THE RELATIVE MERITS OF THE WANKLYN AND THE ADAMS METHODS IN THE ESTIMATION OF FAT IN MILK ANALYSIS.

By Joseph F. Geisler.

The enactment of laws regulating the quality of milk necessarily involves the adoption of minimum limits or standards. The analytical methods used to ascertain the data must be practical and accurate, and must not involve too great an expenditure of time. Since the adoption of milk standards, especially the minimum limits as to solids and fat, many methods of more or less merit have come into use. The method of Wanklyn, with slight modifications, has been most generally adopted, and in fact has served in determining the standards in many countries. Up to the time of the introduction of the Adams or *coil method*, it was generally considered that the Wanklyn method, and the gypsum or sand methods, gave sufficiently accurate results for all practical purposes. This opinion is still retained by some chemists. The extensive introduction of the coil method and the exhaustive investigations by the Society of Public Analysts in England called attention to great discrepancies between the per cents. of fat ascertained by the coil method and those determined by other methods. It has been generally supposed that the Adams method would usually extract 0.2 to 0.4 per cent. more fat than could be found by the Wanklyn method.

Those who have had experience in the analysis of a great variety of milk and who have made comparative tests by the different analytical methods, have probably obtained differences greater than these.

Having made many such comparative analyses I present herewith some of the analytical data obtained in the analysis of both pure and adulterated milk.

THE WANKLYN METHOD.

In this method about five (5) cubic centimetres of milk are accurately weighed in a tared platinum (flat bottomed) dish and then dried at a temperature of 100° C. to practically constant weight. The dry residue is then exhausted by repeated portions of boiling ether, or petroleum ether, and the extracted fat weighed direct or by difference, *i. e.*, loss in weight of the dry residue first obtained. Carefully worked the duplicate determinations of the per cent. of fat agree well with each other. Unless the dry residue be thoroughly broken up with a glass rod during the treatment with ether the results are, at times, liable to fall considerably below the truth, as will be shown in the comparative analyses cited below.

The platinum dishes used are usually of 1⅝ inches diameter at the base, or the bottom presents about 2 square inches of surface over which the milk solids forming the dry residue are distributed. There are many reasons for the opinion that the fat cannot all be extracted from such a residue by a solvent without first breaking up the residue mechanically. Quite a number of circumstances may influence the results obtained. Milk is extremely variable in composition. Not only does the fat vary widely in percentages, but the other contstituents, and the relative proportions of these to one another, may also vary considerably at times. These, together with the fact that there is considerable difference in the size of the fat globules of the milk of different breeds of cows, are the main causes. It must be quite generally known to those who handle milks to any extent that the individual fat globules of the milk of Jersey cows are considerably larger than those of the milk of Holsteins. For this reason the cream from the milk of the former rises much more quickly and perfectly. This illustration applies to other milks as well. During the evaporation of the milk in the flat bottomed platinum dish the bulk of the fat rises to the surface and forms a layer from which the fat is easily dissolved by the given solvent. The more perfect the initial separation, the more complete and perfect will be the subsequent exhaustion on the application of the proper solvents. There is, however, good reason to believe that in some milks, owing to peculiar combinations of conditions, considerable fat is retained in the

dry residue, so completely incased in the hardened sugar and casein that it is impossible for the solvent to get at it in this condition. Such a residue when pulverized will frequently be found to yield 0.3 to .4 per cent. more fat.

That there is great variation in the time required for the cream to rise in different milks is a fact quite well known. In the author's experience a sample of milk was brought to him as a skimmed milk having shown but very little cream by the cream test. The sample upon analysis was found to contain over 4 per cent. of fat.

THE ADAMS OR COIL METHOD.

In this method many mechanical difficulties are overcome and the data obtained answer all requirements as to accuracy. The method is used principally in the estimation of *fat*. It is a vast improvement over the Wanklyn and similar methods inasmuch as the milk solids are distributed over so large a surface that the solvents used are enabled to extract *all* the fat. The method is, briefly, as follows:

White demy blotting paper, mill 428, weighing about 38 pounds per ream is cut into strips 22 inches long and 2½ inches wide. Each strip is rolled into a loose helical coil having a diameter a little less than an inch. The coils must be exhausted with ether and finally dried at 100° C.

