Report of the Committee on Analysis of Commercial Fats and Oils

October, 1944

Thiocyanogen Values

Last year this Committee attempted to determine if thiocyanogen constants, stoichometrically calculated from fatty acids to glycerides, could be used with satisfactory accuracy. In that program the Committee was unable to obtain agreeing results in the several laboratories. This year we undertook to find out why. Accordingly, samples were sent out and reagents were supplied from two sources so that all collaborators used identical materials. The thiocyanogen values were run using these reagents and the reagents regularly used by each member. The results are shown in the following tabulation:

Laboratory	Cottonseed Oil		Peanut Oil		Soybean Oil	
	Regular	Special	Regular	Special	Regular	Special
1	68.2	67.5	72.0	71.8	86.0	86.0
2	66.9	67.3	71.5	71.8	85.9	86.1
3	65.2	.....	69.9	.....	83.1	.....
4	66.8	67.0	71.1	71.4	84.9	85.4
5	66.4	.....	70.8	.....	83.9	.....
6	68.7	67.6	73.1	71.8	86.0	86.4
7	67.0	67.0	72.0	71.7	85.2	85.6
Average	67.5	67.3	72.0	71.7	85.6	85.9
Av. deviation	0.7	0.3	0.5	0.1	0.4	0.4

Laboratories 3 and 5 not included in averages.

Two hundred per cent excess reagent and 1.66 gms. of powdered potassium iodide were used in all of these determinations.

It is to be noted that for the most part these results are in much better agreement than previous figures.

Some samples, especially the higher melting point fats, are not completely soluble in the reagent. Their solubility is improved by the addition of carbon tetrachloride. Therefore, a comparison has been made of thiocyanogen results with and without the addition of carbon tetrachloride. The carbon tetrachloride was purified by a method supplied by one of the Committee members. The method follows:

PURIFICATION OF CARBON TETRACHLORIDE: *Removing Reducing Substances.* The carbon tetrachloride is shaken in a separatory funnel with about 50 ml. of concentrated sulfuric acid (A.C.S. grade), per liter of carbon tetrachloride and allowed to stand for two hours. This acid treatment is repeated with fresh charges of acid until a color no darker than a light straw develops in the acid layer on standing for two hours. After the acid layer is separated, the larger portion of the acid remaining in the carbon tetrachloride is washed out with water. The last traces of acid are removed by two consecutive washings with 50% aqueous KOH, (50 ml. per liter of carbon tetrachloride). The carbon tetrachloride is then partially dried by allowing it to stand several hours over pellets of potassium hydroxide. It is then decanted into a distilling flask and distilled. At this stage the carbon tetrachloride is suitable for use in iodine number determinations but must be freed of the last trace of moisture before use in the thiocyanogen reagent.

Drying. To remove the last traces of moisture, the carbon tetrachloride is placed in a flask with phosphoric anhydride (50 gms. per liter of carbon tetrachloride), and allowed to stand several hours with occasional shaking. The phosphoric anhydride is then filtered off, the filtrate collected in a distilling flask with another charge of phosphoric anhydride (10 gms. per liter of carbon tetrachloride), and the dry carbon tetrachloride distilled off. All equipment used in distilling the carbon tetrachloride must be dried for at least one hour at 120°C., and all connections in the distillation apparatus should preferably be made with ground glass joints. The use of a two- or three-neck receiving flask to collect the distillate is recommended. One outlet should be fitted with a drying tube.

Data showing effect of carbon tetrachloride:

Laboratory	Sample	Regular	Carbon tetrachloride added			
			25%	40%	10 ml.	5 ml.
1	Cottonseed Oil	67.5	66.3			
1	Peanut Oil	71.8	70.7			
1	Soybean Oil	86.0	85.3			
4	Cottonseed Oil	67.0	66.9			
4	Peanut Oil	71.4	71.1			
4	Soybean Oil	85.4	85.2			
2	Not designated	24.2	23.5	24.1	23.7	
2	Not designated	44.5	45.5	46.1	45.0	
2	Not designated	55.9	57.7	59.3	56.2	
1	Soybean Oil	85.2	85.7			
1	Peanut Oil	70.9	71.2			
		(1)	(1)	(1)	(2)	
4	Glycerides	87.0	85.5	89.4	83.5	
4	Glycerides	84.5	84.2	86.8	83.5	
4	Fatty Acids	91.3	89.3	90.0	86.6	
4	Fatty Acids	24.2	23.4	22.7	22.9	
			(3)			
7	Cottonseed Oil	66.7	66.3			
7	Peanut Oil	71.7	69.7			
7	Soybean Oil	85.5	82.5			
7	Tallow No. 1	47.3	47.0			
7	Tallow No. 2	42.4	42.5			
7	Tallow No. 3	47.0	46.2			
7	Fatty Acids—Tallow No. 1	48.2	45.9			
7	Fatty Acids—Tallow No. 2	44.2	43.1			
7	Fatty Acids—Tallow No. 3	47.2	46.7			
5	Not designated	70.9				69.3
5	Not designated	61.3				60.2
5	Not designated	62.2				61.0
5	Not designated	56.2				56.8
5	Not designated	69.1				68.4
5	Not designated	73.2				70.7

