Report of the Committee on Analysis of Commercial Fats and Oils

October 1946

Determination of Ash in Fats and Oils

E. W. BLANK, Subcommittee Chairman

Six samples were distributed to the subcommittee members with the request that the ash content be determined by the following procedure:

> Heat a clean 100-ml. platinum dish to redness, allow to cool in a desiccator and weigh. Add approximately 50 grams of sample, weighed to ± 0.1 gram, and heat the contents of the dish gently over a Bunsen burner until the oil can be ignited at the surface. Reduce the size of the burner flame until there is just sufficient heat to keep the sample burning quietly. When sufficient sample has burnt away to permit the addition of more sample, remove the heat source, allow to cool sufficiently to extinguish the burning sample, and add a second weighed quantity of the sample. A total weight of about 75 grams of sample should be ignited. After the second portion of sample has been added to the dish, continue the ignition to a black char. Transfer the dish and contents to a muffle. Ignite at 550-650°C. to constant weight. Allow to cool in a desiccator and weigh.

The results reported appear in the following tabulation:

Sample No.	Sample Designation	% Ash							
		Collaborator							
		6a	6b	6c	8	4	9	10	11
1	Red Oil	0.019	0.018	0.019	0.019	0.019	0.018	0.018	0.018
2	Sulfur Olive Oil Foots	0.186	0.170	0.193	0.184	0.184	0.182	0.182	0.183
3	Grease	0.058	0.046	0.053	0.058	0.051	0.052	0.052	0.052
4	Tallow	0.005	0.004	0.005	0.005	0.005	0.004	0.005	0.005
5	Hardened Fish Oil	0.011	0.010	0.014	0.012	0.012	0.010	0.011	0.011
6	Coconut Oil containing added Na Soap	0.032	0.028	0.043	0.039	0.036	0.034	0.038	0.028

There were no adverse criticisms of the procedure and the results indicate that the reproducibility was satisfactory, therefore, the Committee recommends the adoption of this method for the determination of ash in fats and oils.

Analysis of Drying Oils

J. C. KONEN, Subcommittee Chairman

A subcommittee was organized for the purpose of developing or adopting methods suitable for the analysis of drying oils. An A.S.T.M. committee on drying oils met at the A.S.T.M. convention in Buffalo during the past summer. Messrs. Bolley, Scofield, and Konen attended this meeting and report that it was agreed that uniform methods should and could be adopted by the American Oil Chemists' Society, the American Society for Testing Materials, and the Federation of Paint & Varnish Production Clubs. This subcommittee has no data or recommendations to present at this time. Work is in progress on methods for the determination of color, viscosity, refractive index, acid number and specific gravity.

Analysis of Lecithin

W. K. HILTY, Subcommittee Chairman

A subcommittee for the analysis of lecithin was formed the past spring to investigate analytical methods for the evaluation of soybean lecithin and to develop such new methods as are deemed necessary. A sample was sent out to the subcommittee members for the determination of moisture, acetone soluble and insoluble, and benzene insoluble. The results reported appear in the following table:

Collaborator	Moisture	Acetone Soluble	Acetone Insol. (by difference)	Benzene Insoluble
	%	%	%	
6	0.95	38.84	60.21	Nil
2	0.95	38.30	60.70	.....
3	0.82	37.97	61.16	0.051
5	0.86	38.15	61.01	Nil
4	0.76	37.80	61.33	0.010
1	0.93	38.22	60.85	Nil
Average	0.88	38.21	60.85	0.034

Since the results are in good agreement and since these methods are already in common use in the industry, we now recommend their adoption. Copies of the methods follow:

Procedure: **Moisture in Lecithin**

Tare a 500-ml. balloon flask and into it weigh a quantity of the sample. (Not less than 50 grams and not more than 100 grams.) Weigh the sample accurately to .1 grams. Connect the condenser to the distillation tube by means of a tight fitting cork, the distillation tube to be previously treated with cleaning solution, washed with distilled water, alcohol and ether, and dried. To the oil in the flask add 100 ml. of toluene, pouring it through the condenser and allowing it to overflow into the flask below, filling the trap at the same time. Before applying the heat, place a wad of cotton loosely into the upper end of the condenser to retard an initial passage of vapor into the atmosphere.

