on thus distilling 100 c.c. of liquid containing 0.01 per cent. of formic aldehyde, that the first 50 c.c. of the distillate contained only one-fourth of the total amount of aldehyde added, while less than three-fourths had passed over even when 300 c.c. of distillate had been collected. Simple distillation, though rather more troublesome, was therefore resorted to. The results of three experiments with milk are here tabulated. In each case 100 c.c. of milk was distilled, the distillate being collected in fractions of 20 c.c., each of which was titrated with permanganate solution. The residue remaining in the retort was examined for formic aldehyde by Hehner's test. In the second and third experiments, the liquid was rendered acid and alkaline by the addition of a few drops of dilute sulphuric acid and of caustic soda solution respectively :

			Neutral. Grammes CH_2O .		Acid. Grammes CH_2O .		Alkaline. Grammes CH_2O .
First 20 c.c.	...	...	·0015	...	·0026	...	·0011
Second 20 c.c.	...	...	·0006	...	·0019	...	·0004
Third 20 c.c.	...	...	·0002	...	·0011	...	·0003
Residue...	...	...	none	...	present	...	none
Aldehyde added	...	...	·0090	...	·0090	...	·0094

It will be noticed that the presence of acid greatly facilitates the expulsion of the aldehyde, while that of alkali tends to retard it. Moreover, the aldehyde was only detected in the residue of the second experiment, in which acid was added. These facts indicate, perhaps, the formation of compounds of the aldehyde with some constituent of the milk, such compounds being broken up, or their formation prevented, by addition of acid.

In these experiments we were somewhat struck by the slowness with which the formic aldehyde, commonly regarded as a very volatile body, distilled over, and we therefore carried out three similar distillations of *aqueous* solutions of the aldehyde. The results are given below. The aldehyde contained in the residue remaining in the retort was in each case determined :

			Neutral. Grammes CH_2O .		Acid. Grammes CH_2O .		Alkaline. Grammes CH_2O .
First 20 c.c. ...	...	...	·0024	...	·0023	...	·0026
Second 20 c.c. ...	...	...	·0021	...	·0018	...	·0020
Third 20 c.c. ...	...	...	·0017	...	·0017	...	—
Fourth 20 c.c. ...	...	...	·0011	...	·0012	...	—
Residue ...	...	...	·0005	...	·0006	...	·0031
Total ...			·0078	...	·0076	...	·0077
Aldehyde added ...			·0078	...	·0078	...	·0078

The presence of acid or alkali is here seen to exert little or no influence upon the rate of distillation ; and it appears that the aldehyde is not completely expelled from its solutions by anything short of distillation to dryness. This result might perhaps have been anticipated if we may reason by analogy from the results obtained by Duclaux, and also by Richmond, in the distillation of the fatty acids of the acetic series.

Our experiments lead us to conclude that :

(1) The distillate from fresh milk exerts no appreciable action on alkaline permanganate, and can therefore be used for the estimation of formic aldehyde, the absence of other volatile organic bodies being assumed.

(2) The separation of formic aldehyde from milk by distillation is facilitated by acidulation with sulphuric acid. Under these conditions, the first 20 c.c. of distillate from 100 c.c. of milk will contain about one-third, and the first 40 c.c. about one-half, of the total amount of aldehyde present.

(3) The fact, which has often been adverted to, that the formalin contained in the distillate from milk does not represent the whole of that originally added, is to a great extent explained by the behaviour of solutions of formic aldehyde on distillation, and is only partially due to any specific action of the aldehyde on the constituents of milk.

DISCUSSION.

The PRESIDENT thought it would be interesting if the authors of the first paper could furnish any observations upon the application of their process to milk and other products. So far the paper only dealt with the estimation of formaldehyde in aqueous solution.

In the second paper it seemed to be implied that there was a combination between the formaldehyde and the milk. It was a known fact that formaldehyde polymerized on heating, and it might be that, during the operation of distilling, the formaldehyde polymerized into a molecule more condensed, and more difficult to decompose, than the original molecule.

Mr. HEHNER, alluding to a paper which he had some time previously read before

the Society, describing the method which had been referred to as his, said that many people had found difficulty, at first, in obtaining the special reaction with sulphuric acid in the case of milk containing formaldehyde. A suggestion made by one of the authors of the second paper had led to this difficulty being overcome. The suggestion related to the addition of a trace of ferric chloride, which greatly facilitated the reaction.

Apart from the difficulty of distilling formaldehyde from aqueous solution, there was no doubt that formaldehyde combined with certain albuminous substances. He had no experience of its action upon casein, but it certainly combined with albumin to yield a substance which did not coagulate by heat. A solution of albumin containing formaldehyde could be evaporated to dryness, the residue left being completely soluble in water. A process involving this principle had lately been patented. The inventor's conclusion was that two molecules of the albumin were condensed by formaldehyde, the resulting compound being a methylene derivative albumin.

