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THE DETECTION, DETERMINATION, AND RATE OF DISAPPEARANCE OF FORMALDEHYDE IN MILK.

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IT IS well-known that when very small amounts of formaldehyde are added to milk, the latter is not permanently preserved and the color reactions indicating the presence of formaldehyde gradually become less distinct, and may finally fail. The suggestion has frequently been made that milk may be preserved for market with such a small proportion of formaldehyde that the latter will have disappeared before a sample can be tested by the analyst, who will thus fail to detect the adulteration. So far as we are aware, however, no direct evidence of such cases has been advanced. Apparently, but little attempt has been made to study the disappearance of the formaldehyde by quantitative methods. Smith[1] states that if milk containing formaldehyde is kept cool, it may stand one or two days, at least, without alteration in the amount obtained on analysis, even when the original amount was only 1 : 50,000. He adds that a trial proved that when milk containing formaldehyde is subjected to a warm and varying temperature, the amount of formaldehyde recovered by distillation is only 55 to 60 per cent. of that recovered from the same sample when fresh. On the other hand, Rivas[2] reports that even when kept in a refrigerator, mixtures of formaldehyde and milk 1 : 10,000 or 1 : 20,000 showed a marked decrease of the formaldehyde after two days, while if only 1 : 50,000 was added, the disappearance of the preservative was more rapid, being so nearly complete at the end of two days that only a weak or doubtful reaction was obtained. At higher temperatures the formaldehyde disappeared somewhat more rapidly.

Rivas' results thus indicate a much more rapid disappearance of formaldehyde than was found by Smith. In view of this discrepancy and of the fact that preservatives are added to milk mainly for the sake of saving the cost of refrigeration, we have

[1] This Journal, **25**, 1037 (1903).

[2] *Univ. of Penn. Medical Bulletin*, **17**, 175 (1904).

studied the detection and determination of formaldehyde with special reference to the rate at which it disappears from milk kept at ordinary room temperatures.

QUALITATIVE DETECTION.

The hydrochloric acid and ferric chloride test, as developed by Leach, has been found very satisfactory in this laboratory. Ten cc. of the milk to be tested are mixed, in a porcelain casserole, with an equal volume of concentrated hydrochloric acid containing about 2 mg. of ferric chloride, and the mixture heated slowly, rotating the casserole occasionally to insure solution of the curd, and finally kept at a temperature just below boiling for about a minute, unless a distinct reaction is previously obtained. In the presence of formaldehyde a violet color develops, otherwise the solution slowly turns brown. Regarding the delicacy of this test Leach states:[1] "By this test 1 part of formaldehyde in 250,000 parts of milk is readily detected before the milk sours. After souring, the limit of delicacy proves to be about 1 part in 50,000."

In an experiment to test the question whether the sourness of the milk in itself affected the delicacy of the test, we obtained two samples from the same source, one fresh and sweet showing a total acidity equivalent to 0.18 per cent. lactic acid, the other four days old, sour, curdled, and showing an acidity equivalent to 0.92 per cent. lactic acid. To each of these samples formaldehyde was added in the proportion of 1:100,000. On applying the test as given above, perfectly distinct reactions were obtained in both cases, the test being apparently just as delicate in one case as in the other. We therefore interpret Mr. Leach as claiming, not that the test is less delicate for the detection of formaldehyde in sour milk, but that (1) the delicacy of the test is about 1:250,000; (2) when 1 part of formaldehyde is added to 50,000 parts of milk and the mixture allowed to stand until the milk has become sour, enough of the preservative will still be present to be shown by this test. We have confirmed each of these claims. Sometimes, however, the browning of the heated mixture renders indistinct the violet color produced by such minute quantities of formaldehyde. In these cases, more satisfactory indications are obtained on carrying out the test with the fol-

[1] "Food Inspection and Analysis," p. 140.

lowing slight modification.[1] After heating the milk with the acid reagent as described, keeping the temperature just below the boiling-point for about a minute, add quickly from 50 to 75 cc. of cold water and observe the color carefully at the moment of dilution. The purplish violet color, which becomes apparent upon dilution, fades very rapidly, so that the advantage of this modification is entirely lost unless great care is taken to note the appearance immediately upon adding the water.

The gallic acid test, while less convenient, is, in our experience, fully as characteristic as the hydrochloric acid and ferric chloride test, and considerably more delicate. The sample of milk to be tested is acidulated with sulphuric acid and distilled in the same way as for the quantitative determination of the formaldehyde. To 5 cc. of the distillate, add 0.2 to 0.3 cc. of a saturated solution of gallic acid in alcohol and float the mixture upon pure concentrated sulphuric acid in a test-tube. In the presence of formaldehyde a blue color develops gradually at the plane of contact. The reaction is shown distinctly by pure solutions containing 1:500,000 of formaldehyde, and there is no reason to doubt that it is equally delicate when applied to the detection of formaldehyde in milk. A sample of milk which originally contained 1:50,000 formaldehyde ceased to give any reaction by the hydrochloric acid and ferric chloride test after five days, but the distillate subsequently obtained from 30 cc. of this sample gave an unmistakable formaldehyde reaction when tested with gallic acid.

