THE VALUE OF A TITRATION TEST FOR ACIDITY AT THE RECEIVING PLATFORM

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Recently the maintenance of an acidity standard for fresh milk by condenseries and powdered milk manufacturers has been the object of adverse criticism, based on the established fact that any titration test applied to milk fresh from the cow will indicate an apparent acid condition, which cannot be due to lactic acid, the cause of sour or curdled milk, since the presence of this acid indicates bactericidal action on the milk sugar, a process requiring a lapse of more or less time, according to conditions. Brew (1) has pointed out that this apparent acidity may be as high as 0.25 per cent and yet the milk be processed successfully, though his evidence on that score is negative. Sommers and Hart (2) found in one herd variations on titrable acidity of 0.102 to 0.257 per cent, 52 per cent being above 0.18 per cent, and showed that this bears no relation to the heat coagulation of milk. McInerney (3) found one herd of five cows varying from 0.175 to 0.205 per cent acidity with a composite of 0.19 per cent, and in another mixed herd averages of 0.123 to 0.18 per cent according to breed, with milk from individual cows as high as 0.22 per cent. Van Dam (4) holds that titrating milk leads to wrong conclusions as this measures "potential" acidity, while hydrogenion methods measure the "actual" acidity. Henkel (5), in 10,000 determinations on the milk of individual cows, found variations of 0.1375 to 0.225 per cent, though mixed herd milk had much narrower limits. Baragiola (6) emphasizes the necessity of differentiating between the degree of acidity or concentration of the hydrogenion, expressed in millimoles per liter, and the acid content (total acid, titrable acid, or acid value), expressed in cubic centimeters of normal solution or grams of lactic acid per liter.

The cause of the acid reaction of fresh milk to phenolphthalein has been the object of much investigation, which has resulted in narrowing down the probabilities to two or three sources, or a combination of them. Van Slyke and Bosworth (7) have presented good evidence to substantiate their theory that the apparent acidity is due to the acid phosphates present. Richmond (8) attributes it partly to acid phosphates and partly to dissolved carbon dioxide, though Van Slyke and Baker (9), on the contrary, found that the degree of acidity, as measured by titration tends to decrease with increasing CO_2 content, a condition which Baker and Breed (10) believe is due to the entrance of bicarbonate from the blood of the cow. Bordas and Touplain (11) investigated the titrable acidity, with phenolphthalein, of milk serum, the coagulum containing the insoluble salts, the casein plus the insoluble salts, and the pure casein separated by the alcoholic method. They concluded that the original acidity is due to casein and that no free acid or acid salts exist in milk at the outset. Bordas (12) made further studies and reported that the increase in acidity is due to casein liberated from combination with calcium by the formation of calcium lactate.

This conflicting evidence as to the cause of titrable acidity in fresh milk is of less importance from the standpoint of factory practice than the question of the justice of an acid standard to the factory patrons. If it is true that any considerable number of cows or any one breed of cattle consistently give milk which has a higher titrable acidity than the standard maintained or if the acid test fails to measure the quality of the milk at the receiving platform, the contention of Brew, Hart and others that manufacturers of milk products are in error in maintaining a rejection test based on titrable acidity must be acknowledged and every effort bent toward development of some other test which may distinguish poor milk with more certainty and yet be as rapid of manipulation, as the titration method. Up to the present time no substitute has been devised which meets the latter requirement, the vital one from the manufacturing standpoint. This being the status of the question, the attention of this laboratory was turned to an investigation of the titrable acidity of individual cows and of herds.