(1) Effective normality of thiocyanogen reagent 0.194-0.206
(2) Effective normality of thiocyanogen reagent 0.140
(3) Effective normality of thiocyanogen reagent 0.200

A summary of results obtained to date indicates that the use of carbon tetrachloride is undesirable except possibly in the case of high melting point fats which are difficultly soluble in the regular reagent. More work is contemplated.

In a previous report this Committee recommended that the amount of reagent be increased from an excess of 100-150% to 150-200%. It is now recommended that the quantity of potassium iodide be increased from 1 gm. to 1.66 gms.

Fat Stability Test

Additional work has been done on the Fat Stability Test. This work has been concentrated on further standardization of the details of the method.

Samples were distributed among Committee members who reported the following results:

Laboratory	Sample			
	2	3	4	5
8	30	45	34	35
2	22-20-26-21	46	31	28
7	29	45	33	30
9	28	45	35	30
12	35	48	40	34
6	31	52	35	33
4	28	47.5	31	31
5	26	....	31	33
11	25	42	29.5	25.5
10	24	47.5	32	21
Average	26	46	33	30
Av. deviation	3.5	1.9	2.3	2.2

While there are some individual differences that are large, the average deviations are much improved over previous results. More work is contemplated on this method.

The Army Quartermaster Corps requested that the Committee supply them with a method for the Fat Stability Test, incorporating the best technique known at this time. Therefore, a procedure has been written and approved by the Committee and submitted to the Quartermaster Corps. While this procedure has not yet been accepted as final by the Committee and may require modification, it is agreed that it represents an acceptable method. The method follows:

Apparatus (1)

The apparatus consists of an aerating train, which is designed to supply washed air to the samples and a bath to keep the samples at constant temperature. The entire unit is calibrated in such a way that a constant volume of air (2.33 cc. per second) passes through each sample. The apparatus and procedure of standardization of the air flow are illustrated and described in the original paper (2).

The bath consists of a water jacket in which water is kept at the boiling point, using a reflux condenser to keep the volume constant. This water jacket encloses a mineral oil bath in which is contained a rack accommodating 25- by 200-mm. test tubes. The bath is maintained at such a temperature that the samples within the tubes will remain at 208°F. ± 0.5°F. (97.7°C.). The temperature of the outer bath may be regulated by the addition of alcohol to lower or glycerin to raise the boiling point. The bath is preferably insulated with about 1.5 inches of asbestos. This facilitates the maintenance of a uniform temperature. The bath may be heated with either gas or electricity. The heating must be arranged so as to give uniform heating throughout the length of the bath. It is important to be sure the temperature is the same over all.

The only modification to the original design of the aerating train is that a reflux condenser is inserted in bottle E which contains the air-washing liquid. The air passes from bottle E through the condenser to remove as much water as possible. From the condenser the air passes to the regular manifold distributing bottles G and F. A satisfactory arrangement is described by Riemenschneider, Turer and Speck (3). Bottle B and cylinders C and D contain water. Bottle E contains a solution of 2% potassium dichromate in 1% sulfuric acid.

All glass aeration tubes as described by Riemenschneider, Turer and Speck are permissible but not required (3).

Solutions

1. Sodium thiosulfate 0.1 N accurately standardized.

2. Sodium thiosulfate 0.01 N accurately standardized.

Use reagent grade thiosulfate, freshly distilled water and store in brown glass bottles. Add 10 ml. isoamyl alcohol and 0.1 gm. sodium carbonate per liter to stabilize the solution. Prepare a solution approximately 0.1 N and standardize as follows:

Prepare 0.1 N potassium dichromate by dissolving 2.452 gms. of finely powdered and dried reagent grade potassium dichromate in distilled water and make up to 500 ml. Pipette 25 ml. of this solution into glass-stoppered Erlenmeyer flask, add 5 ml. conc. hydrochloric acid, 5 ml. potassium iodide solution (150 gms. per liter) and 50 ml. distilled water. Add the thiosulfate slowly with continuous and vigorous swirling until the yellow color has almost disappeared. Add about 1 ml. of starch indicator and continue the titration, shaking as before, until the blue color just disappears. Adjust the thiosulfate solution to exactly 0.1 N.