With the cooling water flowing through the condenser, apply the heat and regulate it so that the condensed distillate will fall from the end of the condenser at the rate of 2 to 5 drops per second. The distillation shall be continued at the specified rate until no water is visible on any part of the apparatus except at the bottom of the trap. At the end of 30 minutes, 45 minutes, and 1 hour interrupt the distillation and work down the water globules which persist in hanging to the side of the tube, by means of a copper wire with a loop on the end. At the time of working down the water globules, also wash down through the condenser with about 10 ml. of fresh toluene. A persistent ring of condensed water in the condenser tube shall be removed by increasing the rate of the distillation for a few minutes.

At the end of 1 hour, disconnect the receiving tube and permit the contents to come to room temperature.

When room temperature has been reached, read the volume of water in the trap below the toluene layer, to .01 ml., multiply by 100 and divide by the weight of the sample. The result is the per cent water present in the original oil by weight, it being assumed that 1 ml. of water equals 1 gram.

Note:

Inasmuch as there is decomposition read to total layer below the toluene considering the light milky layer as water.

Example:

$$\frac{\text{Volume of layer in ml.} \times 100}{\text{Grams material weighed}} = \% \text{ water.}$$

Typical Problem:

$$\frac{.83 \times 100}{52} = 1.6\%.$$

Acetone Soluble and Acetone Insoluble in Lecithin

Procedure:

Weigh 2 grams of the material to be tested into a previously tared centrifuge tube containing a glass rod tared with the centrifuge tube. Weigh to .0005 gram. Dissolve in 3 ml. of petroleum ether aiding solution by means of the stirring rod. This will take about 15 minutes. When dissolved, run into the mixture from a burette 15 ml. of acetone. Mix thoroughly with the diluted sample and transfer to a dish containing ice water. Then gradually add chilled acetone with constant stirring to the 50-ml. mark. Remove the stirring and chill for 15 minutes in an ice bath. Transfer to a power centrifuge and centrifuge for about 10 minutes at such a speed as will cause the mixture to be clear.

After centrifuging 15 minutes decant the acetone soluble portion into a 250-ml. tared beaker. Now refill the tube with acetone to the mark, stir, chill, and centrifuge as before. Combine the two acetone soluble portions in the tared beaker. Evaporate the acetone carefully on a hot plate. Aspirate the residue well, dry in oven at 105°C. for 1 hour, desiccate, and weigh. Report as acetone soluble, calculating as follows:

$$\frac{\text{Grams residue} \times 100}{\text{Grams original material}} = \% \text{ Acetone Soluble.}$$

Calculation of Acetone Insoluble:

Acetone Insoluble equals 100—(% Acetone Soluble plus % Moisture, plus % Benzene Insoluble).

Benzene Insoluble Matter in Lecithin

Procedure:

Weigh into a tared 250-ml. Erlenmeyer flask 10 grams of the material to be tested. Add 100 ml. of benzene and shake until thoroughly dissolved. Filter through a previously tared filtering funnel. Wash the flask and filter twice with 25-ml. portions of benzene. Dry in oven at 105°C. for 1 hour. Desiccate and weigh to .0005 gram. Calculate increase in weight to % and report as Benzene Insoluble.

Separation of Liquid and Solid Fatty Acids

F. G. DOLLEAR, Subcommittee Chairman

The subcommittee on the separation of liquid and solid fatty acids is carrying out an investigation on five samples of oil which are also under investigation by the thiocyanogen subcommittee and by the spectroscopy committee. These samples are linseed oil, soybean oil, cottonseed oil, lard, and beef fat. The saturated acid content of these oils will be determined by three different methods, the American Oil Chemists' Society lead salt-alcohol method, a solvent crystallization method, and a modified Bertram oxidation method. This will permit a comparison of the results obtained by these different methods, and will indicate whether certain modifications will be necessary in the procedures to obtain reliable results on various types of oils. Work of this subcommittee has not progressed to a point where results can be reported at this time.

Determination of Unsaponifiable Matter

C. P. LONG, Subcommittee Chairman

The work this year has been centered on cooperative work on two samples. These were a high grade tallow and the same tallow to which has been added enough mineral oil denaturant to form 1% of the sample.