"The milk to be examined is shaken, and with a pipette, 5 c.c. are discharged into a small beaker 2 inches high by 1¼ diameter, of a capacity of about 30 c.c., weighing about 12 grams. This charged beaker is first weighed, and then a paper coil gently thrust into the milk very nearly to the bottom. In a few minutes the paper sucks up nearly the whole of the milk. The paper is then withdrawn by the dry extremity of the coil and gently reversed, and stood dry end downwards on a clean sheet of glass. With a little dexterity all but the last fraction of a drop can be removed from the beaker and got upon the paper. The beaker is then again weighed, and the milk taken estimated by difference. It is of importance to take up the whole of the milk from the beaker, as I am disposed to consider that the paper has a selective action, removing the water constituents of the milk by preference over the fat.

"The charged paper is next placed in the water oven on the glass plate, milk-end upwards, and roughly dried. Mismanagement may possibly cause a drop to pass down through the coil on to the glass. This accident ought never to occur, but if it does, it is revealed in a moment by inspection of the surface of glass, and the experiment is thereby lost. In about an hour it is rough-dried and in a suitable condition for the extraction of the fat."

Many modifications have been introduced but only in minor details. Some chemists use a different filter paper, others use asbestos fibre or asbestos paper. The use of coils of a good quality of filter paper has the advantage of exposing comparatively a very large surface over which the dry milk solids are distributed and thus exposed to the action of the solvent. A paper $22\frac{1}{2} \times 2\frac{1}{2}$ inches has at least $56\frac{1}{4}$ sq. in. surface, or $112\frac{1}{2}$ sq. in. for the two sides, as the smallest surface exposed. When it is further considered that the milk is distributed over the individual fibers of the paper it is at once seen that the surface is still more increased. It is probable that the surface thus exposed in a coil ranges from 300 to 400 square inches. This large surface enables the complete extraction of the fat in the shortest possible time.

I have preferred to modify the details somewhat as follows:

The coils* are prepared from Schleicher & Schüll's filter paper No. 597, the strips cut to the usual size $22\frac{1}{2} \times 2\frac{1}{2}$ inches. The coils are thoroughly exhausted by repercolation with hot ether, and when necessary also with hot alcohol, until all soluble matter has been extracted, then dried and kept ready for use. For an analysis a coil is unrolled, the edges turned up about $\frac{1}{4}$ inch for the full length of the strip, and then, by suitably fastening the ends, it is hung up at an angle of about 45 deg. Into a small tared beaker of about 18 c.c. capacity, about 6 c.c. of milk are accurately weighed and then immediately transferred to the inclined strip by gradually dropping the milk upon the same. The beaker and glass rod are then wiped dry with a small piece of filter paper and this is hung up with the strip. In this manner with a little care

* S. & S. now manufacture specially for milk analysis a grade of paper, No. 571, which is guaranteed free from fat.

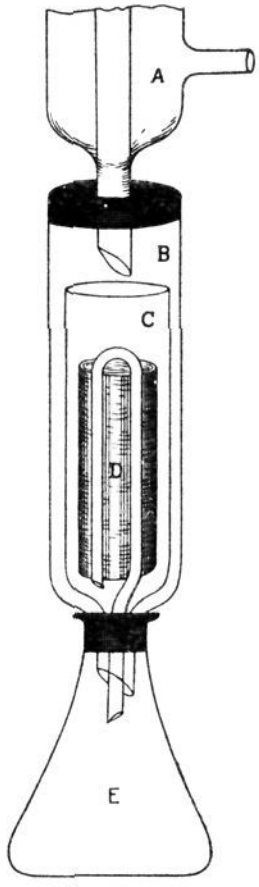
not a particle of the weighed quantity of milk taken need be lost. The coil, before the milk is transferred to the same, is marked with a number agreeing with the number of the milk sample so that it can be indentified. It is then hung perpendicular and allowed to hang for 1 to 3 hours until dry, finally rolled into a loose coil and transferred to an air bath and dried at 100° C., for about ¾ hour to 1 hour or until thoroughly dry. The coil is then transferred to a repercolation apparatus having an intermittent syphon in which the constant repercolation of the ether extracts all the fat from the coil.*

When the extraction is complete the coil is removed, the ether recovered, and the residual fat remaining in the tared flask first dried a few minutes on the water bath, the flask wiped off clean and dry, transferred to an air bath, dried at 100° C. for 20 to 30 minutes, and, after cooling 10 to 15 minutes, weighed. To ensure accuracy it is well to dry the flask a second time for about 20 minutes and reweigh as before.