The practical experience of a number of milk inspectors was reviewed at the outset and the gleanings summarized into three pertinent facts. First, that the average acidity of herd composite milk as received at the factory was well below 0.18 per cent, though it was probably true that individual cows of certain herds or breeds gave milk higher than that in acidity. Second, that milk was not rejected on the basis of titrable acidity alone, for an acid test was resorted to only when the odor and flavor of the milk suggested to the experienced inspector that it was questionable. In other words, the acid test is applied mainly as an adjunct to the senses of the trained inspector. This is in line with the best practice of the day. As Hunziker (13) states:

> Experience has shown that, while it is necessary for the condenseries to decide on a maximum acidity of milk above which all milk be rejected, the nose and the palate of the experienced inspector are better criterions than the acid test alone, as to the fitness of milk for condensing. Acid tests are valuable in the case of uncertainty and suspicion as to the quality of any given can of milk. . . . . What has been stated concerning the necessity of high quality of fresh milk in the successful manufacture of condensed milk is equally true in the manufacture of milkpowder. . . It is especially essential that it arrive at the factory perfectly sweet, since acidity tends to lower the solubility of the finished product.

This has been confirmed by our own experience during the past twelve years, during which approximately 10,000,000 cans of milk have been taken in at our receiving platforms. During the flush of the past season an average of 12,000 cans were handled daily, with complete freedom from curdled milk or sour cream. Third, our wide experience has demonstrated clearly that it is impossible to manufacture a heavy cream of less than 0.09 to 0.095 per cent acid or a light cream of less than 0.11 to 0.115 per cent from milk testing 0.17 per cent at the receiving room. Before this fact had been established thousands of pounds of fresh cream became sour during transportation to market. This shipping quality of the fresh cream is an important item. It has been repeatedly demonstrated that heavy cream of 0.10 per cent or a light cream of 0.12 per cent acid may

be apparently in excellent shape when it leaves the factory, but it invariably sours, more quickly in the warm months, before it reaches the retail customer. To insure a cream that will stand up in such shape as to meet the exact demands of the trade, it is essential that the milk as received at the factory be below 0.17 per cent titrable acid. More important, probably, than the souring of this fresh cream is the high acid flavor and the greater tendency toward curdling which appears in milk powdered from fluid milk of high acidity. Maintaining an uniformly high standard of quality in powdered milk means efforts beginning at the farm and this necessitates constant supervision of production conditions. The acid titration test provides one method of checking up on these, as any marked bacterial growth or lack of proper cooling is reflected in increased acidity. Long experience has shown that high acid milk taken in at the receiving platform continues to develop acidity so rapidly that milk powder dried from it has a peculiarly disagreeable acid flavor and, when used for cooking, will curdle easily.

To ascertain definite facts concerning the apparent or titrable acidity of fresh milk and of milk at the receiving stand, a series of investigations were carried on by the department during the year of 1920. Herds in seven different territories in western New York and Pennsylvania were tested during the months of January, March, July, September and October. For the most part the cattle were mixed, with Holstein, Guernsey and Jersey the predominant breeds. In one territory practically all of the cows were Jerseys and in another mostly Holsteins. A total of 766 herds were tested.

The initial work was done on the milk of individual cows, the first titration being run at the farm immediately upon the completion of each milking. Marshall's method (14) was used, the 0.1 N alkali having been carefully prepared and standardized against standard N/5 HCl, previously tested by precipitation with $AgNO_3$ and ignition. The milk was allowed to stand for a few minutes after being drawn to allow the froth to subside, a 9 cc. sample being then withdrawn with a pipette and placed in a white china cup. Titration was made with 3 or 4 drops of

1.25 per cent phenolphthalein, with no added water, with 9 cc. of added water and with 18 cc. of added water. Sufficient tests were run to determine that the addition of water did not affect the titration value expect to make the end point more easily visible. Alkali was added till a faint pink, permanent for one minute, was apparent. The milk from each cow was next strained into a can through filter cloth and a pint sample placed in a sterilized, glass-stoppered bottle. Upon the completion of the whole milking these jars were cooled and taken to the factory, where the development of acidity was followed closely Titrations were made at the end of 16, 20, 24, 40, 44, 47, 50 and 60 hours, souring being induced in one series by elevating the temperature at the end of forty-four hours from 54° to 72°. The effect of pasteurization on the acidity of the milk was tried. In one series this was done at the end of twenty-four hours by raising the temperature to 145° for thirty minutes. The samples were in glass-stoppered jars, giving no outlet for any volatile gas, to which may be due the average increase of 0.005 to 0.01 per cent in the acidity of this series. In another group pasteurization was carried out in open glass jars after forty-eight hours in a similar manner. Here there was a decrease in acidity of as much as 0.055 per cent in one case and an average decrease of 0.015 per cent.