From previous work it was obvious that the manner of evaporating the petroleum ether extract in the present method and the time and manner of drying were two of the most important factors in securing or preventing accurate results. This, in part, is indicated by the amount of the denaturant that is recovered in the unsaponifiable determination. The effect of placing a weighed amount of stearine in the flask was also included. The results were somewhat disappointing because their wide variation particularly as to the amount of denaturant recovered. They did point out some definite trends.

The following are some of these:

1. Stearine retards the loss of mineral oil denaturant and possibly other volatile unsaponifiable material.
2. Drying on the steam bath is much more preferable than oven drying at 105°C. to constant weight.
3. The time of holding the sample flask on the steam bath after the last of the solvent has evaporated should be probably 10 minutes, certainly not over 30 minutes. If moisture in the extract presents a difficulty, the extract should be dried with anhydrous sodium sulfate before evaporation.
4. The loss of mineral oil denaturant and probably of most other volatile unsaponifiable material increases as the volume of solvent increases.

Work is continuing on these samples with comparisons by drying in a vacuum desiccator at room temperature.

Since the Swift continuous extraction method allows the use of about ¼ the volume of petroleum ether that the regular method requires, the glass apparatus for this method has been distributed to the subcommittee, with an outlined method for handling the samples. This involves the use of stearine in the flask and drying one set in the vacuum desiccator. Work will continue on this method.

Determination of the Refined and Bleached Color of Tallow

L. B. PARSONS, Subcommittee Chairman

Work has been in progress for some time in an effort to find a suitable method of determining the refined and bleached color of tallow. There is a need for this method in connection with the manufacture of soap in order to more properly evaluate tallow intended for soap production. Samples have been tested in previous years and the data included in previous reports. Three samples were distributed to the subcommittee during the past year for refining and bleaching test. The results appear in the following tabulation:

Laboratory	Sample No. 12		Sample No. 13		Sample No. 14	
	F.A.C. Color	Refined & Bleached Color (red)	F.A.C. Color	Refined & Bleached Color (red)	F.A.C. Color	Refined & Bleached Color (red)
12	5	0.27	5	2.3	11A	0.7
4	5	0.35	5	2.4	15	0.9
9	5	0.20	5	2.0	11A	0.6
13	5	0.55	5	2.7	13	1.0

Another sample, No. 15, was also sent out for the same determination. The refined and bleached samples were exchanged between collaborators for color reading in order to determine whether or not the difficulty lay in the bleaching test or in the color reading. The results of this test appear below:

Laboratory	Collaborators R. and B. Color	13's Readings on Collaborators R. and B. Samples	Collaborators' Readings on 13's R. and B. Sample
13	1.8	1.8	.....
4	1.5	1.6	1.5
12	1.5	1.5	1.7
9	1.0	1.2	1.4

A majority of the results obtained have been in reasonable agreement and it is the opinion of the Committee that much of the difficulty in instances where results do not agree lies in the difficulty in reading colors by the color reading method rather than in the actual refining and bleaching test. The Committee believes that the method is satisfactory as compared with other bleaching methods and recommends its adoption.

Refining and Bleaching Test

Place 500 grams of the thoroughly mixed sample of crude tallow or grease in a refining cup and heat in a water bath to 125-130°F. Stir rapidly at approximately 250 r.p.m., and add the calculated amount of 20° Bé caustic soda solution. Some excess of caustic soda is necessary to insure a satisfactory separation of the foots. Experience indicates that the percentage of excess actual NaOH calculated on the basis of the fat weight must be increased with increasing percentages of F.F.A. in the stock. In general, satisfactory foots separation results when caustic soda in excess of the amount required to react with the F.F.A. (calculated as oleic acid) is added as follows:

% Excess NaOH Basis Weight of Stock	% F.F.A. in Stock
0.2	.1- 4.00
0.3	4.01- 6.00
0.5	6.01- 8.00
0.6	8.01-15.00

Stirring of the mixture is continued at 250 r.p.m. for 5 minutes. The speed of stirring is then decreased to approximately 70 r.p.m. and the temperature of the bath quickly raised to 142-147°F. Stir under these conditions for 10-15 minutes, or until the foots appear to be ready to settle. It may sometimes be necessary to add a small amount of water to the mixture of tallow and foots to hasten the coagulation and to insure complete precipitation. After the stirring, allow the mixture to stand at 142-147°F. until the foots settle and the fat is clear.

