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Report of the Smalley Committee, 1952-53

FOLLOWING custom the reports of the four subcommittees of the Smalley Committee represent the complete report. These reports will be individually recorded, but before doing so the chairman would like to offer some general comments.

Some 3,215 samples were distributed and the results tabulated during the year. While the members of the committee and subcommittees have been fully cooperative and effective and the chairman expresses his thanks for their work and guidance, certain organizations and individuals merit special note.

The American Oil Chemists' Society and the fat and oil industry are indebted to the following for the preparation and distribution of the samples:

G. Conner Henry and Law and Company for the Oil Seed Meal and Oil Seed Samples.
J. P. Hewlett and the HumKo Company for the vegetable oil samples.
K. H. Fink and Armour and Company for the tallow and grease samples.

Special appreciation is also expressed to:

A. S. Richardson for tabulating the cottonseed oil results.
F. R. Earle for tabulating the soybean oil results.
R. T. Doughtie for tabulating and grading the oil seed results.
R. A. Decker for calculating the grades on the vegetable oils.

The chairman has been fortunate in having excellent committee support.

SMALLEY COMMITTEE
R. W. BATES, chairman

Subcommittee on Oil Seed Meal

We present herewith the 35th report of the subcommittee on Oil Seed Meal. This year 15 samples were distributed to 110 collaborators. The samples were sent to 27 states, 5 Canadian provinces, and 2 South American countries.

A graph has been prepared, showing the number of collaborators (based upon the percentage of the total) who were within the recognized tolerance of the accepted average. The general average of all samples was also calculated and the values of the past five seasons listed for comparison.

It will be noted that the moisture results were not quite as good this season, 52% being within the tolerance. The oil and nitrogen results were in line with past seasons, being 52.1 and 50.2%, respectively.

Sample No. 10 was a soybean meal, and there was a lack of knowledge on the part of some of the collaborators as to the method applicable for the determination of moisture. This resulted in poor agreement, and the collaborators were not graded on moisture results of this sample.

To eliminate ties for second place on the determination of moisture the results of those tied for second place were recalculated, using no tolerance.

Those collaborators with the highest grades this season were:

1. *On Oil and Nitrogen.* The American Oil Chemists' Society Cup for the highest proficiency in the determination of oil and nitrogen will be awarded to P. D. Cretien (#1) of the Texas Testing Laboratory, Dallas, Tex., with a grade of 99.985%. Mr. Cretien won the cup in 1951 and again in 1952 and, in accordance with custom, will be given permanent possession of the cup. He joins the select group consisting of The Battle Laboratories, E. H. Tenent Sr., D. B. McIsaac, the late W. F. Hand, and R. R. Haire who in years gone by have won the cup at least three times.

In second place was Edward R. Hahn (#8) of the Hahn Laboratories, Columbia, S. C., with a grade of 99.982%.

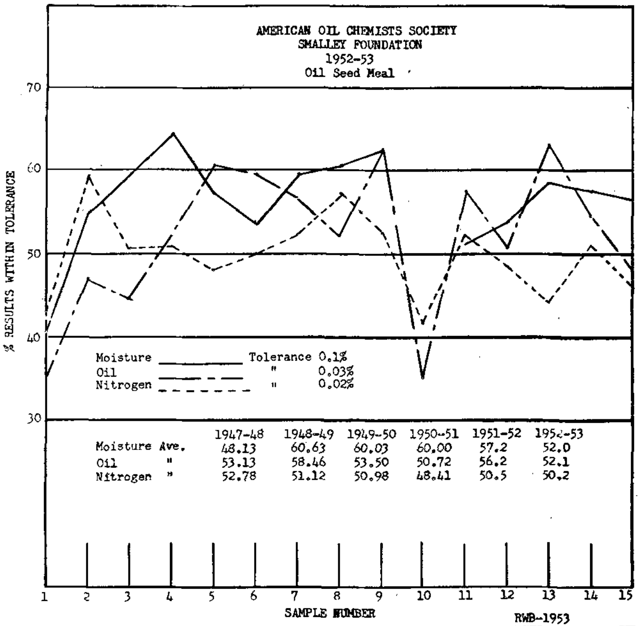
Honorable mention (no certificate) is given to R. C. Pope of the Pope Testing Laboratories of Dallas, Tex., with a grade of 99.971%.