QUANTITATIVE DETERMINATION.

For the determination of formaldehyde, 300 cc. of milk in a round-bottomed flask of about 1 liter capacity are acidulated with 3 cc. of dilute (1:3) sulphuric acid and distilled over a small rose-top burner until 60 cc. of distillate are obtained. The formaldehyde in this distillate is determined by the potassium cyanide method.[2] About one-third of the formaldehyde[3] in the milk is recovered in this way.

The following results were obtained upon freshly prepared solutions:

[1] Sherman: *School of Mines Quarterly*, **26**, 408 (1905); "Methods of Organic Analysis," p. 228.

[2] Romijn: *Z. anal. Chem.*, **36**, 18 (1897); Smith: This Journal, **25**, 1028 (1903); Williams: *Ibid.*, **27**, 598 (1905).

[3] Leonard and Smith: *Analyst*, **22**, 5 (1897).

FORMALDEHYDE IN WATER.

1 : 1000 distilled at once ; 36.1 per cent. recovered.
1 : 5000 " " " 36.6 " " "
1 : 10,000 " " " 34.0 " " "
1 : 40,000 " after 2 days ; 38.9 " " "

FORMALDEHYDE IN MILK.

1 : 10,000 distilled at once ; 31.9 per cent. recovered.
1 : 20,000 " " " 34.3 " " "

These results agree so closely with those obtained by Smith[1] that further tests of the method upon fresh solutions seemed unnecessary.

RATE OF DISAPPEARANCE.

Quantitative determinations show a gradual disappearance of formaldehyde even from its solutions in distilled water, the rate of disappearance being more rapid the more dilute the solution. For example:

Solution in distilled water 1 : 1000 after 168 days[2] showed 99.6 per cent. of the formaldehyde originally present.

Solution in distilled water 1 : 5000 after 168 days showed 56.8 per cent. of the formaldehyde originally present.

Solution in distilled water 1 : 10,000 after 168 days showed only traces of the formaldehyde.

These determinations were made by the potassium cyanide method which has been shown[3] to include as formaldehyde any paraformaldehyde which may be present. Hence the low figures obtained upon the more dilute solutions show an actual destruction, and not merely a polymerization of formaldehyde. In the experiments upon the disappearance of formaldehyde in milk, parallel determinations upon water solutions of the same concentration have been made by the distillation method described above, distilling until the distillate measures one-fifth the volume of sample taken.

The principal results obtained in studying the rate of disappearance of the formaldehyde are given in the following tables, the first of which shows the figures obtained by the approximately quantitative method outlined above, while the second shows the intensity of the color reactions obtained by the hydro-

[1] This Journal, **25**, 1036 (1903).
[2] The bottles containing these solutions had been opened several times.
[3] Williams : This Journal, **27**, 598 (1905).

chloric acid and ferric chloride test, at different intervals after adding the formaldehyde to the milk. The account of experiments by Bigelow[1] indicating a somewhat more rapid disappearance of this reaction was received during the writing of this paper.

DISAPPEARANCE OF FORMALDEHYDE AS SHOWN BY APPROXIMATELY QUANTITATIVE ESTIMATIONS.

Series No.	Description of sample.		Distilled after standing.	Proportion of original formaldehyde recovered in distillate (one-fifth volume). Per cent.	Proportion of original formaldehyde estimated to have disappeared. Per cent.
1.	Formaldehyde added to :				
	Milk	1 : 10,000	2 days	25	38
	"	1 : 20,000	2 "	23	42
	"	1 : 40,000	2 "	10	75
	Water	1 : 40,000	2 "	39	—
	Milk	1 : 10,000	4 "	20.5	48
	"	1 : 20,000	4 "	3.7	90
	"	1 : 40,000	4 "	Trace	(Nearly all)
	Water	1 : 40,000	4 "	36	8
	"	1 : 40,000	9 "	25	38
	"	1 : 40,000	18 "	16	60
	"	1 : 40,000	28 "	10	75
2.	Formaldehyde added to :				
	Milk	1 : 10,000	17–25 days	5–6	85
	Water	1 : 10,000	11 "	37	5
3.	Formaldehyde added to :				
	Fresh milk	1 : 1000	117 "	21	43
	Sour milk	1 : 1000	133 "	20	45
	Water	1 : 1000	149 "	39	—
	Fresh milk	1 : 5000	117 "	3.9	90
	Sour milk	1 : 5000	135 "	3.1	92
	Water	1 : 5000	156 "	22	42
4.	Formaldehyde added to :				
	Diluted milk[2]	1 : 20,000	1 day	[3]	25
	Water	1 : 20,000	11 days	[3]	25
	Diluted milk[2]	1 : 40,000	1 day	[3]	25
	Water	1 : 40,000	11 days	[3]	45

[1] Bull. 90, Bur. Chem., U. S. Dept. Agriculture.