Decant through a 60-mesh screen 300 grams (±1.0) of refined tallow or grease into an unchipped enameled refining cup, on a Torsion balance. Heat the tallow or grease with a Bunsen burner to 105°C.-110°C. Add 3% (9 grams) of A.O.C.S. Activated Earth. Stir mechanically for 5 minutes at a speed sufficient to keep the earth in suspension, maintaining the temperature between 105° and 110°C. by heating with the Bunsen flame. Immediately filter the fat or oil, transferring as much of the Activated Earth as possible through a coarse, dry, 25-cm. filter paper of Whatman No. 4 grade (Reeve Angel No. 230 filter paper is also satisfactory), using a corrugated galvanized-iron funnel. Discard the first portion that filters through, as it is usually cloudy. When the fat or oil filters through clear, collect in an oil sample bottle or tube and read the Wesson color in a 5¼" column.

Stability of Sodium Thiosulfate

The Committee has been investigating various methods of stabilizing sodium thiosulfate solution. The methods compared were as follows:

1. 0.1 *N* $Na_2S_2O_3$ as usual.
2. 0.1 *N* $Na_2S_2O_3$ + 0.01 g. Na_2CO_3 per liter.
3. 0.1 *N* $Na_2S_2O_3$ + 0.1 g. Na_2CO_3 per liter.
4. 0.1 N $Na_2S_2O_3$ + 3 drops $CHCl_3$ per liter.
5. 0.1 *N* $Na_2S_2O_3$ + 10 ml. isoamyl alcohol per liter.
6. 0.1 N $Na_2S_2O_3$ + 0.01 g. Na_2CO_3 and 3 drops $CHCl_3$ per liter.
7. 0.1 *N* $Na_2S_2O_3$ + 10 ml. isoamyl alcohol and 0.1 g. Na_2CO_3 per liter.

The following comparisons were made:

a. Determine pH of water from which solns. were made.
b. Determine pH of each prepared soln.
c. Determine pH and titer vs. 0.1 *N* $K_2Cr_2O_7$ at beginning and monthly thereafter for six months.
d. Compare titer on actual iodine and SCN No. with fresh 0.1 *N* $Na_2S_2O_3$ at start and monthly thereafter.
Store in dark bottles with rubber stopper at room temperature.

The conclusions were:

1. All solutions were of good stability, even those without preservation.
2. There was not unanimity of opinion as to the best preservative. Results were not consistent.
3. Decomposition of 0.1 *N* sodium thiosulfate solution is not as serious as suspected.
4. The Committee does not anticipate any further work on this project.

Determination of Thiocyanogen Values

R. T. MILNER, Subcommittee Chairman

On June 4, 1946, five samples of oils (linseed, soybean, cottonseed, lard, beef fat) were sent to six laboratories for collaborative study of the thiocyanogen determination. The method prescribed was a modification of the present official A.O.C.S. method and in both the preparation of reagent and procedure followed closely the two articles by Dollear and fellow-workers [Oil and Soap *22:* 226 (1945) and *23:* 97 (1946)]. The chief departure from the A.O.C.S. method was the use of carbon tetrachloride in the reagent. Each collaborator was requested to make duplicate determinations and to repeat these after at least one day's interval.

Results were received from five laboratories by October 1. Three of these laboratories were in agreement with each other and also had no apparent difficulties in obtaining agreement on successive days with the same sample. For example, on linseed oil these three laboratories reported, as an average of four results (two on each of two days), 120.4, 120.6, and 121.8, while on beef fat they reported 42.2, 42.0, and 42.3. The other two laboratories had difficulty in checking themselves on successive days and their results were not in good agreement with each other or with the other three laboratories.

Since further work will be necessary to obtain agreement between collaborating laboratories and since several minor points such as the use of potassium iodide solution must be studied, no detailed report will be given at this time. Further work will be carried out as promptly as possible.

One disconcerting fact has been demonstrated by the present work. These same five oil samples have been studied by the Spectroscopy Committee and the Liquid-Solid Acids Subcommittee. The Spectroscopy Committee furnished iodine values on these oils with 8 out of 12 values for each oil in close agreement. Saturated acids have been measured by two laboratories on the linseed, soybean, and cottonseed oils by the crystallization procedure, and the results are in agreement. If these averaged values for iodine values and saturated acids are used, together with the thiocyanogen values as determined in this work, to calculate the composition of the linseed, soybean, and cottonseed oils, then composition are found which are not in agreement with those found by other methods of analysis such as the spectrophotometric.