2. *On Oil.* Two were tied for the highest standing in the determination of oil with grades of 100.0% proficiency. These were:

R. C. Pope (#22), Pope Testing Laboratory, Dallas, Tex.
E. R. Flack (#72), Allied Mills, Peoria, Ill.

Honorable mention is given to the following with grades of 99.988%:

P. D. Cretien, Texas Testing Laboratories, Dallas, Tex.
W. H. Kesler, Woodson-Tenent Laboratories, Little Rock, Ark.
W. F. Beedle, Geo. W. Gooch Laboratory, Los Angeles, Calif.



	1947-48	1948-49	1949-50	1950-51	1951-52	1952-53
Moisture Ave.	48.13	60.63	60.03	60.00	57.2	52.0
Oil "	53.13	58.46	53.50	50.72	56.2	52.1
Nitrogen "	52.78	51.12	50.98	48.41	50.5	50.2

Geographical Distribution

Tex.	22	Iowa	2	Pa.	1
Ill.	9	Ohio	3	N.H.	1
Calif.	8	Ariz.	4	N.Y.	1
Ga.	6	Minn.	1		
Ala.	3	Kas.	2		
S.C.	5	N.C.	2	Canada	8
Mo.	4	Wisc.	1	Brazil	1
Miss.	5	Ind.	1	Argentina	1
La.	4	Conn.	1	Total	110
Tenn.	4	Wash.	1		
Ark.	3	Va.	1		
Okla.	4	Neb.	1		

3. *On Nitrogen.* Edward R. Hahn (#8) was first with a grade of 100%. A. G. Thompson Jr. (#52) of the Southern Oil Company of Columbia, S. C., was second with a grade of 99.991%

Honorable mention is given to: P. D. Cretien (#1) and C. E. Worthington, Barrow-Agee Laboratory, Cairo, Ill., who each had a grade of 99.981%.

4. *On Moisture.* Edward R. Hahn (#8) was first with a proficiency of 100.0%. A. G. Thompson (#52) won a certificate for second place with a grade of 99.910%.

Honorable mention is given to: G. R. Thompson (#53) of the Southern Cotton Oil Company, Savannah, Ga.; H. L. Tamborini (#57) of the California Cotton Oil Corporation, Los Angeles, Calif.; and W. M. Martin (#64) of the Western Cotton Oil Company, El Paso, Tex., with grades of 99.910%.

A detailed report has been mailed to all collaborators, showing their standings in comparison to those of their fellow chemists.

R. W. Bartlett R. R. Haire
R. T. Doughtie Jr. T. C. Law
T. L. Rettger P. D. Cretien
E. H. Tenent Sr. R. W. Bates,
chairman

Subcommittee on Oil Seeds

During the 1952-53 season cottonseed, soybean, and peanut samples were distributed to the collaborators. There were 45 collaborators on cottonseed, 22 on soybeans, and 15 on peanuts. Overall there were two less than the previous year. The accuracy of the work compared very favorably with that of previous years. It will be noted that those attaining first place in each series had a grade of 100%.

Smalley certificates for proficiency will be awarded to the following:

Cottonseed Series

First place, analyst No. 19, Edward R. Hahn, Hahn Laboratories, Columbia, S. C., with a grade of 100.00%.

Second place, analyst No. 31, G. R. Thompson, Southern Cotton Oil Company, Savannah, Ga., with a grade of 99.88%.

Soybean Series

First place, analyst No. 8, L. R. Brown, A. E. Staley Manufacturing Company, Decatur, Ill., with a grade of 100.00%.

Second place, analyst No. 11, W. N. Kesler, Woodson-Tenent Laboratories, Little Rock, Ark., with a grade of 99.40%

Peanut Series

First place, analyst No. 1, Thomas C. Law, Law and Company, Atlanta, Ga., with a grade of 100.00%.

Second place, analyst No. 4, C. L. Manning, Fort Worth Laboratories, Forth Worth, Tex., with a grade of 99.60%.