Dilute thiosulfate solution (0.01 N) may be prepared by accurately pipetting 100 ml. 0.1 N thiosulfate solution into a 1,000-ml. volumetric flask and diluting to volume with boiled and cooled distilled water.

3. Starch indicator solution. Make a homogeneous paste of 10 gms. of soluble starch (Lintner) in cold distilled water. Add to this 1 liter of boiling distilled water, stir rapidly and cool. Salicylic acid (1.25 gm. per liter) may be added to preserve the indicator solution. If long storage is required, the solution should be kept in a refrigerator.

4. Air washing solution. An aqueous solution containing 2% potassium dichromate and 1% sulfuric acid. This solution must be changed at least weekly.

5. Potassium iodide solution. Saturate distilled water with reagent grade potassium iodide. Be sure solution remains completely saturated. This is best indicated by the presence of crystals of undissolved salt in the solution bottle. Store in the dark. This solution turns a light brown on standing and may become faulty with age.

6. Acetic acid-chloroform solvent. Mix 60% reagent grade glacial acetic acid and 40% U.S.P. chloroform by volume.

7. Cleaning solution. Place 5 to 10 grams of technical potassium dichromate in a 1-liter Erlenmeyer flask with about 50 ml. of water. Warm the flask under the hot water tap to dissolve as much dichromate as possible. Add concentrated sulfuric acid slowly and carefully until the volume is about 200 ml. Allow the hot solution to stand for about five minutes, then dilute to 1 liter with concentrated sulfuric acid.

The life of the cleaning solution depends upon the thoroughness of removal of the fat from tubes, beakers, etc. The solution is discarded when the distinctly red chromic acid color has changed to brown. If the fat has been well washed away, the solution can be used for 3 or 4 weeks. Its life may be still longer if not in daily use.

Sampling

All equipment and containers must be scrupulously clean. The containers may be new (unused) tinned cans or glass jars. Metals such as copper, bronze and brass must, under no circumstances, be allowed to come in contact with samples. Glass containers are cleaned with cleaning solution, thoroughly rinsed with distilled water and dried by heat. Mason fruit jars with rubber gaskets are satisfactory but all parts must be cleaned as described above. Jars with plastic or enameled tops, or covers containing paper liners are not recommended.

Samples are removed from tierces or similar packages with a stainless steel trier (butter type 18" to 36" long) which has previously been well cleaned with soap and water, thoroughly rinsed with distilled water and completely dried by heat or with new paper towel. Samples shall be so taken that none of the shortening will be taken less than 2 inches from the wall of the container or from the surface.

Samples must be packed and transported to the destination laboratory in such a way that they will arrive in a solid state. Samples that have been melted or partially melted at any time are not to be used.

Porcelain or stainless steel spatulas are used in the laboratory for removing the test portion from the container. Clean the spatula between samples in a stream of *hot* water and wipe with paper towel. Select a portion for the test, after removing the top surface and discarding, in such a way as to avoid taking any fat which has been in contact with the sample container. Place in a beaker which has been cleaned with cleaning solution, thoroughly rinsed with distilled water and dried with heat. Completely melt the contents of the beaker but do not allow the temperature to rise more than a few degrees above the melting point of the sample.

Aeration of Sample

Caution. The control of temperature, maintenance of absolute cleanliness and elimination of any chance of contamination cannot be overemphasized. If these factors are not well guarded, the results are likely to be incorrect.

Pour 20 mls. of liquefied sample into each of three 200-mm. test tubes, which for convenience, should be calibrated at the 20-ml. level. Place one of the tubes in the oil bath, which has previously been brought to the desired temperature and make necessary connections to start the air flow. Record time of starting. Stopper the second and third portions and hold at a cool temperature until the time arrives for their incubation. At the desired time after starting the first portion, start the second portion of the sample and similarly the third portion.

The time spacing of tubes is conveniently regulated as follows:

Keeping Time	Space Tubes
0-16 hrs.	1 hr. apart
16-32 hrs.	2 hrs. apart
32-50 hrs.	3 hrs. apart
Over 50 hrs.	4 hrs. apart

The tubes must be maintained at 208°F. ± 0.5°F. (97.7°C.) and inspected regularly to be sure that the air is flowing properly. Incubations may be conducted in two ways depending on whether the exact keeping time is desired or whether a given minimum keeping time is to be met.