The present work shows that much more work must be done before a satisfactory determination of the composition of vegetable oils can be made.

Stability Test

V. C. MEHLENBACHER, Subcommittee Chairman

Progress this year on the Fat Stability Test has concentrated on the redesign of the apparatus which is now under construction. A report of results with this apparatus will be made available at another time.

Insoluble Impurities Determination

It was called to our attention during the year that some laboratories disliked using petroleum ether for washing the residue in the insoluble impurities determination. It was disliked because of the hazard involved. Several members of the Committee made a comparison between petroleum ether and carbon tetrachloride on a variety of fats. The results appear in the following tabulation:

Laboratory 14		Laboratory 13		Laboratory 6		Laboratory 12		Laboratory 4	
P.E.	C.T.	P.E.	C.T.	P.E.	C.T.	P.E.	C.T.	P.E.	C.T.
0.15	0.15	0.10	0.09	0.52	0.55	0.29	0.25	0.16	0.15
1.10	1.18	0.17	0.15	0.72	0.70	0.14	0.17	0.66	0.73
0.08	0.06	0.18	0.22	0.02	0.01	0.22	0.39	0.66	0.65
0.39	0.36	0.20	0.19	0.02	0.01	0.32	0.30	1.10	1.05
0.18	0.17	0.50	0.53	0.02	0.01	0.11	0.13	.....	.....
0.80	0.80	0.70	0.66	.....	.....	0.36	0.39	.....	.....
.....	.....	.....	.....	.....	.....	0.74	0.68	.....	.....
.....	.....	.....	.....	.....	.....	0.23	0.25	.....	.....
.....	.....	.....	.....	.....	.....	0.13	0.17	.....	.....
.....	.....	.....	.....	.....	.....	3.68	3.16	.....	.....
.....	.....	.....	.....	.....	.....	1.26	1.42	.....	.....
.....	.....	.....	.....	.....	.....	0.45	0.47	.....	.....

P.E.—Petroleum Ether.
C.T.—Carbon Tetrachloride

The above results indicate that carbon tetrachloride and petroleum ether are equally satisfactory. On the basis of these results the Committee recommends that carbon tetrachloride be permitted as an alternative washing agent for use in the insoluble impurities determination.

Analysis of Tall Oil

The agreement at the Committee meeting a year ago was to follow the progress of the A.S.T.M. in their development of methods for the analysis of tall oil. The activities of the A.S.T.M. during the past year have concentrated on other products so that no progress has been made in the case of tall oil.

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New Techniques in Glycerine Distillation*

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IN recent years significant improvements have been made in distillation equipment and technique. Glycerine refiners have been aware of the need for modernized equipment in order to realize economies in consumption of fuel, to produce C. P. grade without resorting to multiple distillations, and to achieve economy of space by increasing the productive capacity per unit. "Sweetwater" produced in the older type stills was undesirable since these weak concentrations—ranging from 2.5-5.0% glycerol— had to be re-evaporated and redistilled, and even then the distillate was of poor quality, being rich in trimethylene glycol and saleable only as "Yellow Distilled." A further disadvantage of the older units was the necessity for concentrating the distillate up to 98.7%, the minimum standard for "Dynamite" glycerine.

The purpose of this discussion is to review some recent advances in solving these difficulties. More specifically, we will describe the design features and the operation of a distillation unit which has been used successfully in commercial operation for several years and which has not heretofore been described in the literature. Recognizing the need for improvements, Dr. M. H. Ittner was successful in designing a unit (now known as the "Ittner Still") which eliminated the undesirable features of the older stills, and which will be described here (1). Dr. Ittner touched upon it, but very briefly, at the time he received the Perkin medal in 1942 (2). An improved type of glycerine still has also been described by Wurster (3).

With the aid of the chart we can follow the sequence of flow. Beginning at the left we note the feed tank "A." This has a capacity of 20,000-25,000 pounds and is mounted on a scale (for accounting purposes) and is provided with a steam jacket for partial pre-heating of the crude. The crude is drawn into the still by means of a vacuum in the still system, first passing through the main pre-heater "B." This is a

* Presented at the 20th annual fall meeting, American Oil Chemists' Society, Chicago, Oct. 30-Nov. 1, 1946.