The washed ether used for such extractions must be redistilled or tested, to make sure that it does not yield any residue, which would otherwise be calculated as fat. A suitable size of extraction apparatus is described herewith.

*It is best to cover the top of the coil with a small piece of exhausted filter paper so as to prevent the condensed ether from mechanically removing particles of the solidified material from the coil.

EXTRACTION APPARATUS.*



A. Liebig Condenser.

B. Percolator. Diameter (int.) 1½ inches; Length of body, 6½ to 7 inches. Lower stem about 2 inches long, cut off obliquely, and not less than ⅜ inches int. diameter.

C. Extractor. Length of body, 4¼ to 4½ inches, internal diameter, 1 inch. Lower stem about 3 inches long, and cut off obliquely. Internal diameter of lower stem and intermittent syphon, about ⅛ inch. Height of syphon, 3¼ to 3½ inches, with inner end, which must reach to near the bottom of the extractor, cut off obliquely.

D. Coil of paper.

E. Erlenmeyer Flask. Flask about 4 inches high, wide neck, and measuring about 150 c. c.

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* Although this apparatus was designed by the author, he makes no claim as to originality of the same.

Analytical Data.

The following analyses were made by the "Wanklyn" method. In the series *A* petroleum ether was used for the fat extraction and in the duplicates, series *B*, purified ether. It will be observed that there is no material difference in the percentages of fat obtained, so that either answers equally well as a solvent.

A	No. 1.	*B*, duplicate
Spec. Grav. at 15.5° C.	—1.0261—	
Water 89.442%		89.446%
Total Solids 10.558%		10.554
100.000%		100.000
Fat 3.056		3,038
Casein and Sugar 6.931		6.924
Ash .571		.592
Total Solids 10.558%		10.554%
	No. 2.	
Sp. Gr. at 15.5° C.	—1.030—	
Water 88.518		88.527
Total Solids 11.482		11.473
100.000		100.000
Fat 3.243		3.240
Casein and Sugar 7.582		7.568
Ash .657		.665
Total Solids 11.482%		11.473%
	No. 3.	
Sp. Gr. at 15.5° C.	—1.025—	
Water 89.240		89.227
Total Solids 10.760		10.773
100.000		100.000
Fat 3.588		3.488
Casein and Sugar 6.572		6.678
Ash .600		.607
Total Solids 10.760%		10.773%

In the above fat determinations, as well as all the following fat estimations by the "Wanklyn method," a glass rod was used to

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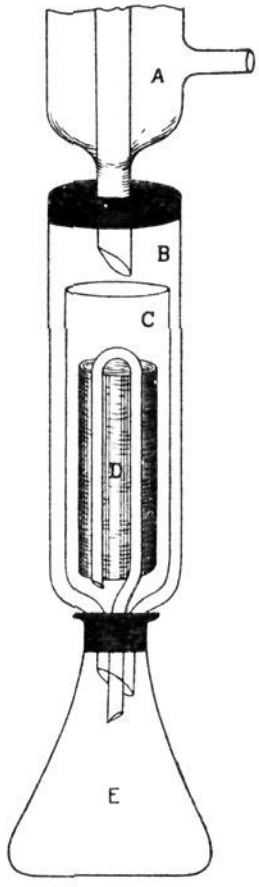

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In the above analyses of 20 milks the average difference amounts to +.294% in favor of the coil method, with the differences ranging from +.08% to +.60%. In the following 5 samples recently analyzed in duplicate by both the Wanklyn and *coil* methods the results were as given below. It must be noted, however, that in these fat determinations by the Wanklyn method the dry residues were not manipulated with a glass rod to any extent, but the fat was "exhausted" by repeated application of boiling ether until the latter failed to extract any more fat. All are the average of duplicate determinations.

Water.	Solids.	Ash.	Wanklyn. Fat.	Coil. Fat.	Difference in % Fat.
87.420	12.580	.753	3.359	3.816	+.457
87.905	12.095	.765	2.905	3.625	+.720
87.102	12.898	.734	4.125	4.707	+.582
87.554	12.446	.750	3.398	3.806	+.408
88.226	11.774	.730	3.030	3.602	+.572

The coil method extracted in the five samples an average of .547% more fat than the Wanklyn, the range being from .408 to .720%. Such differences certainly deserve recognition.