For Exact Keeping Time. Incubation is continued to definite peroxide levels corresponding to the point of inception of rancidity. These levels are:

Lard and oleo oil..... 20 me. peroxide/kg. of fat
Hydrogenated and blended shortening.....
100 me. peroxide/kg. of fat

It is convenient, with long keeping samples, to run a "pilot tube" 12-15 hours in advance of the three test tubes to get an approximation of the keeping value. Successive small samples (1 gm.) may be withdrawn from this tube to test for peroxide value as the rancid point is approached. This should not be continued after a total of 5 gms. have been removed from a single tube. The pilot tube serves a two-fold purpose, first, it enables the operator to safely carry the incubation overnight and second, it eliminates most of the guesswork from choosing the time for making titrations (see note below). It is desirable to incubate samples continuously until they have reached a stage at which, if continued throughout the night, rancidity will have developed before morning. When this stage has been reached, the tubes are removed from the batch and immediately chilled. They must be held in the chilled condition until incubation under constant supervision can be resumed.

All tubes are titrated when the end-point has been reached. Results are reported in terms of hours to the nearest hour at which the peroxide value just fails to exceed 20 me. or 100 me. as the case may be.

Hydrogenated or Blended Shortening

Tube No.	Hours	me. peroxide/Kg.
1	120	110
2	116	90
3	112	80

It will be seen from a simple graph of the results that at the end of 118 hours the peroxide value just reaches 100 me. peroxide/kg. *Report 118 hours.*

For Minimum Keeping Time. To determine whether a sample meets a specified keeping time requirement it is necessary to conduct the incubation of the three tubes as outlined above for Exact Keeping Time except that the incubation may be interrupted when the specified time has elapsed. It will be seen that the pilot tube is not needed if the operator arranges his work so as to be able to stop the incubation at the proper time.

Note: After a little practice, the odor of the air from the exhaust tube can be taken as a good indicator of the end-point but because of the large personal variation in organoleptic testing, the odor is *not* accepted as final.

Determination of Peroxides

Weight 5 grams (±.05) of sample into 200-300 ml. Erlenmeyer flask and dissolve in 30 ml. of the acetic acid-chloroform. Add 0.5 ml. of saturated potassium iodide solution and shake until the solution becomes clear. After 2 minutes, add 30 ml. of distilled water and titrate with standard sodium thiosulphate. Add starch indicator when near the end-point. The flask should be shaken vigorously near the end of the titration to liberate all the iodine from the chloroform layer. The number of milli-equivalents of peroxide present per 1,000 grams of sample is calculated from the amount of sodium thiosulphate solution required to titrate the liberated iodine.

Milli-equivalents of peroxide per 1,000 grams of sample equals:

$$\frac{\text{Ttitration (ml.)} \times \text{normality} \times 1{,}000}{\text{wt. of sample (5 gm.)}}$$

A blank titration should be made daily on all reagents and should never exceed 0.1 ml. of sodium thiosulfate.

Cleaning Procedure

Wash the used tubes from the stability determinations with soap and water and rinse with tap water. Place on a test tube rack and nearly fill with cleaning solution. Wash off the air inlet and outlet assembly including the rubber stopper with ethyl ether or light gasoline before washing with soap and water. This solvent wash is necessary on the inside of the glass tubes since the small diameter makes it impossible to scour the inside with a brush. After the soap and water wash and several rinses, place the inlet and outlet assambly in the test tubes containing cleaning solution. By means of a rubber tube and a vacuum line draw some of the cleaning solution up into the air inlet and air outlet tubes and allow to drain back. Repeat this several times until a film of cleaning solution adheres evenly to the inside of the glass tubes. Then allow the air delivery tubes to stand over night in contact with the cleaning solution within the test tubes.

After soaking as described, pour off the cleaning solution, rinse all parts at least four times with warm tap water and then allow the tubes to stand for at least 2 hours in tap water. Follow with at least six rinses of distilled water. Dry the test tubes in an air oven at 105°C. Dry the air inlet and outlet assembly in a vacuum oven at about 60°C. A low temperature is used to prevent softening of the rubber stoppers. Inspect all glass parts minutely and discard everything not absolutely clean. The units are then ready for use. Protect all glass parts in a dustproof cabinet until ready to use.

Maintenance of Equipment

All equipment and washing solutuions must be kept clean. Oil and water baths must be kept at proper levels. The water should be 1.5 inches from the top and the oil 2 inches from the top. Use distilled water to prevent scale formation and pure white mineral oil.

Keep the capillary tubes clean to insure proper air passage. A very fine wire is convenient for this purpose.

