

accurately by the cyanide process as described by Ricketts and Miller. If other disturbing factors are present the method will have to be modified accordingly, but the method as described gives results sufficiently accurate for all practical purposes on the great majority of commercial pyrites ores. This process is simple, reasonably quick, and gives much more satisfactory results than the other methods we have tried.

Mr. S. H. Sheib who is connected with this laboratory has rendered valuable assistance in perfecting this method of pyrrhotite determination, and its success is largely due to his careful work.

LABORATORY VIRGINIA-CAROLINA CHEMICAL CO.,
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THE ESTIMATION OF FAT IN SWEETENED CONDENSED MILK.¹

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CONDENSED milk, as its name indicates, is a more or less concentrated milk, prepared by evaporating or distilling off a large percentage of the water of the milk. The concentration is usually carried to a degree to meet popular taste and trade requirements, unless the law establishes a specified degree of condensation. Broadly, this class of milk may be divided into the sweetened and unsweetened condensed milk, the former containing a large per cent. of cane-sugar as sweetener and preservative. Aside from its general good qualities, the extreme precaution of cleanliness in the preparation of most of the condensed milks has added much to their popularity, so that the sale and consumption of these milks is assuming vast and rapidly increasing proportions. As an article of food it is therefore more frequently being made the subject of analytical inquiry to determine its quality and freedom from adulteration.

While certain manufacturers pride themselves in turning out a product of uniform color, consistency, and superior keeping qualities and purity, others have deliberately put adulterated goods on the market and were prosecuted and fined for the same.

The analysis of ordinary milk presents no particular difficulties

¹ Read at the Twenty-first General Meeting of the American Chemical Society, June, 1900.

to the experienced analyst, but there is an abundant and cumulative evidence to show that the correct analysis of sweetened condensed milk is difficult and has proved to be a stumbling block to the efforts of many chemists.

Thus, quite recently, an article "A Method of Analysis for Canned Condensed Milk,"¹ by F. S. Hyde, appeared as a "Contribution from the Havemeyer Laboratories of Columbia University, No. 6," and this article has obtained wide circulation.

The results of the analyses of the first 17 samples reported are so utterly out of harmony with the composition of commercial condensed milk that experienced analysts have only to refer to the method whereby the results were obtained to learn the cause of the faulty statements. It is the general experience that the easiest part of analytical work is the writing out of a method. Without going into the details of the article referred to, I would quote² the following, which has a decided bearing in the application of the food laws:

A law of New York State requires that no "condensed milk shall be made,—unless the proportion of milk solids shall be in quantity the equivalent of twelve per centum of milk solids in crude milk and of which solids twenty-five per centum shall be fats." Sec. 25, Chap. 143, L. 1894.

"Generally the amount of fat in condensed milk is less than ten per cent. of the whole, or less than twenty-five per cent. of the forty per cent. (more or less) milk solids of which the fat is a part.

"The original cow's milk used may be considerably above the legal standard and yet the degree of condensation be insufficient to bring the manufactured article within the requirements of the law. Under such conditions the manufacturer might be liable to prosecution, although the product might be perfectly wholesome."

In the writer's experience it is the rare exception rather than the rule for condensed milks to contain less than a proportion of 25 per cent. of fat in the milk solids.

If, as stated, milk above the standard required by law be used

¹ This Journal, 21, 439 (1899).

² *Ibid.*, 21, 444 (1899).

for the condensation, there could be no legal prosecution of a manufacturer since the concentration would not materially alter the ratio of fat to milk solids, and the section of law quoted does not define the degree of concentration. Therefore, whether condensed little or much, the "condensed" product would not be an infraction of the law quoted, and prosecution under the same is out of the question.

Aside from insufficient condensation, it is generally assumed that skimming or the removal of butter-fat is the principal temptation to defraud on the part of the manufacturer. To prove skimming, the first essential is the accurate estimation of the fat, assuming the per cent. of fat obtained to be butter-fat. That is to say, the mere finding of the required per cent. of fat, and ratio of fat to milk solids would not prove such milk unadulterated unless the fat found was actually butter-fat.

Attempts have been made to remove the butter-fat and substitute other fat for the same in condensed milk; hence, the allusion to butter-fat particularly.

