yet there is a certain reliable mean value for both. These values, with the fluidities, are:

	η	φ
Butter.....	0.3200	3.125
Oleomargarine.....	0.3500	2.857

An adulteration of 10 per cent margarine in butter could be readily detected in the apparatus used in any case. Since pure butters from any one creamery vary very little, by finding the mean value for such products, admixture of a foreign fat of different viscosity could be shown if even only 1 per cent were so added.

SUMMARY

1. Oleomargarine fats are always more viscous than butter fats except, of course, where the viscosity of the former is greatly lowered by the introduction of large amounts of liquid fats as indicated by a chemical analysis.

2. On standing, the viscosity of butter probably increases to a maximum due to a loss of volatile acids, and then becomes less viscous as putrefaction sets in.

3. Although the viscosities for both fats vary somewhat in products from different sources, the fluctuation is always about a mean value which might be assumed without great error as a standard.

4. The viscosities of the mixtures are not strictly additive.

5. The fluidities are practically linear functions of the temperature.

6. The fluidities of the mixtures are additive, so that these, and not viscosities, should be the basis for any comparison.

7. Assuming that the fluidity of butter does not vary more than 5 per cent in value, an adulteration of 10 per cent oleomargarine can be detected with assurance by the method of determination used.

CLARK COLLEGE
WORCBSTER, MASS.

THE PROPERTIES OF WATERED MILK

By EDWARD W. LONG AND CLARENCE E. MAY

Received April 2, 1913

Much work in the detection of added water in milk has been done by the usual chemical methods. So far as the authors are aware, no extensive studies have been made of the changes met where hard well water instead of distilled water has been added to milk, or where sucrose has been added to watered milk to build up the refractometer reading, or where additions of sucrose have been made to whole milk serum to build up the immersion refractometer reading.

The standard composition of milk has been well established, and published results of numerous analyses of American cow's milk are well known.¹ In recent years the method of detecting watered milk has been largely a study of the deportment of the given sample of milk when the corresponding milk serum was prepared and examined with the Zeiss immersion refractometer. Various methods have been suggested

for the preparation of the milk serum prior to the examination of the refractive power of the serum. Villiers and Bertault,^{2,3} as early as 1898, devised a method using acetic acid for the removal of milk proteins. Matthes and Müller,³ in 1903, made use of the Zeiss immersion refractometer for the examination of the serum which they obtained from spontaneously soured milk. Leach and Lythgoe,⁴ in 1904, made use of the immersion refractometer in examining milk serum prepared by the Woodman method. To 100 cc. of milk at about 20° C., 2 cc. of 25 per cent acetic acid were added, well mixed and placed on a water bath at 70° C. for 20 minutes. The mixture was then cooled for 10 minutes in ice water and filtered. The main difference between their method and those formerly used was in the heating of the acid-milk mixture for longer times at lower temperatures prior to filtration. Baier and Neumann⁵ used an asapol-citric acid mixture as the precipitating agent. The serum so prepared was examined with the Wollny milk fat refractometer. Ackermann⁶ used calcium chloride as the precipitating agent in the preparation of milk sera. With so many procedures available, it seemed desirable to compare the various methods on samples of known purity. This was done by Lythgoe and Nurenberg.⁷ They found some methods had certain advantages over other methods but for ease of manipulation and getting concordant results, the Woodman acetic acid method as used by Leach and Lythgoe was preferred.

Other methods that have been useful in the detection of added water to milk are dependent on the preparation of the milk serum and the using of this serum in various ways such as the determination of the specific gravity, the nitrate reaction with diphenylamine, the determination of the freezing point, the determination of the electrical conductivity and the determination of the index of oxidation.

Using the specific gravity method of examination, Bull⁸ found that in eight cases 5 per cent added water was distinguishable, in ten cases 10 per cent added water was distinguishable and in fourteen cases (all examined) 15 per cent added water was distinguishable. Although the method seemed more delicate than the refractometer method, the author felt the refraction method more reliable.⁹

Varying interpretations are given to the estimation of nitrates in milk as indicating the addition of water. They are mentioned here to complete the bibliography. Tillman¹⁰ claimed that water containing 10 mg. N₂O₅ per liter could be detected when added to milk in amounts equal to 5 per cent of the milk. Galvagno¹¹ claimed that the nitrate reaction was valueless, while

¹ Reference to Villiers and Bertault, *THIS JOURNAL*, **1**, 38.