Do not use rubber tubing or rubber stoppers that have started to crack or that have become sticky from the heat. Clean all new rubber thoroughly before using. Be sure that the ends of the rubber tubing do not pick up any oil from contact with the bath.

The bath is easily cleaned by wiping with a cloth to which has been added a little carbon tetrachloride.

REFERENCES

(1) The entire apparatus, including calibrated capillary tubes, may be obtained from E. H. Sargent & Company, 155 E. Superior Street, Chicago, Illinois.
(2) Oil & Soap *10*, 105 (1933).
(3) Oil & Soap *20*, 169 (1943).

Insoluble Bromides (Hexabromide Test)

The insoluble bromide test has stimulated considerable interest this year because of its application to the evaluation of soaps intended for use in the production of synthetic rubber. Some time ago this Committee did some work in an attempt to make this test quantitative. While those data were not published, they can be summarized by the statement that the results had no quantitative significance. Several of the members, especially the Southern Regional Research Laboratory, made a very thorough investigation and concluded that the method and several modifications of this method were unreliable.

FAT STABILITY APPARATUS

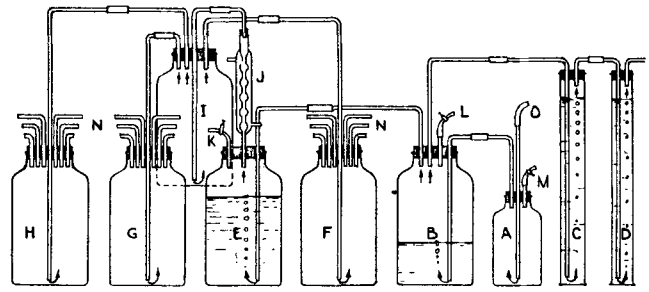

Diagram of Air-Distributing System

A—Device to control pressure of incoming air.
B—Bottle containing water for washing air.
C,D—Water columns. Air in space above water in B is kept under constant pressure sufficient to bypass air through C and D at a steady rate.
E—Bottle containing acid dichromate solution. The air from E passes through condenser J into bottle I, thence into bottles F, G, and H, which distribute air to the tubes N, which lead to the aeration tubes.
M—Screw clamp to regulate flow of air.
O—Connection to source of air pressure.
K, L—Pinchcocks to release pressure when shutting off apparatus.

This time our interest has been in the qualitative aspects of the hexabromide test. The method generally used is as follows:

Procedure. Add approximately one gram (if solid) or 1 ml. (if liquid) of the fatty acids to 25 ml. of acetic acid—ether solvent (4 parts by volume of ethyl ether to 1 part glacial acetic acid) in a Soxhlet flask. Cool to 0° to 5°C. and hold at this temperature for two hours. *If a precipitate forms*, filter the solution cool through a small filter paper into another cool Soxhlet flask which has been rinsed with acetic acid-ether solvent. If there is no precipitate, proceed immediately to the next step.

Add bromine to the contents of the flask from a dropping bottle until a deep red color is imparted to the mixture. Do this under a hood. Cool the mixture again to 0° to 5°C. and hold it in this range for an additional four hours. Examine the contents of the flask again. If a heavy precipitate has formed, report as "Positive." If the solution is clean and brilliant, report as "Negative."

Investigation of the details of this procedure has brought out some of the following facts:

a. The quantity of bromine used is of some significance in determining whether a precipitate will form.

Sample	Color of solution after adding bromine	Precipitate
Tallow—a	Orange	Positive
Tallow—b	Orange	Negative
White grease—a	Orange	Positive
White grease—b	Orange	Positive
Tallow—a	Deep red	Negative
Tallow—b	Deep red	Negative
White grease—a	Deep red	Negative
White grease—b	Deep red	Negative

The melting points of the precipitates obtained from several samples of known purity were:

Tallow glycerides	60- 65°C.
Tallow fatty acids	60°C.
White grease glycerides	65- 70°C.
Soybean glycerides	135-140°C.
Soybean fatty acids	176-180°C.

The melting point data suggest that the precipitates obtained from tallows and greases are not hexabromides.

b. Spectrographic determinations of linolenic acid were made on several samples and these data were used to determine the minimum sensitivity of the insoluble bromide test.

Sample	% Linolenic acid	
	Triglycerides	Fatty acids*
Tallow—1	0.6	0.9
Tallow—2	0.8	1.1
Tallow—3	1.2	1.1
White grease—1	1.7	1.6
White grease—2	1.7	1.9
Soybean oil	6.4	7.2

* Fatty acids were separated according to A.O.C.S. Method for the Titer Determination.

