ON THE DETERMINATION OF ADDED WATER IN MILK.

By A. G. Woodman.

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IN order to estimate the amount of water which has been added to a sample of milk, it is generally necessary to make separate determinations of the specific gravity, the total solids, and the fat. The accurate determination of at least two of these factors is a matter of considerable time, and, although it is possible to shorten the time to a certain extent by the use of such formulas as those of Fleischmann, or of Hehner and Richmond, there can be no doubt that a rapid, and at the same time accurate, method for determining the extent to which milk has been watered would find extensive application.

The most successful of the various methods by which it has been proposed to effect this direct determination of added water are based, in general, upon the fact that under certain conditions the serum or liquid portion of sour milk possesses a fairly constant composition, much more so than the milk itself. The methods by which the milk serum is obtained depend for the most part upon the coagulation of the milk by means of dilute acid. Vieth[1] recommends letting the milk sour spontaneously by standing at the room temperature for two or three days and then separating the serum from the coagulum at 65° C. Other investigators prefer to coagulate the milk directly by the addition of an acid. Dietsch[2] and Radulescu[3] use dilute acetic acid and warm the milk. Reich[4] recommends the use of a small quantity of glacial acetic acid and final heating of the milk to 100° C. Sambuc[5] heats the milk to 40°–50° with two cc. of an alcoholic solution of tartaric acid of a specific gravity of 1.030–1.032, approximately the same as that of the milk serum itself. The whole question has been investigated quite thoroughly by Radulescu, who has made a study of the conditions necessary in regard to the strength of acetic acid employed, the temperature

[1] Forschungen auf dem Gebiete der Viehhaltung und ihrer Erzeugnisse, *1884*, (15), 334.

[2] *Chem. Ztg.* (*1884*), 323.

[3] Mitt. aus dem pharm. Ins. und Laboratorium für ang. Chem. der Univ. Erlangen, (*1890*), III, 93.

[4] *Milch Ztg.*, (1892), 274.

[5] Jour. de Pharm. et de Chim., (*1884*), 95.

to which the mixture should be heated, and the time required, in order to obtain satisfactory results. The method recommended by Radulescu is as follows: To 100 cc. of the milk is added two cc. of twenty per cent. acetic acid, and the mixture is heated in a water-bath at 85° C. for five or six minutes, as a result of which the casein separates in the form of a compact cake and is easily filtered off. After being thoroughly mixed the filtrate is cooled to 15° C. and its specific gravity taken. The acid used is variously stated in different portions of Radulescu's paper to be "twenty per cent. acetic acid," "twenty-five per cent. acid," and acetic acid having a specific gravity of 1.0294, which is about twenty-two per cent. strength. In the determinations which I have carried out, using practically the same method as that proposed by Radulescu, I have found that for the richer samples of milk the twenty per cent. acid is too dilute, failing to entirely precipitate the casein, but that the acid of twenty-five per cent. strength is sufficient in all cases.

After a number of experiments, following at first as nearly as possible the procedure recommended by Radulescu, subsequently making such modifications in the method as were found advisable in order to secure more nearly uniform results, I have adopted the following procedure: 100 cc. of the milk, which should be at a temperature of about 20° C., are thoroughly mixed with two cc. of a twenty-five per cent. solution of acetic acid, specific gravity 1.0350, in a small beaker. The beakers, kept covered with watch-glasses, are heated for twenty minutes in a water-bath kept at a temperature of 70° C., the temperature of the milk samples being brought gradually by this means to about 65° C. The beakers are then removed from the water-bath and placed immediately in ice-water, where they are allowed to remain for ten or fifteen minutes, after which the solutions are filtered through small, dry, plaited filters, the first portion of the filtrate, which generally comes through cloudy, being returned to the filter. After the filtrate has been thoroughly mixed it is cooled to 15° C. and its specific gravity taken by means of a Westphal balance. It occasionally happens, more especially with normal milk or milk to which only a slight amount of water has been added, that the serum which is thus obtained has a slight cloudiness or opalescence, but I have not

observed that it causes any appreciable difference in the specific gravity. For assistance in studying the conditions upon which the above procedure is based, I am indebted to Mr. J. W. Brown and Miss J. H. Bartlett.