² Villiers and Bertault, *Bull. Soc. Chim.*, **19**, 305.

³ Matthes and Müller, *Z. oeffentl. Chem.*, **10**, 173.

⁴ Leach and Lythgoe, *J. Am. Chem. Soc.*, **26**, 1195.

⁵ Baier and Neumann, *Z. Nahr. Genussm.*, **13**, 369.

⁶ Ackermann, *Ibid.*, **4**, 186; *Chem. Abstr.*, **1**, 1588.

⁷ Lythgoe and Nurenberg, *THIS JOURNAL*, **1**, 38.

⁸ Bull, *Ibid.*, **3**, 44.

⁹ Woodman, *J. Am. Chem. Soc.*, **21**, 503.

¹⁰ Tillman, *J. Soc. Chem. Ind.*, **30**, 44.

¹¹ Galvagno, *Chem. Abstr.*, **3**, 2838.

¹ Leach, Textbook, "Food Analysis," 2nd Ed., p. 127.

Rothenfasser^{1,2} concluded that the nitrate reaction was given too little rather than too much attention.

Fischer^{3,4} found the freezing point of whole milk to be fairly constant, and when the watering of milk was not greater than 5 per cent, he was not able to detect with certainty the presence of the added water. With greater degrees of watering he was able to notice differences in the freezing points of the mixtures.

Flohil,^{5,6} on the one hand, found that even with 20 per cent added water no marked change in the electrical conductivity sufficient to throw the sample of milk outside of the limit for undiluted milk was noticed, while on the other hand Binaghi^{7,8} maintained that the electrical conductivity afforded a valuable indication of the presence of added water.

Comanducci^{9,10} devised a method for the determination of the extent of watering or skimming of milk based on the fact that the number of cubic centimeters $N/10$ $KMnO_4$ (H_2SO_4) necessary to oxidize a given quantity of genuine milk was nearly constant. The author claimed that this method could be used to determine the percentage of water added or the percentage of cream removed, providing the milk had not been both watered and skimmed.

Further, Burr and Berberich¹¹ have proposed a method for determining the watering of milk by means of examining the ash content of the milk serum. They have found this figure to be in between 0.797 per cent and 0.817 per cent for whole milk and for naturally-soured milk the figure was quite constant.

Richmond¹² has found that the amount of water added to milk can be determined by adding the difference between the specific gravity of the sample and 1000 to the figure representing the percentage of fat in the milk. Unadulterated milk was found to give a value of 36, but 34.5 was considered a safer limit. This method is perhaps of less value.

In the present investigation, the authors have used the acetic acid method for the preparation of the milk serum. This involved treating 100 cc. of milk with 2 cc. 25 per cent acetic acid, mixing thoroughly and heating stoppered in a water bath at 70° C. for 20 minutes. Besides using the whole milk sera, we have used various dilutions of milk and have employed various temperatures for reading the Zeiss immersion refractometer.

Using a number of samples of milk, we have studied the effect of temperature on the readings when they were taken at 15° C. and each respective degree of temperature up through 20° C. The following results will serve as an example; corrected readings are given:

¹ Rothenfasser, *Chem. Abstr.*, **3**, 2988.

² Rothenfasser, *Z. Nahr. Genussm.*, **18**, 353.

³ Fischer, *Chem. Abstr.*, **2**, 1166.

⁴ Fischer, *Pharm. Ztg.*, **53**, 48.

⁵ Flohil, *Chem. Abstr.*, **5**, 3598.

⁶ Flohil, *Chem. Weekblad*, **8**, 605.

⁷ Binaghi, *J. Soc. Chem. Ind.*, **29**, 1404.

⁸ Binaghi, *Biochem. Ztg.*, **26**, 60.

⁹ Comanducci, *Chem. Abstr.*, **1**, 1588.

¹⁰ Comanducci, *Gazz. chim. ital.*, **36**, II, 813.