Since measurements of the acidity of milk from individual cows indicated no unusually high values attention was turned to an investigation of mixed herd milk as received at the factory. The method used was to mix the milk in each can, as received, with a dipper and then to take an aliquot sample from each can of the milk brought in from any one herd, the whole being mixed to give a herd composite. These samples were placed in sterilized glass-stoppered jars and determinations made as soon as possible. Ordinarily double titrations were made with 9 cc. of milk and 18 cc. of water with occasional check runs with no added water. In all cases where the milk showed 0.17 per cent or higher acid an investigation was made of any conditions which might have been responsible for it and a check-up was run on the fresh milk from the individual members of the herd at the farm. In order

to ascertain whether high acid corresponded with high solids not fat, as contended by some observers, the current ten-day butterfat test of each herd as regularly run in the factory was recorded and used as a criterion, since high butterfat usually accompanies high solids not fat.

In table 1a are given the results of tests on the individual milk of one group of cows. Temperatures of the samples at time of titration are recorded at the foot of each column. These cows were tested on January 29. Table 1b shows the results obtained from a second group of cows tested on March 26. The dates when the cows freshened are shown in column 2. Temperatures of samples are recorded as above.

Variations in acidity range from 0.10 to 0.175 per cent with an average of 0.136 per cent, ten being below and eight above that figure. The composite of the mixed milks is 0.145 and 0.14 per cent respectively. In six cases, cows 8, 9, 10, 11, 14 and 17, the acidity was lower after sixteen hours than when the milk was freshly drawn, a phenomenon previously observed by Koning. That there is some relation between acidity and the period of lactation is indicated by the fact that the cows that were farthest along, cows 11, 12, 14, 15 and 16, show the lowest acidities. The slow development of acidity when milk is quickly cooled and kept at low temperature is worthy of note. The results obtained are somewhat lower than the majority of those reported by other observers. In only one case, cow 7, would any of these milks have been rejected on a standard of 0.17 or 0.18 per cent and in neither case would the composite milk have been refused, the most important conservation from the standpoint of factory practice or of the producer.

In table 2 are given the results obtained on mixed herd milk in seven territories as received at the factory. Under each 0.005 per cent of acid are listed the number of herds showing that amount, with the average butterfat test of the group immediately below.

In checking up the herds where values higher than 0.165 were in recorded the following results were obtained. The one sample territory A was 0.36 per cent when tested and was curdled four

hours after being received. Of the two samples showing 0.17 in territory C, in both cases improper cooling in conjunction

TABLE 1

(*A*)

COW NUMBER	ACIDITY AT MILKING	AFTER 16 HOURS	AFTER 20 HOURS	AFTER 24 HOURS
	per cent	*per cent*	*per cent*	*per cent*
1	0.14	0.15	0.155	
2	0.10	0.125	0.115	
3	0.12	0.14	0.15	
7	0.11	0.15	0.13	
5	0.13	0.15	0.15	
6	0.115	0.135	0.135	
7	0.17	0.18	0.18	
8	0.13	0.12	0.125	
Composite of above.....	0.145	0.145	0.145	0.145
Temperature of above	70°F.	58°F.	57°F.	58°F.