Mixture of Palmitic and Soybean Oil Acids:

% Linolenic acid	Precipitate formed with insoluble bromide test
1.1	Negative
1.8	Negative
3.0	Positive
4.0	Positive

These data indicate that the Insoluble Bromide Test is not reliable for quantities of linolenic acid below 2-3%.

It has been suggested that when the fatty acids are separated they should be protected at all times by a blanket of nitrogen and that any heating should be done only in vacuo. A few samples of soap were sent out and the results obtained were as follows:

Laboratory	1		2		3		4	
	NP	P	NP	P	NP	P	NP	P
7	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.
2	Neg.	Trace	Neg.	Pos.	Neg.	Trace	Neg.	Pos.
1	Neg.	Pos.	Neg.	Pos.	Neg.	Pos.	Neg.	Pos.
Collaborator	—	Pos.	—	Pos.	—	Pos.	—	Pos.

NP indicates not protected. P indicates protected.

In no case were the positive results confirmed by a melting point. The literature indicates that the melting point of the hexabromide derivative of linolenic acid is approximately 180°C. The indications are that a positive test should always be confirmed by a melting point of the precipitate.

There is some evidence that in the separation of fatty acids from soap, the procedure of splitting the fatty acids may have some significance. Spectrographic determinations were made of linolenic and linoleic acids on several samples of pure soap, and fatty acids separated from these soaps. The fatty acids were separated according to the A.O.C.S. method.

Sample	Linolenic acid		Linoleic acid		Total	
	Soap	Fatty acid	Soap	Fatty acid	Soap	Fatty acid
1	.87	.50	2.20	2.56	3.07	3.06
2	.52	.29	2.68	2.97	3.20	3.26
3	.51	.51	2.14	2.47	2.65	2.98

All results calculated to the same basis for comparison.

It should be pointed out that while these differences are significant from the viewpoint of accurate analyses, they are not so in terms of the sensitivity of the insoluble bromide test. Further work is required before the hexabromide test can be accepted with any degree of certainty. Motion was made, seconded, and carried that no further work be done on this hexabromide method because it has been demonstrated to be inexact and unreliable.

Note: Spectrographic determinations were made by Drs. Urbain, Kauffman and Lingard in the Research Laboratories of Swift and Company.

Laboratory	A.O.C.S. Method		Proposed Method	
	Cloud	Congeal	Cloud	Congeal
Sample No. 1				
2	31.4	32.0	26.8	31.9
12	.....	.....	27.1	32.6
4	30.2	30.7	27.4	32.4
13	.....	.....	30.0	32.6
7	29.6	30.4	27.5	32.2
Sample No. 2				
2	30.9	31.3	26.8	31.1
12	.....	.....	26.5	31.5
4	.....	.....	26.2	31.4
13	.....	.....	29.7	32.3
7	28.8	29.6	26.4	30.9
Sample No. 3				
2	32.1	32.2	27.1	30.6
12	.....	.....	.....	.....
4	.....	.....	27.4	31.8
13	.....	.....	30.0	32.1
7	28.0	28.6	27.8	31.4
Sample No. 10				
2	33.2	33.6	28.5	34.4
12	32.0	32.8	30.2	34.9
4	30.7	31.2	29.1	34.8
13	.....	.....	31.4	35.2
7	30.1	31.3	29.2	33.7
Sample No. 11				
2	34.2	34.6	29.5	36.2
12	34.2	35.0	30.8	35.9
4	34.4	34.7	29.6	35.7
13	.....	.....	31.4	36.4
7	30.6	31.8	29.9	34.9
Sample No. 12				
2	30.7	30.8	22.4	31.9
12	29.0	31.2	23.2	31.7
4	27.2	29.2	22.4	31.5
13	.....	.....	24.4	32.0
7	27.1	30.6	22.6	31.5
Sample No. 13				
2	24.1	24.2	15.5	22.3
12	24.0	24.2	18.1	23.5
4	17.6	18.4	16.6	22.2
13	.....	.....	15.3	21.6
7	22.0	22.7	16.4	22.0
Sample No. 14				
2	30.2	30.8	26.8	32.0
12	30.1	31.0	28.4	32.1
4	27.9	28.2	27.4	32.0
13	.....	.....	29.8	32.4
7	28.6	29.4	27.4	29.8
Sample No. 15				
2	27.8	27.9	26.0	28.8
12	27.5	28.6	21.3	28.8
4	23.9	26.1	20.6	28.5
13	.....	.....	22.3	29.0
7	28.6	29.4	21.0	27.4

Congeal Point

The Committee has done considerable work in an attempt to standardize some method for the congeal point. It was found that the methods in use in the industry were much alike in principle but varied in detail. Therefore, we standardized these details and submitted samples to several Committee members. The method in general was as follows: The temperatures, apparatus and lighting were standardized and a definite quantity of sample was stirred to the clouding point in a water-cooled bath. The sample was then transferred to an air-cooled bath, the thermometer fixed in one position and allowed to remain stationary until temperature increased to a maximum.