In the following table (Table I) will be found the results obtained on samples of pure milk obtained from various sources, and on mixtures of these milks containing varying percentages of water, by the method that I have outlined above. All determinations of specific gravity have been made at 15° C., using a delicate Westphal balance, which gave the specific gravity of pure water at 15° C. as 1.0000.

TABLE I.

		Specific Gravity.					
			Serum.				
No.	Milk.	Normal.	Ten per cent. water.	Twenty per cent. water.	Thirty per cent. water.	Forty per cent. water.	Fifty per cent. water.
1.....	1.0337	1.0297	1.0263	1.0237	1.0206	1.0180	1.0153
2.....	1.0334	1.0294	1.0260	1.0232	1.0203	1.0174	1.0151
3.....	1.0340	1.0295	1.0264	1.0232	1.0206	1.0175	1.0151
4.....	1.0324	1.0293	1.0259	1.0233	1.0202	1.0178	1.0148
5.....	1.0336	1.0296	1.0262	1.0235	1.0205	1.0177	1.0153
6.....	1.0328	1.0293	1.0258	1.0233	1.0202	1.0174	1.0148
7.....	1.0334	1.0292	1.0260	1.0233	1.0202	1.0175	1.0149
8.....	1.0325	1.0294	1.0260	1.0234	1.0201	1.0175	1.0152
9.....	1.0339	1.0296	1.0262	1.0236	1.0206	1.0178	1.0153
10.....	1.0335	1.0296	1.0261	1.0235	1.0204	1.0174	1.0148
11.....	1.0329	1.0292	1.0259	1.0234	1.0203	1.0173	1.0148
Av....	1.0335	1.0294	1.0261	1.0234	1.0204	1.0175	1.0150

The specific gravity of the serum from milk at a given dilution is shown by the table to be a fairly constant quantity, the average decrease for each ten per cent. of water being 0.0031.

The specific gravities given in Table I were obtained on samples in which the per cent. of water *in the mixture* varied by ten. As might naturally be expected, if the results are calculated on the basis of percentage of *added* water the differences in specific gravity are not so great. In Table II are given the results obtained on samples of pure milk to which varying percentages of water have been added.

TABLE II.

Samples varying by ten per cent. *added* water.

		Specific Gravity.					
			Serum.				
No.	Milk.	Normal.	Ten per cent. water.	Twenty per cent. water.	Thirty per cent. water.	Forty per cent. water.	Fifty per cent. water.
1....	1.0336	1.0294	1.0259	1.0239	1.0219	1.0199	1.0189
2....	1.0333	1.0295	1.0260	1.0240	1.0220	1.0200	1.0190
3....	1.0334	1.0294	1.0259	1.0239	1.0220	1.0200	1.0190
4....	1.0330	1.0295	1.0260	1.0239	1.0221	1.0201	1.0190
5....	1.0324	1.0294	1.0259	1.0239	1.0220	1.0199	1.0190
6....	1.0328	1.0294	1.0260	1.0239	1.0220	1.0200	1.0190
7....	1.0340	1.0294	1.0260	1.0239	1.0220	1.0200	1.0190
8....	1.0337	1.0296	1.0261	1.0240	1.0221	1.0201	1.0190
9....	1.0330	1.0294	1.0259	1.0239	1.0221	1.0200	1.0190
10....	1.0335	1.0295	1.0260	1.0239	1.0220	1.0199	1.0189
Av...	1.03327	1.02945	1.02597	1.02392	1.02202	1.01999	1.01898

These results confirm the conclusion reached by Radulescu, that the specific gravity of the serum from normal milk is never below 1.027, and in no case of those examined was it found to be below 1.0290. The decrease in specific gravity caused by the addition of ten per cent. of water varied from 0.0035 to 0.0010. The statement is made by Radulescu,[1] that the addition of each ten per cent. of water to normal milk lowers the specific gravity of the serum by 0.0005 to 0.0010 and this value is also given by König.[2] This is evidently an error, for from the preceding table it will be seen that the decrease actually obtained is considerably higher and as a matter of fact the differences shown in Radulescu's tabulation of results vary from 0.0029 to 0.0012. I do not consider it advisable to determine the amount of total solids and of fat in the milk serum, as recommended by Radulescu, because if this is done the method offers no special advantages as far as regards economy of time and ease of execution over those ordinarily used.