(*B*)

COW NUMBER	WHEN FRESHENED	ACIDITY AT MILKING	AFTER 16 HOURS	AFTER 20 HOURS	AFTER 24 HOURS	AFTER 40 HOURS	AFTER 44 HOURS	AFTER 47 HOURS	AFTER 50 HOURS	AFTER 60 HOURS	CONDITION OF MILK
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
9	February	0.17	0.15	0.155	0.16	0.155	0.155	0.155	0.155	0.20	Turning
10	January.....	0.175	0.155	0.16	0.16	0.165	0.16	0.16	0.16	0.165	Sweet
11	September...	0.145	0.14	0.14	0.14	0.145	0.14	0.14	0.14	0.165	Turning
12	September...	0.135	0.135	0.14	0.14	0.14	0.14	0.14	0.14	0.32	Sour
13	January.....	0.155	0.16	0.165	0.165	0.175	0.18	0.175	0.175	0.185	Turning
14	September...	0.11	0.105	0.115	0.115	0.155	0.115	0.115	0.115	0.15	Sweet
15	September...	0.12	0.125	0.125	0.13	0.13	0.13	0.13	0.13	0.14	Sweet
16	December....	0.125	0.14	0.13	0.135	0.135	0.135	0.135	0.135	0.175	Turning
17	January.....	0.145	0.13	0.14	0.14	0.135	0.14	0.145	0.145	0.225	Sour
18	March	0.15	0.16	0.165	0.165	0.165	0.165	0.165	0.16	0.205	Turning
Composite of above.....		0.14	0.14	0.145	0.15	0.15	0.15	0.15	0.16	0.55	Sour
Temperature of above.....		70°F.	52°F.	53°F.	53°F.	54°F.	54°F.	72°F.	74°F.	76°F.	

with hot weather was found to be the cause. Tests made at the farm at milking time showed composits of 0.135 and 0.14 re-

spectively, with no individual cows of high acid. The one sample higher than 0.17 when received was composed of milk from two cans, one of which was rejected as sour after the sample had been mixed. Of the high acid herds in territory D, of which there are two, tests made at the farm showed an acidity on the composite of 0.15 per cent in one case. The other herd consisted of three cows, which gave fresh milk testing 0.15, 0.175 and 0.18 per cent respectively. The farmer was keeping the milk

TABLE 2

FACTORY	0.11	0.12	0.125	0.13	0.135	0.14	0.145	0.15	0.155	0.16	0.17	0.17–0.36
A.....			1	6	13	31	18	17				1
Average butterfat...				3.46	3.65	3.52	3.55	3.72				
B.....	1		2	12	15	15	16	9				
Average butterfat...	5.0		3.92	3.82	4.03	4.16	4.00	4.01				
C.....			5	11	31	41	37	43	28	2	2	1
Average butterfat...			3.5	3.55	3.52	3.51	3.50	3.54	3.57	3.52	3.50	
D.....			1	22	18	25	12	14	2	6	1	1
Average butterfat...			3.5	3.95	3.93	3.89	3.91	3.77	3.60	3.52	4.30	5.0
E.....	5	14		28		39		15		2	1	
Average butterfat...	3.73	3.70		3.85		3.89		3.93		3.70	3.60	
F.....				14		42		20		18	5	
Average butterfat...				3.71		3.74		3.83		3.93	3.82	
G.....	2	14		37		23		19		7		
Average butterfat...	3.98	3.70		3.93		3.93		3.80		4.00		

from the first cow at home for his own use. The mixed milk of the other two cows gave a value of 0.18 per cent. This is an unusual condition. The only herd showing as high as 0.17 in territory E was tested first at the farm for a composite with 0.16 per cent acid apparent. A check-up made the following night on the milk from the individuals of the herd gave results as follows: 0.15, 0.15, 0.12, 0.11, 0.18, 0.16, 0.15, 0.10, 0.13, 0.16 and 0.18 per cent, an average of 0.145 per cent. In con-

nection with these results it may be mentioned that these tests being made in October when the pasture was very short, this farmer was feeding sweet corn to his cows just prior to milking. In territory F tests were made at the farm on the milk from the five herds showing 0.17 per cent acid at the factory. Composites taken at milking time gave 0.14, 0.14, 0.15, 0.16 and 0.17 per cent respectively. Conditions prevented tests on the individual cows of this last herd.