In the unsweetened condensed milk the estimation of the fat presents no particular difficulty, especially since the introduction of the Adams' coil method,¹ when the necessary precautions are taken. The large surface over which the milk solids are spread in the paper, a minimum of 110 sq. in., offers a medium from which solvents ordinarily rapidly extract² the fat.

The coil method has found general favor among analysts and were it not for the inconvenience of preparing "fat-free" coils it would be *par excellence*, and with certain modifications, the best method for the purpose. The preparation of the coils is tedious, but where accuracy is required the previous extracting of the coils to be used must be resorted to, as the quality of paper varies, some lots containing considerably more extractable matter than others.

Chemists were quick to avail themselves of the advantages of the coil method and use it in the estimation of fat in sweetened condensed milk, for the large surface offered advantages to overcome the difficulties experienced and pointed out by Hehner,³

¹ *Analyst*, March, 1885.

² See Vieth: *Analyst*, 16, 127; Geisler: "The Relative Merits of the Wanklyn and the Adams Methods in the Estimation of Fat in Milk Analysis," this Journal, 12, 488-500.

³ *Analyst*, 4, 45 (1879).

who stated "that it is quite impossible to extract the fat from the total solids by means of ether, or benzoline, the large amount of cane-sugar effectually protecting the fat."

Adams' method was not available until some years later. In the light of recent published analyses of sweetened condensed milk, Hehner was a "martyr" considering the abuse heaped on him by the manufacturers for the analyses, for it will presently be shown that even the extreme advantages of the *coil method*, unless certain precautions are taken, has its pitfalls. In the application of the coil method it is customary among a large number of chemists to proceed as follows: Thus Cornwall¹ and Wallace² state in following out the method:

"Rather thick, white filter-paper was thoroughly extracted with ether in a Soxhlet apparatus and 5 cc. of the diluted milk (equal to 2 grams of the condensed milk) dropped on a nearly square strip of this paper³ large enough to conveniently soak up the milk. To avoid the formation of candied spots the milk was uniformly spread over the paper by brushing with a small narrow strip of the same kind of paper. After drying in the air the paper was rolled into a loose cylinder and dried in the air-bath at 100° C. for about an hour and a half.

"The fat was then extracted with ether, for two hours, in a Soxhlet apparatus, and a second extraction was made, lasting for an hour to an hour and a half longer. The second extraction usually yielded less than 4 milligrams more of fat, and often none at all. The fat determination was made in duplicate. The greatest difference was 0.2 per cent., usually only a hundredth of a per cent."

In brief, the Adams' method, as applied to sweetened condensed milk, consists in transferring about 2 grams of milk diluted to 5 or 6 cc., to a paper coil of 50-60 sq. in. (100-120 sq. in. of surface, both sides), and extracting the fat by means of ether or petroleum ether.

The quantity of milk taken for the extraction is not a matter

¹ Cornwall: Rep. Dairy Com., N. Y. State, 1890, p. 408; N. J., 1887.

² Wallace: Rep. Dairy Com., N. J., 1899, pp. 43-47.

³ Cornwall: Rep. Dairy Com., N. J., 1891, p. 90; filter-paper of medium thickness 10 × 5 inches. Wiley: Rep. Dairy Com., N. J., 1891; thick filter-paper strips 24 × 24 inches.

of indifference, nor is the solvent, or the method of extraction. Unless the ether is dry and free from alcohol, the coils get too soggy to permit the full extraction of the fat. Even with dry ether or petroleum ether, losses may occur even as high as 0.5 per cent. as against an occasional maximum of about 1 per cent. in a direct extraction. Evidence of this may be obtained by treating the thoroughly exhausted coil after drying, to a thorough soaking in water until all soluble matter is removed, drying the coil, and again exhausting with ether or petroleum ether, when additional fat will be found in the majority of cases.

Direct exhaustion by ether for four hours leaves variable percentages of fat in the residuum on the coils. This is true of other solvents as well. If 2 grams of the condensed milk are used per coil, the coil, after the first exhaustion, which presumably should yield all the fat, should be dried and exhausted with water, again dried and exhausted with the volatile solvent. Forty-nine separate examinations showed differences for the second exhaustion of 0.27 to 1.2 per cent. of which nine ranged from 0.27 to 0.49 per cent. ; twenty-three from 0.50 to 0.75 per cent. ; and the remainder from 0.75 to 1.2 per cent. That is to say, if the precaution of exhausting the coils with water had not been taken, the fat in the milks would have been underestimated from 0.27 to 1.2 per cent. in actual per cent. of fat by the coil method.