The following investigations were made with a view of determining the merits of some of the objections raised against the *coil* method.

Amount of Substances Soluble in Ether.

A paper coil, not previously exhausted by ether, submitted to continuous repercolation in the extraction apparatus for four hours, yielded a residue amounting to 0.008 g., which figured on basis of 6 grms. of milk would have shown a maximum increase of .13% apparently, fat. In another lot of paper (Schleicher & Schülls, No. 597) the *average* of 16 coils amounted to 0.0025 g. per coil, which on the above basis of 6 grms. would show an apparent increase of .041%.

Rate at which the Fat is Extracted.

The milk used for this series of tests had the following composition :

	Water.	Total Solids.	Fat.	Cas. and Sugar.	Ash.
(Sp. Gr. 1.0274)....	87.847	12.153	4.294	7.163	.696

The coil used was previously exhaused by both ether and alcohol.

Total ether used=40 grms. Milk taken=6.073 grms.

13 syphonings yielded	0.2608 grms.	fat	=4.294 % fat.
6 additional syphonings yielded	0.0003 "	"	=0.004 % "
6 " " "	0.0000 "	"	=0.0 "
			4.298 % fat.

In this case, therefore, thirteen syphonings extracted practically all the fat, and the additional twelve syphonings yielded scarcely a weighable quantity of anything, which goes to show that the ether does not extract any appreciable quantity of milk sugar, or milk constituents other than fat. In a number of cases where the coil method seemed to give very high results as to per cent. of fat, the residues of "fat" in the flask were completely soluble in petroleum ether.

Effect of Dropping or Absorption in the transfer of the Milk to the Coil for the Extraction of Fat.

A pure milk was used for this test:

	Water.	Total Solids.	Fat.	Cas. & Sug.	Ash.
(Sp. Gr. at 155°C.=1.0315)	86.376	13.624	4.540	8.320	.764

% Fat yielded when milk was absorbed in coil as per Adams..... =4.550
% Fat yielded when milk was dropped upon the unfurled strip.... =4.530

It is thus seen that the difference here amounted to only 0.020 %, considerably within the limits of experimental error.

Does the Fat Oxidize during the Drying?

Some have tried to account for the increased yield of fat by the coil method by attributing it to oxidation of the fat. Direct experiments fail to prove this, and in fact show that if oxidation does take place it is not appreciable under the conditions of the test. A sample of pure milk was taken for the test:

COMPOSITION.

	Water.	Total Solids.	Fat.	Cas.& Surg.	Ash.
(Sp. Gr. at 15.5°C.=1.033)	86.969	13.031	3.864	8.417	.750

Of this milk three different portions were weighed, transferred to the coil paper as usual by dropping and each treated further as indicated below.

The coils, previous to pouring the milk upon the same, had been extracted with ether and alcohol and dried as usual.

A. The strip with milk hung up and air dried at the temperature of the atmosphere, about 22° C. for 3 hours.

B. Dried in open air with the heat from a burner at a temperature of 40° to 55° C. for 4 hours.

C. First dried same as *B*, but in addition thereto 3¼ hours at 100° to 103° C. in an air bath.

If the fat is oxidised during the drying, it is reasonable to expect that the longer the drying and the higher the temperature the greater will be the amount of oxidation and the apparent increase in the percentage of fat obtained. The following data were obtained :

	Milk taken.	Fat obtained by Syphoning.	% Fat.
A	5.8875 g.	0.2285 g.	=3.881 %
B	6.0325	0.2327 g.	=3.859 %
C	6.089	0.2347 g.	=3.854 %

Test *C*, which was subjected to the most thorough drying, gave 0.027 % less fat than *A*, and .005 % less than *B*, all of which are within the limits of experimental error. There is, therefore, no evidence that any increase in fat was caused by oxidation, in fact according to the above data the reverse would be the case. It was also found that drying the fat contained in the Erlenmeyer flask in the air bath for 30 to 45 minutes did not give any evidence of oxidation of the fat.

INFLUENCE OF THE EXHAUSTION OF THE COILS BY ETHER AND ALCOHOL.

For this purpose coils (S. + S. 597 paper) were prepared by exhausting them for 2 hours in the repercolation apparatus and then dried = "ether" coils.

Some of the "ether" coils were then exhausted by repercolation with hot alcohol and dried = "alcohol" coils.