It has been the practice of some to use a congeal point procedure which is according to the A.O.C.S. Titer Method except that the test is made on the glycerides instead of on the fatty acids. The samples sent out were run by both methods. Some of the results are shown above.

It is quite apparent that neither procedure is satisfactory. Further work is planned.

Unsaponifiable Matter

Time has not permitted much work on the unsaponifiable method, although two samples were sent out. These samples were run by the Official A.O.C.S. Method, the Continuous Extraction Method (Oil & Soap, Nov. 1938, page 287) and the English S.P.A. Method (The Analyst, *58*, 203 (1933). The results are shown below:

Laboratory	Continuous extraction		Official A.O.C.S.		S.P.A.	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
14	1.49	1.44	1.22	1.18	1.85	1.81
8	1.16	1.10	1.10	1.28	.....	.....
15	1.29	1.02	1.21	0.95	.....	.....
16	1.22	1.19	1.25	1.22	.....	.....
6	1.31	1.36	1.25	1.27	.....	.....
7	1.18	1.27	1.05	1.06	.....	.....
2	1.06	1.23	1.10	1.04	.....	.....

Dr. Fitelson of our Committee, who is Referee on Oil, Fats, and Waxes for the A.O.A.C., comments as follows: "We are now conducting A.O.A.C. collaborative work on methods for unsaponifiable matter, and it appears, from the results obtained so far, that the S.P.A. method will be recommended as the official A.O.A.C. method. Although the continuous extraction method may be satisfactory for many fats, we are convinced that the S.P.A. method has wider applicability and gives higher and more accurate results."

Two members reported no significant difference between results when the extract was dried according to the A.O.C.S. official procedure and in a vacuum oven at 80°C., providing the latter is continued to constant weight. Additional work is required.

Table of Interpretation of F. A. C. Color Standards

About one year ago this Committee published a table indicating the visual relationship in intensity between the F.A.C. Color Standards. It is now recommended that this table be incorporated in the method

RELATIONSHIP BETWEEN F.A.C. COLOR STANDARDS

F.A.C. tube No.	Tubes listed below are equal to or lighter than the corresponding tube in the left-hand column
1	1
3	1, 3
5	1, 3,5
7	1, 3, 5, 7
9	1, 3, 5, 7, 9
11	1, 3, 5, 7, 9, 11
11A	1, 3, 5, 7, 9, 11, 13, 11A
11B	1, 3, 5, 7, 9, 11, 13, 11A, 11B
11C	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 11A, 11B, 11C
13	1, 3, 5, 7, 9, 11, 13, 11A
15	1, 3, 5, 7, 9, 11, 13, 15, 11A, 11B
17	1, 3, 5, 7, 9, 11, 13, 15, 17, 11A, 11B
19	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 11A, 11B, 11C
21	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 31, 33, 11A, 11B, 11C
23	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 31, 33, 35, 11A, 11B, 11C
25	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 31, 33, 35, 37, 11A, 11B, 11C
27	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 31, 33, 35, 37, 39, 11A, 11B, 11C
29	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 11A, 11B, 11C
31	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 31, 11A, 11B, 11C
33	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 31, 33, 11A, 11B, 11C
35	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 31, 33, 35, 11A, 11B, 11C
37	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 31, 33, 35, 37, 11A, 11B, 11C
39	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 31, 33, 35, 37, 39, 11A, 11B, 11C
41	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 31, 33, 35, 37, 39, 41, 11A, 11B, 11C
43	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 11A, 11B, 11C
45	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 45, 11A, 11B, 11C

for the evaluation of color, using the F.A.C. Color Standards.

F. A. C. Color Comparator

The Committee has been considering the adoption of some instrument which would furnish standard lighting conditions and a uniform method of reading F.A.C. colors. One such instrument was constructed by the Fisher Scientific Co., Pittsburgh, Pa., according to the design of Whyte [Oil & Soap, *19*, 199 (1942)] and circulated to several members of the Committee. This model was not satisfactory. Mr. Whyte then submitted an improved modification of his original instrument which was also sent to several members of the Committee. The principal objections raised to this instrument were that the sample and standards are not viewed under identical conditions of illumination, and that light from standards other than the one selected for the comparison may reach the observer's eye. We plan to go further in our search to find a suitable instrument with which to read F.A.C. colors.