[2] Milk diluted with an equal volume of distilled water.

[3] Figures not comparable with those given in this column on account of differences in experimental methods.

DISAPPEARANCE OF FORMALDEHYDE IN MILK AS INDICATED BY COLOR REACTION WITH HYDROCHLORIC ACID AND FERRIC CHLORIDE.

Formaldehyde added in proportion of	Tested after standing.	Reaction obtained.	Condition of sample.
1 : 250,000	½ hour	Fair	Fresh
1 : 250,000	2 days	None	Very sour, completely curdled
1 : 100,000	½ hour	Strong	Fresh
1 : 100,000	2 days	Faint	Sour and curdled
1 : 100,000	5 "	?	Curd separated
1 : 50,000	2 "	Fair	Sour and curdled
1 : 50,000	5 "	?	Curd largely separated
1 : 40,000	4 "	Fair	Sour
1 : 40,000	14 "	Faint	Curdled and separated
1 : 20,000	4 "	Strong	Curdled, very sour, some gas
1 : 20,000	46 "	Faint	Curd dissolving
1 : 20,000	66 "	"	" "
1 : 20,000	216 "	None	Curd mostly dissolved
1 : 15,000	150 "	"	" " "
1 : 10,000	46 "	Distinct	Sour and curdled
1 : 10,000	66 "	"	" " "
1 : 10,000	216 "	Faint	Curd largely dissolved
1 : 5000	216 "	Strong	Curdled
1 : 1000 (A)	350 "	"	Normal
1 : 1000 (B)	15 months	"	Slight evidence of digestion
1 : 1000[1] (C)	3 years	Distinct	Curd largely digested
1 : 1000[1] (D)	3 "	None	" " "
1 : 1000[1] (E)	4 "	"	" " "
1 : 800[1]	3 "	Distinct	" " "
1 : 600[1]	5 "	Strong	Loose precipitate of curd, no apparent digestion

SUMMARY OF PRINCIPAL RESULTS.

By the method here used an approximate estimation of formaldehyde in milk can be made at any concentration greater than 1 : 160,000 and the rate of disappearance can be studied quantitatively until this dilution is reached.

Aqueous solutions containing 1 : 5000 to 1 : 40,000 of formaldehyde lost strength steadily on standing at room temperature, the loss increasing with the dilution and being due to an actual destruction and not merely to polymerization of the formaldehyde.

Formaldehyde added to milk in such proportions as are most likely to be used commercially (1 : 10,000 to 1 : 40,000), disappeared ten to twenty times as rapidly as from water solutions

[1] In these cases the amount of formaldehyde added is only approximately known.

of the same concentration. Thus formaldehyde added to distilled water in the proportion of 1:40,000 had diminished to 1:160,000 in twenty-eight days, while in a parallel experiment with milk it showed the same diminution in two days.

Stronger solutions are much more stable. Formaldehyde in water 1:1000 showed no appreciable loss in five months. The rate of disappearance of formaldehyde from milk containing 1:1,000 was practically the same as from water containing 1:5,000.

The rate of disappearance did not seem to be affected by allowing the milk to become sour before adding the formaldehyde.

The hydrochloric acid and ferric chloride test for formaldehyde in milk is sensitive to a dilution of 1:250,000. Sourness of the milk does not in itself diminish the delicacy of the reaction, but when milk is preserved by means of formaldehyde the latter will have largely disappeared before the milk becomes sour. In all of the cases here studied, however, distinct reactions were obtained at least as long as the milk remained sweet and of normal appearance. That these results indicate a less rapid disappearance of formaldehyde than was found by Rivas or by Bigelow is thought to be due mainly to the greater delicacy of the test as modified for our experiments, though doubtless differences in laboratory temperature and in the nature of the milk used may also have affected the results.

The gallic acid test is much more delicate than the hydrochloric acid and ferric chloride test and gives more conclusive results with samples which have stood until the formaldehyde has largely disappeared.

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THE PHOSPHATES OF CALCIUM. I.[1]

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WHEN the phosphates of calcium are brought into contact with water they are partially decomposed, owing to hydrolysis. At ordinary temperatures this decomposition generally proceeds at a very slow rate, and in consequence equilibrium conditions

[1] Published by permission of the Secretary of Agriculture.