The milk used in the first series had the following composition :

	Water.	Tot. Solids.	Cas. & Sugar.	Fat.	Ash.
(Sp. Gr. at 15.5 % =1.0318)	87.155	12.845	8.195	3.890	.760

		Milk taken.	Fat obtained.	% Fat.	Average.
"Ether" Coils	No. 1	6.178g	0.2414g	= 3.907 %	3.917 %
	No. 2 duplic.	6.017g	0.2363g	= 3.927 %	
"Alcohol"	No. 3	6.045	0.2337g	= 3.866 %	3.864 %
	No. 4 duplic.	6.004	0.2319g	= 3.862 %	

Average difference = .053 %

The milk for the second series contained :

	Water.	Tot. Solids.	Cas. & Sugar.	Fat.	Ash.
(Sp. Gr. at 15.5 % = 1.0312)	87.152	12.848	7.928	4.181	.739%

		Milk taken.	Fat obtained.	% Fat.	Average.
"Ether" Coils	No. 5	6.000	0.2509	= 4.181 %	4.197 %
	No. 6 duplic.	6.0635	0.2555	= 4.213 %	
"Alcohol" Coils	No. 7	6.1195	0.2524	= 4.124 %	4.152 %
	No. 8	5.946	0.2486	= 4.180 %	

Average difference = .045 %

A comparison of the above data will show the fact that coils prepared from S. & S. filter paper No. 597 and thoroughly exhausted by ether answer for all practical purposes, the difference of .045 % and .053 % as above obtained being quite insignificant. As already stated each lot of paper must be tested to guard against error.

I append herewith a number of results of duplicate estimations of fat by the coil method.

% Fat Miscellaneous Milk		% Fat Skimmed Milk	
a.	b. duplicate.	a.	b. duplicate.
		0.345	0.343
3.831	3.855	0.319	0.351
3.828	3.847	0.305	0.302
3.691	3.604	0.502	0.505*3
3.876	3.842	0.484	0.508*3
2.801	2.776*1	0.672	0.694
5.342	5.394*2	0.601	0.568

*1 An adulterated milk.

*2 A pure sample of milk from a herd of 6 cows fed on some bran and pasture. The analysis of the milk showed

Water.	Total Solid.	Fat.	Cas. & Sug.	Ash.
85.838 %	14.162 %	5.368	8.058	.736

This milk was very high colored, owing to the richness in fat. The Sp. Gr. of the milk at 15.5° C. was found to be 1.0305.

*3 In these skimmed milks the Wanklyn method failed to show more than .15 % fat.

SUMMARY.

In the data presented most of the data are stated with three decimal figures. It is almost needless to add that beyond the second decimal the figures have but little practical value except in making up averages, but the figures were here retained so as to agree with the data of other tables in which some of the results had to be used.

Attention should also be called to the distinction between the terms—"Wanklyn" and—Wanklyn—method as used thoughout the article. In the "Wanklyn" method the dry milk residues were more or less broken up by means of a glass rod, while in the —Wanklyn method no particular attempt is made to mechanically break up the residue during the action of the solvent.

As to the relative merits of the Wanklyn and Adams, or coil method, for the extraction of the fat of milk it must be conceded :

(1) That the duplicates by either method agree well with each other.

(2) That the Adams' or coil method may yield as much as 0.72, per cent. more fat than the Wanklyn method, the variation, depending much upon whether or not the dried residue of milk solids in the Wanklyn method is mechanically broken up during the action of the solvent.

(3) That the *ratio of fat extracted by the Wanklyn method* (or similar methods) *does not bear a uniform ratio to the total percentage of fat contained in the milk*, which fact in itself is sufficient to condemn the method where accuracy is required.

Milk analyzed by the Adams' or coil method should be required to show at least 0.35 per cent. more fat than the standard adopted for the Wanklyn method. From the fact that the coil method extracts more fat than the Wanklyn method it is evident that by the former the "solids not fat" will be found to be lower, frequently as low as 8.5 per cent. In several instances in the pure milk of cows fed on grass pastures the "solids not fat" were found as low as 8.30 to 8.00 per cent.

Although the *average* difference between the Wanklyn and the Adams' (or coil) method may be considered as 0.3 to 0.5 per cent., yet it must be borne in mind that *averages* cover up a multitude of sins and that it is the extremes we must guard against.