If this conclusion were correct, it would explain why it was not possible to recover the whole of the formaldehyde added to an albuminous substance like milk, since a portion of it would have undergone change in forming the methylene derivative.

Mr. RICHMOND said that almost all organic compounds containing the —NH_2 (or =NH) group condensed with formaldehyde in the same manner as albumin. Aniline, for instance, gave a compound which was known by the name of anhydro-formaldehyde-aniline, $\text{C}_6\text{H}_5\text{NH}_2 + \text{CH}_2\text{O} = \text{CH}_2\text{NC}_6\text{H}_5 + \text{OH}_2$.

The figures given by Messrs. Leonard and Smith, in relation to fractional distillation, showed that formaldehyde conformed to the law which he had worked out for the volatile acids of the acetic series.

It was curious that higher results should be obtained from acid solutions. The substance liberated by the acid was probably not formaldehyde, but some substance which distilled at about the same rate as water. It would be interesting if some knowledge could be obtained as to the exact nature of this substance, as it would probably throw some light on the changes taking place when formaldehyde and milk were mixed and kept for some time.

Mr. CASSAL said there was no doubt that the addition of formaldehyde to milk profoundly affected the casein. He had made experiments with a view to finding whether the casein was subsequently soluble, and would submit to peptic digestion, and had found that the treatment of milk with the formaldehyde solution in the quantity prescribed by the vendors made the milk indigestible. It curdled into a condition of practical insolubility to peptic digestion. A similar effect was produced on gelatin, which was converted, by weak solutions of formaldehyde, into a hard material resembling brittle horn.

With regard to the separation of formaldehyde from milk, there could be no doubt that, as Mr. Hehner had said, it would be impossible to recover the whole amount added to a sample of milk. It was perfectly obvious that if the formaldehyde entered into combination, something must be done to liberate it.

He would like to ask if Messrs. Leonard and Smith had tried repeated distillations by steam. He understood there was only one continuous distillation in their process.

Some time previously Mr. Bevan had called attention to the fact that an increase in the weight of the residue obtained in milk analyses was found when formaldehyde had been added. As a matter of fact, if a solution of formaldehyde were allowed to evaporate spontaneously, a solid substance remained. How far that might account for what Mr. Bevan found he did not know. He believed, however, that complete reproduction of the formaldehyde could be arrived at by means of repeated distillation with water.

Mr. RICHMOND asked to be allowed to submit to Mr. Cassal a question regarding the indigestibility of casein, viz., whether Mr. Cassal had attempted to prove that the undigested casein was not the well-known dyspeptone. It was a matter of common knowledge that, on submitting casein to peptic digestion, especially in milk which contained a large quantity of lime, an insoluble substance in combination with lime was formed. Had Mr. Cassal made any comparative experiments before and after the treatment with formaldehyde? He, in conjunction with Mr. Boseley, had raised the same question with regard to the experiments of Weigle and Merkel on the same lines as Mr. Cassal.

Mr. CASSAL said that his experiments were carried out side by side, the one with milk containing formaldehyde, the other without. He had not done more than this.

Mr. HEHNER said it was a curious fact that the compound formed by the action of formaldehyde on albumin was eminently digestible. He had seen the results of experiments, which he had every reason to believe were carefully performed, showing that the compound was more digestible than ordinary albumin.

Mr. CASSAL pointed out that Mr. Hehner had said that only a certain amount of the formaldehyde entered into combination, and this combination he considered was somewhat theoretical; consequently there would still be a definite proportion of formaldehyde remaining. He suggested that it was to this extra amount that the preservative effect was due, and also the injurious effect which he referred to.

Mr. BEVAN said that, considering the large quantity of casein present in milk, and the small quantity of formaldehyde usually added, it was surprising that any of the latter was obtained at all.

Mr. LEONARD, referring to the President's remarks, said that he understood the product of polymerization was readily converted back into the aldehyde by warming with hot water.

In reply to Mr. Cassal, in the case of the steam distillation, a current of steam was passed into the milk, the operation being continued for several hours. It was not repeated, but was a single continuous operation.

The PRESIDENT, in returning the Society's thanks to the authors of the two papers, remarked upon the important part which formaldehyde played in organic nature, instancing its effects upon gelatin, which had been applied in the practical processes of photography, and its quite different action, which Mr. Hehner had pointed out, in relation to albumin. There were many points requiring elucidation in connection with the subject, which offered an encouraging field of research for young investigators.