The average acidities in the various territories were: A—0.141, B—0.139, C—0.44, D—0.141, E—0.135, F—0.144, G—0.136. The average acidity of the 766 herds, using the values originally obtained at the factory and including the two cases where the milk was palpably sour, was 0.140 per cent. Examination of the butterfat contents and the deduced solids not fat of the various herds, territories and groups indicate that there is no consistent dependence of high acidity upon high solids-not-fat content. In fact, territory B, where the cattle are practically all Jerseys, was third from the lowest in average acidity and had no values higher than 0.15 per cent. Among the 766 herds examined only two showed conditions, existent in the cows themselves causing an apparent acidity of 0.17 per cent or higher, and one of these might have been eliminated had it been possible to make further tests. Stated differently, only 0.26 of one per cent of all the herds tested, representing 7700 cows, furnished milk which would have been rejected on the basis of an apparently high acid condition, provided the milk was properly and sanitarily handled. Where this was not done such a test proved of value in detecting milk which was improperly cooled or contaminated in some manner.

To summarize the results obtained we may say that the normal acidity of fresh milk of individual cows is from 0.14 to 0.145 per cent, that the normal acidity of composite herd milk as received at the factory is 0.140 per cent and that where milk is handled in a cleanly and careful manner it will not be rejected on the basis of any acid test now in use by the manufacturers of milk products. The value of the acid test in checking the methods of production is, accordingly, clearly demonstrated and

its ease of application combined with this demonstrated reliability warrants its use until such time as some other equally rapid and more dependable method of determining the quality of milk shall have been perfected. Granted that the acid test occasionally detects milks which naturally have an acidity higher than the standard, it must be admitted that such milk is abnormal and comes from abnormal cows. That the quality of this milk may or may not be poorer does not enter into the question. Such milk is abnormal and no practical working scheme can allow for all abnormalities. Milk is occasionally found with butterfat or total solids content below the legal minimum, but who would argue therefrom that the standards maintained by Federal, State and Municipal authorities should be lowered? The percentage of cows and herds showing abnormally high acid is so small as to be negligible and the manufacturer is doing no injustice to the producer when he insists that all milk must be delivered with an acidity below 0.17 or 0.18 per cent, particularly when such a test is applied as an adjunct to the nose and palate of the experienced inspector.

REFERENCES

(1) BREW, J. D.: Milk Dealer, April, 1920.
(2) SOMMER, H. H., AND HART, E. B.: Jour. Biol. Chem., xl, 137–149.
(3) MCINERNEY, T. J.: Jour. Dairy Sci., iii, 227–229.
(4) VAN DAM, W.: Verslag. Land. Onderzoek., Ryklandbouwproefstat, 1918, v, 24.
(5) HENKEL, TH.: Milchwirtsch. Zentr., 3, 340–69 (1907).
(6) BARAGIOLA: Mitt. Lebensm. Hyg., 3, 13–22.
(7) VAN SLYKE, L. L., AND BOSWORTH: Jour. Biol. Chem., xix, 73–76.
(8) RICHMOND: Dairy Chemistry.
(9) VAN SLYKE, L. L., AND BAKER, J. C.: Jour. Biol. Chem., xl, 345–356.
(10) BAKER, J. C., AND BREED, R. S.: Jour. Biol. Chem., xliii, 221–236.
(11) BORDAS AND TOUPLAIN: Ann. fals., 4, 297–301.
(12) BORDAS: Orig. Comm. 8th Intern. Congr. Applied Chem., 18–67.
(13) HUNZIKER, O. F.: Condensed Milk and Milk Powder, 11th edition, 45, 236.
(14) MARSHALL: Wisconsin Agric. Expt. Station Bull. 129.