The large variation is due principally to the varying per cent. of cane-sugar in the different samples. As the time of extraction for these varied from two and a half to four hours for the first extraction, a separate set of extractions under fixed conditions was made. The coils (filter-paper strips 22×2.5 inches, were "alcohol-ether" coils, and each coil again exhausted for five hours with the solvent with which it was to be subsequently treated. Simple exhaustion of the coils by ether alone does not remove all the extractable matter from the same. The extractive matter obtained for the eight individual coils varied from 1 milligram to a maximum of 2.5 milligrams. The latter was extracted by petroleum ether from a coil not previously treated with this solvent.

The eight coils were therefore free from extractable matter. Two were taken to be extracted with petroleum ether, and two with a mixture of petroleum ether (15 per cent.) and ethyl ether. The first extraction lasted three hours and the second two hours.

After the first three hours' exhaustion, the coils were taken out and dried, and then exhausted with water until all soluble matter was removed. The coils were again dried and again subjected to their respective solvents for two hours. The results obtained were as follows :

PETROLEUM ETHER.			
Amount taken.		Fat.	
Grams.		Gram.	Per cent.
2.0355	First extraction.....	0.160	7.86
	Second "	0.013	0.63
			8.49
2.0815	First extraction.....	0.158	7.59
	Second "	0.015	0.72
			8.31 ¹
" ETHER-PETROLEUM" ETHER.			
Amount taken.		Fat.	
Grams.		Gram.	Per cent.
2.0645	First extraction.....	0.156	7.55
	Second "	0.017	0.82
			8.37
2.035	First extraction.....	0.1605	7.88
	Second "	0.012	0.58
			8.46

Results by taking about 1 gram of milk and treating as above :

1.0235 grams taken gave 0.0854 gram fat or 8.35 per cent.

1.084 grams taken gave 0.0917 gram fat or 8.46 per cent.

Direct exhaustion with petroleum ether for five hours for the first exhaustion, and two hours further exhaustion after the water treatment, gave :

Amount taken.		Fat.	
Grams.		Gram.	Per cent.
2.0395	First extraction.....	0.159	7.795
	Second "	0.0135	0.661
			8.456
2.013	First extraction.....	0.155	7.699
	Second "	0.0155	0.769
			8.468

The actual time limit will not in all cases do justice to extraction where petroleum ether is used to any extent, as the siphonings are

¹ Water slightly milky, indicating loss of fat.

not always regular. Anhydrous ether, *i. e.*, water-washed ether shaken with concentrated glycerine and redistilled after separation has taken place, shows differences as great as those. The mixture of petroleum ether and ethyl ether was a water-washed ethyl ether mixed with 15 per cent. of petroleum ether prepared by thoroughly shaking and mixing the mixed ether with about 25 per cent. of concentrated glycerine and redistilling the thoroughly separated ether mixture. Coils treated with an anhydrous ether are usually quite crisp when taken out of the extraction apparatus.

Chemists who have made comparative tests have no doubt found that 1 gram of the condensed milk per coil will usually yield all the fat to within 0.2 to 0.3 per cent. on four or five hours' extraction with petroleum ether, or dry ethyl ether, or a mixture of ethyl and petroleum ether, and that the loss rarely exceeds 0.2 per cent.

The amount of milk¹ used per coil is quite a variable one among chemists.

The method of taking a sample and transferring it to the coil may be minor details but important as to possible variation in results by the coil method. While the quantity of original milk will be noticed to vary from 0.5 to 2 grams per coil, it must be apparent that the margin of safety may be overstepped in either direction, for while the maximum quantity may be too large for complete direct extraction, the minimum quantity is too small, as a difference of 1 milligram in fat obtained represents at once 0.2 per cent. For the general run of fat estimation, little fault will be found with results obtained by exhausting the fat from 1 gram of the condensed milk from a *fat-free* coil by the direct exhaustion for four to five hours with petroleum ether, or ether-petroleum ether.