The method as originally proposed by Radulescu has been criticised by E. Reich[3] on the ground that only a partial clarification of the milk is effected, the precipitation and removal of the albumen not being complete at the temperature to which the

[1] *Loc. cit.*

[2] Die Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe, Ed. (*1898*), 361.

[3] *Milch Ztg.*, (*1892*), 274.

mixture is heated. The following modification of the method has been proposed by Reich: 100 cc. of the milk is thoroughly shaken in a 200 cc. flask with four-tenths cc. glacial acetic acid, the mixture heated for five or six minutes at 60°–65°, cooled, and the liquid portion poured off into fifty cc. Erlenmeyer flasks. These are hung for five or six minutes in a boiling water-bath, then rapidly cooled in ice-water. The casein and albumen are removed by filtering through a small dry Swedish filter and the specific gravity of the filtrate taken at 15° C. I have determined the specific gravity of the serum from five samples of milk diluted with varying percentages of water by Reich's method and also of the same samples by the modification of Radulescu's method previously described. These results are given in the following Table (III):

TABLE III.

		Specific gravity. Serum.					
No.	Milk.	Normal.	Ten per cent. water.	Twenty per cent. water.	Thirty per cent. water.	Forty per cent. water.	Fifty per cent. water.
		According to Radulescu's Method Modified.					
1.....	1.0337	1.0294	1.0259	1.0239	1.0220	1.0199	1.0190
2.....	1.0319	1.0294	1.0260	1.0240	1.0220	1.0199	1.0190
3.....	1.0338	1.0295	1.0260	1.0239	1.0220	1.0200	1.0189
4.....	1.0340	1.0294	1.0259	1.0239	1.0219	1.0200	1.0189
5.....	1.0328	1.0294	1.0260	1.0240	1.0220	1.0200	1.0190
		Same Samples According to Reich's Method.					
1.....	1.0337	1.0293	1.0266	1.0240	1.0224	1.0205	1.0196
2.....	1.0319	1.0289	1.0257	1.0234	1.0219	1.0200	1.0182
3.....	1.0338	1.0292	1.0264	1.0245	1.0226	1.0207	1.0199
4.....	1.0340	1.0296	1.0264	1.0243	1.0225	1.0205	1.0198
5.....	1.0328	1.0295	1.0270	1.0247	1.0217	1.0210	1.0199

The claim of Reich that his method yields concordant results which are uniformly lower than those obtained by Radulescu's method is not borne out by the figures shown in the above table. It has been my experience that the method offers no advantages over that of Radulescu, being more tedious to carry out and giving results which vary more widely.

As an illustration of the degree of accuracy with which the amount of added water in milk may be estimated from the specific gravity of the milk serum I give the following results

obtained on two samples purchased at a city grocery and supposed to be pure milk:

	1.	2.
Specific gravity milk	1.0282	1.0263
" " " serum	1.0257	1.0234

The specific gravity of the serum indicated in one case ten per cent. and in the other twenty per cent. of added water. The amount of added water calculated from careful determinations of the total solids and of the fat was very close to this, being 9.8 per cent. for the first sample and 19.6 per cent. for the second. The method is easy to carry out and should prove to be of considerable value.

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DETERMINATION OF CALCIUM AND MAGNESIUM IN ASHES.[1]

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THOSE who have had any considerable number of ash samples to analyze according to the method adopted by the Association of Official Agricultural Chemists, cannot help having been struck with the extreme difficulty of determining calcium and magnesium. The whole trouble consists in washing the voluminous precipitate of basic acetate of iron and phosphate of iron, which is not only so bulky as to be troublesome, but also commences to run through the filter soon after washing is begun.

The following work was undertaken with the idea of showing that this washing can be entirely done away with, without seriously affecting the accuracy of the results. To do this the precipitation of the phosphoric acid and iron from the solution of calcium and magnesium was made in a 500 cc. flask, the solution then cooled to room temperature, made up to the 500 cc. mark, and *well shaken*. 250 cc. of this solution were then filtered off through a dry filter, keeping the funnel covered to prevent evaporation, evaporated to a small volume, ammonia added to get rid of any small traces of iron that might have dissolved in

[1] Read at the meeting of the Washington Section, March, 1899.