¹¹ Burr and Berberich, *Chem. Abstr.*, **2**, 3115.

¹² Richmond, Leffman and Beam, "Food Analysis," p. 216 (reference).

DILUTION	15° C.	16° C.	17° C.	18° C.	19° C.	20° C.
Whole milk.....	46.05	46.0	45.8	45.6	45.3	45.1
20 parts added water.....	40.4	40.15	39.9	39.65	39.4	39.15
40 parts added water.....	33.8	33.7	33.55	33.3	33.1	33.0
60 parts added water.....	27.85	27.7	27.5	27.3	27.15	27.0

We have examined ten samples of milk obtained from a local dairy. The same milk on being diluted with water until the added water amounted to 20, 40 and 60 per cent, respectively, of the mixture was acidified and the serum examined with the refractometer. The following results were obtained at 20° C:

Sample	Whole milk	20 per cent H ₂ O	Diff.	40 per cent H ₂ O	Diff.	60 per cent H ₂ O	Diff.
1	46.45	39.4	7.05	33.3	6.1	27.05	6.25
2	45.6	39.15	6.45	33.0	6.15	27.0	6.0
3	45.2	39.05	6.15	32.8	6.25	26.8	6.0
4	45.8	38.2	7.6	32.8	5.4	26.9	5.9
5	44.1	37.1	6.0	32.5	4.6	26.8	5.7
6	43.5	37.9	5.6	31.5	6.4	26.4	5.1
7	40.9	35.4	5.5	30.3	5.1	25.3	5.0
8	44.2	38.2	6.0	32.2	6.0	26.2	6.0
9	42.5	36.8	5.7	31.0	5.8	25.7	5.3
10	43.1	37.4	5.7	31.3	6.1	25.8	5.5

The average differences in refractometer reading for each 20 parts of added water as shown by the above table was 5.88° on the scale of the Zeiss immersion refractometer.

In order to ascertain what differences there might be when well water instead of distilled water was used for dilution of the milk, a number of samples of milk were diluted with well water and distilled water, respectively. The following table shows the readings with the different waters:

DILUTION	Distilled water	Well water
Whole milk, 42.6		
20 parts added water.....	36.7	36.7
40 parts added water.....	30.9	31.0
60 parts added water.....	25.9	26.0

The well water used contained 0.030 gram of total solids per 100 cc. From the table it is evident that there is but little difference in the readings. From the different samples examined it seemed that with a water containing 0.030 gram solids per 100 cc. there was an increase of about 0.1° above the refractometer reading observed when using distilled water. This difference is scarcely large enough to exceed the error possible in making the readings.

Amount of sugar per 100 cc. Grams	SAMPLE A Whole milk readings	Difference per gram of sucrose
0.0	42.8	...
1.0	46.6	3.8°
2.0	50.6	4.0°
3.0	54.6	4.0°
Amount of sugar Grams	SAMPLE B Whole milk readings	Difference per gram of sucrose
0.0	44.15	...
1.0	48.00	3.85°
2.0	52.05	4.05°
3.0	56.1	4.05°

In studying the influence of sucrose added to milk, whole milk was adulterated with 1.0, 2.0, and 3.0 gram portions, respectively, of ordinary granulated sugar per 100 cc. of milk and treated in the usual way to prepare the corresponding sera. Great care was exercised in getting all the sugar dissolved and the solution well mixed. Fourteen samples of milk

yielded an average increased reading of 3.98° on the immersion refractometer scale for each gram of sugar per 100 cc. of milk. The average difference per gram of sucrose was approximately the same whether 1.0, 2.0 or 3.0 grams per 100 cc. of milk were used. The above will serve as representative samples.

Seventeen samples of milk were adulterated by additions of sugar and water. The samples were prepared by filling 100 cc. flasks with milk, withdrawing 20 cc. by means of a pipette, adding 1.0, 2.0 and 3.0 grams, respectively, of ordinary granulated sugar, dissolving and mixing the sugar solution carefully and then filling to the graduation mark with water. The samples were then heated with acetic acid as usual for defecation. In 17 samples, an average difference of 4.02° instrument reading per gram of sugar added was obtained. Following this, samples of whole milk were diluted to contain 60 parts milk and 40 parts of added water. Five samples gave an average difference in reading of 4.1° instrument reading for each gram of sugar added per 100 cc. of milk. Five samples of milk containing 40 parts of milk and 60 parts of added water yielded a difference of 4.04° (average) for each gram of sugar added.