Accuracy in fat estimation to within 0.2 per cent. in sweetened condensed milk is certainly attainable where the necessary precautions are taken. Where 2 grams of the condensed milk are taken the results cannot be depended upon, however, as repre-

¹ T. H. Pearman and C. G. Moor (*Analyst*, 20, 268) use 5 cc. of a 10 per cent. solution; A. H. Allen ("Commercial Organic Analysis," Vol. IV., 2nd ed., p. 235) recommends 5 cc. of a 10 per cent. solution; J. H. Shenstone (*Analyst*, 13, 222) uses 2 grams; Wallace (N. J. State Dairy Com. Rep., 1899, pp. 43-47) uses 2 grams; Cornwall (N. J. State Dairy Com. Rep., 1887, 1890, p. 408) uses 2 grams; H. Throop Richmond and L. K. Boseley (*Analyst*, 18, 170) use 5 cc. of a 15-30 per cent. solution.

senting the full yield of fat, unless the exhausted and dried coil is exhausted with water, and again exhausted with the volatile solvent. Water-washed ether mixed with 10 to 15 per cent. petroleum ether and distilled after shaking out with concentrated glycerine, answers the purpose as well as petroleum ether, as a solvent, and possesses other advantages if the petroleum ether has the proper boiling-point. The commercial petroleum ether is not suitable for this purpose, but suitable fractions of the same may readily be obtained on distillation.

The effective manner in which the cane-sugar prevents the action of the solvents upon the fat is well illustrated in the asbestos-tube method for fat estimation, in which 20 cc. of a 20. per cent. solution of the milk (4 grams) is deposited upon asbestos fiber, and, after drying, exhausted with petroleum ether. This method¹ has been the means of the unjust and unwarranted condemnation of quite a number of condensed milks. It has been proved that the method failed to exhaust all the fat, often 2 to 3 per cent. remaining in the residue, as has been amply demonstrated by exhausting the residue with water and recovering the shortage of fat in the residuum. The asbestos method has found favor in many quarters and was the direct cause of condemnation of pure milks in several instances.

The recurring frequency of unjust condemnation of condensed milk makes it particularly necessary for chemists to exercise great caution in expressing opinions upon whether a milk is skimmed or not. There are instances on record where sweetened condensed milks with high content of cane-sugar and of unquestioned purity were condemned as adulterated on the strength of the analysts finding low percentages of fat (3.8 per cent. lowest and a considerable number ranging from 5.5 to 6.8 per cent.) when more accurate methods demonstrated the presence of over 8 per cent. of fat in all the samples.

A difference of 0.5 per cent. fat has a very important bearing in the enforcement of a law defining the fat contents in milk solids. This is particularly true when the Ritthausen method is used for the estimation of the albuminoids, any error in the fat estimation reflecting its deficiency in increase of the albuminoids (the albuminoids being determined by difference) so that the

¹ Bulletin No. 54, Condensed Milk, Inland Revenue Department, Canada.

ratio between fat and albuminoid is distorted to a degree which would reflect seriously upon the milk under examination, and indicate probable skimming in the minds of some chemists.

This no doubt accounts for the discrepancy in quite a number of published analyses of the excess of albuminoid over fat in what probably were unskimmed milks. When such discrepancies are noticed in an analysis it is advisable to check the results by a nitrogen estimation by the Kjeldahl method, if this was not used in the first instance.

CONCLUSION.

In conclusion I would add that where as much as 2 grams of the sweetened condensed milk is used per "Adams' coil," the full extraction of the fats cannot be depended upon in a direct exhaustion of the coil by a four or five hours' treatment. For general usage 1 gram of milk per *fat-free* coil and four or five hours' exhaustion will give results which will rarely exceed the experimental errors common to complicated methods in which many minor details all must add their perceptible quota to a final result. The asbestos-tube¹ method, without water exhaustion, cannot be considered as giving acceptable results, as the shortage of fat by the same renders the results worthless. Three or four hours' exhaustion of the dried residue with petroleum ether, drying the exhausted mass and reexhausting with petroleum ether, will recover most of the fat.

The details of *modus operandi* especially as to proportion of milk taken to asbestos can no doubt be adjusted so that with the precaution of water exhaustion indicated the results will be fully as reliable as those by other methods. The many factors entering into any method for fat estimation in sweetened condensed milk would indicate that maximum variations of ± 0.1 are possible, and that any method yielding uniform results within that range would be acceptable for all ordinary purposes, as to accuracy.

¹ Bulletin No. 54, Condensed Milk, Inland Rev. Dep't, Canada.