Titer Stirring Device

The Committee examined a mechanical stirring device for titers which was made by the Fisher Scientific Co., Pittsburgh, Pa. This unit was motor driven and permitted vertical stirring of three samples of fatty acids at a time. With a few exceptions, the apparatus permitted stirring as required by the A.O.C.S. method. The rate of stirring did not exactly conform to requirements. The transite top of each individual bath needed redesigning so as to allow easy addition or removal of water. Several samples were stirred in this instrument and the results ob-

tained compared with figures obtained by the official method. The agreement was satisfactory. Several minor suggestions were made, all of which were passed on to the Fisher Scientific Co.

Miscellaneous

The Committee has been requested to study some procedure by which to better evaluate fats for soap production with respect to color. This problem is being considered but we have no data to present now.

The following people have collaborated with the Committee in some part of this program: R. T. Milner, G. W. Agee, J. J. Ganucheau and B. W. Beadle.

E. W. Blank — J. E. Maroney
E. W. Colt — L. B. Parsons
F. G. Dollear — H. A. Schuette
J. L. Laing — S. O. Sorensen
J. Fitelson — L. M. Tolman
C. P. Long — F. C. Woekel
V. C. Mehlenbacher, *chairman*

Report of the Committee On Uniform Methods and Cooperative Work

Fall Convention—1944

Only two committee reports were submitted for consideration of the Committee on Uniform Methods and Cooperative Work at this Fall Meeting in Chicago, Oct. 25-27.

Soap Analysis Committee:

The Soap Analysis Committee report as submitted by M. L. Sheely, chairman, contained two recommendations. These were as follows:

1. That the complete set of methods for soaps containing synthetic detergents be adopted as tentative. The committee described these methods in their report.
2. That a new procedure for the determination of potassium hydroxide and potassium carbonate in potash paste soaps also be adopted as tentative.

These recommendations were considered by the Committee on Uniform Methods and Cooperative Work and have their approval. Upon motion by the chairman of the latter committee, and a proper second from the floor, these recommendations were adopted.

The Committee on Analysis of Commercial Fats and Oils:

This committee has done considerable work and has made the following recommendations with reference to changes in the Thiocyanogen method:

1. Increase the reagent from an excess of 100-150% to 150-200%.
2. Increase the potassium iodide from 1.00 gram to 1.66 grams.

With reference to the Fat Analysis Committee color standards they recommended that the table of interpretation, which has been published previously in Oil and Soap, be incorporated as part of the method.

All of the above recommendations were considered by the Committee on Uniform Methods and Cooperative Work and have their approval. Upon motion by the chairman of the latter committee, with a proper second from the chair, these recommendations were unanimously adopted.

J. T. R. Andrews — E. B. Freyer
J. J. Ganucheau — T. C. Law
C. P. Long — H. P. Trevithick
J. J. Vollertsen, Chairman

Solidification Point Curves of Binary Acid Mixtures

IV. Triacontanoic to Tetratriacontanoic Acids[1]

H. A. SCHUETTE, D. A. ROTH,[2] and R. M. CHRISTENSON[3]
University of Wisconsin, Madison, Wis.

In earlier communications (6) from this laboratory on the subject of the analytical chemistry of the fatty acids there have been presented solidification-point diagrams for binary mixtures of consecutive pairs of so-called "even" acids from *n*-decanoic to *n*-triacontanoic and a discussion of the qualitative and quantitative aspects of these diagrams when viewed as analytical tools. With this communication we extend the list to the C_{34} acid, thus enlarging the scope of application of the resulting phase diagrams of binary mixtures to lac wax, cotton wax, and beeswax. The latter probably contains all of the even *n*-fatty acids from C_{24} to C_{34} (2), but a quantitative analysis of even so common a product has not yet been carried out.

The use of solidification-point diagrams in the analysis of fatty acid mixtures is dependent upon the fractional distillation of their methyl or ethyl esters into binary mixtures. Although the problem does not usually arise in the analysis of the glyceride oils, a successful separation of the acids commonly associated with many of the waxes must still be mastered; that it will come through improved distillation techniques is quite probable if our own experiences with Chinese insect wax (6d) may be deemed prophetic of success.

[1] This investigation was supported in part by a grant from the Wisconsin Alumni Research Foundation, whose aid is gratefully acknowledged.
[2] Now Ensign, USNR. His doctoral dissertation, 1944, formed the basis for this communication.
[3] Present address: Pittsburgh Plate Glass Company, Milwaukee, Wis.