The average difference in reading produced by a gram of sugar added per 100 cc. of milk calculated on the total 41 samples including whole milk, milk containing 20 parts added water, 40 parts of added water and 60 parts of added water, respectively, per 100 cc. of milk-mixture, was 4.03° . From these results it seems that 1 gram of granulated sugar added to 100 cc. of milk raises the refraction of the serum about 4° and no great difference is observed when either whole milk or watered milk is used. If this increasing figure is used together with the decreasing figure (2.9°) representing the refractometer reading produced by 10 per cent added water, one should be able to adjust the two figures so that the refractometer reading on the serum would come near that observed for unadulterated milk. Thus by adding the proper amount of sugar, the serum of the watered milk should be capable of yielding a refractometer reading approaching the normal milk before adulteration. We calculated with this in view and found that for every 10 per cent of water added, 0.725 gram granulated sugar (commercial grade) such as we were using had to be added to each 100 cc. of milk in order to make the adulterated sample of milk give the same refractometer reading as the original whole milk.

The following data was obtained from an actual sample of milk that showed a refractometer reading of the serum to be 44.15° and contained total solids amounting to 14.48 per cent. On watering this sample of milk until we had a mixture containing 80 parts of milk and 20 parts of added water, and adding 1 gram of granulated sugar, by calculation, we should have had a mixture yielding a serum with a refractometer reading of 42.35° . By actual experiment, we found 42.15 as the observed reading. Adding 2 grams of sugar per 100 cc. of milk-mixture should have yielded a refractometer reading of 46.35° . By observation, the actual reading was 46.1° . Adding 3 grams of sugar

to 100 cc. of the milk should have given us a serum with a refractometer reading of 50.25° . Exactly this figure was found by experiment.

The experimental part checked fairly well with the calculations. Other samples of milk with which we worked varied from the calculated value as much as 0.5° but the majority of the samples gave readings within closer range of the calculated values.

The sample of milk just described in detail although watered and sugared (1.0 gram per 100 cc.) yielded a refractometer reading safely above the standard usually associated with whole milk. The total solids in the diluted milk, after treatment with sugar, would have been 12.58 per cent, a figure exceeding the usual standard. The milk originally mentioned contained 5 per cent fat. Even on dilution this resulting figure would have been above the standard for butter fat. It is evident that the milk in question when diluted so as to contain 20 per cent added water and 1 gram of granulated sugar for every 100 cc. of watered milk, on being examined in the usual way would have given results that might have baffled the chemist in detecting the added water. Unless the sucrose tests had been applied, the sample might have been passed as unadulterated milk.

It can be shown that this form of milk adulteration is a profitable thing. At the rate of 1 gram of sucrose to 100 cc. diluted milk containing 80 parts of whole milk, one quart of the milk would require 0.025 pound of granulated sugar to bring the refractometer reading up to its original value. With sugar at 6 cents a pound and milk at 8 cents a quart, 0.15 cent spent for sugar would yield a return of 2 cents. The adulteration can be thus carried on profitably by the milk dealer if he is able to escape the chemist's sucrose tests.

CONCLUSIONS

1. The Zeiss immersion refractometer method of testing milk serum is doubtless the most practical method for the detection of water addition, but this method is far from infallible when used alone.
2. This work indicates that for every 10 per cent of water added to milk, the serum when prepared by the acetic acid method gives a refractometer reading about 2.9° lower than the unwatered milk.
3. The addition of 1 gram of granulated sugar to 100 cc. of milk, watered or unwatered, will raise the refractometer reading of the serum about 4° .
4. The adulteration of milk by watering and sugaring can be profitably carried on by adjusting the amounts of the adulterants and adding them to the milk that is well above the standard in solids and fat.
5. This work was carried out to find the actual importance of the desirability of detecting cane sugar as a milk adulterant. It seems that in examining commercial samples of milk it is well worth the chemist's trouble to look out for the presence of this form of adulteration.