Honorable mention is given to D. A. Bradham, Barrow-Agee Laboratories, Leland, Miss., and E. H. Tenent, Woodson-Tenent Laboratories, Memphis, Tenn., who tied for third place on cottonseed; to M. L. Hartwig, Law and Company, Montgomery, Ala., C. L. Manning, Fort Worth Laboratories, Fort Worth, Tex., and E. H. Tenent, Memphis, Tenn., who tied for third place on soybeans; and to Thomas B. Caldwell, Law and Company, Wilmington, N. C., who was third on peanuts.

Complete reports showing all grades were mailed the collaborators.

W. T. Coleman G. Conner Henry
Edward R. Hahn R. T. Doughtie,
chairman

Subcommittee on Crude Vegetable Oils

Six samples of crude vegetable oil were distributed to 85 collaborators. Three were cottonseed and three were soybean oil. Over 57% of the collaborators reported on all samples.

As usual, the grades on the cottonseed oil were based on the refining loss, refined color, and free fatty acid. The spectrophotometric method was used for the refined oil colors.

On the soybean oils the grades were based on the refining loss, bleached color, and free fatty acid. In general, both the Lovibond and spectrophotometric colors were reported, and in these cases the color deduction was the average of the deductions by the two methods.

The cottonseed oil results were not as good as those of previous years. This was partly due to the quality of the samples distributed.

One very significant and disturbing factor was the apparent unfamiliarity of many of the collaborators with the Trading Rules, *viz:* No. 264 and 142 of the N.C.P.A., which involve the selection of the proper settlement results. The subcommittee hopes to clarify this matter in our instructions next season, but we strongly urge all collaborators to study these rules carefully.

The soybean oil results were very good.

As a matter of record the average grades of the collaborators reporting on all samples were:

On Cottonseed Oil	80.6%
On Soybean Oil	94.0%
Combined	87.3%

The collaborators receiving certificates of proficiency are:

First place, analyst No. 67, W. F. Beedle, Geo. W. Gooch Laboratory, Los Angeles, Calif., with a grade of 98.3%.

Second place, analyst No. 9, H. L. Arrington, Procter and Gamble Manufacturing Company, Portsmouth, Va., with a grade of 97.7%.

Honorable mention is given to L. R. Brown, analyst No. 46, of the A. E. Staley Manufacturing Company, Decatur, Ill., with a grade of 95.1%.

R. A. Decker A. S. Richardson
F. R. Earle J. P. Hewlett,
chairman

Subcommittee on Tallow and Grease

Five samples of tallow and grease were distributed to 52 collaborators. Over 70% of the collaborators reported on all samples. The tests requested were free fatty acid, color, titer, insoluble material, unsaponifiable, and the refined and bleached color. The collaborators were not graded on the refined and bleached color.

The color and titer were used as a basis for classifying the samples. The classification of the materials and the average standard deviations are listed here for the record:

Sample No.	Standard Deviation					
	F.F.A.	Titer	Mois.	Insol.	Unsap.	R&B Color
	%	°C.	%	%	%	Red
1. (Prime Tallow)	0.15	0.22	0.05	0.03	0.23	0.87
2. (A.Wh. Grease)	0.11	0.26	0.04	0.07	0.12	0.39
*3. (No. 2 Tallow)	0.81	0.42	0.12	0.05	0.25	......
4. (Ex. Ch. Wh. Grease)	0.12	0.29	0.05	0.04	0.08	0.22
5. (Choice Tallow)	0.07	0.24	0.03	0.04	0.14	0.22
Average	0.11	0.29	0.06	0.05	0.16	0.42

* Contained 61.2% f.f.a., actually a very low grade tallow; the standard deviation was not included in the average.

The accuracy of the result has again shown improvement. The subcommittee also recognizes that the interest in the work has also been quite pronounced.

Smalley certificates of proficiency will be awarded to:

Analyst No. 3, N. W. Ziels, Lever Brothers Company, Hammond, Ind., who was first with a grade of 99.17%.

Analyst No. 35, R. C. Pope, Pope Testing Laboratories, Dallas, Tex., who was second with a grade of 99.14%.

Honorable mention is given to T. S. McDonald, Procter and Gamble Company, Dallas, Tex., who was third with a grade of 98.93%.

The grading system used was that adopted in 1950 except for the following:

Sample No. 1. No deduction was made for color where 13, 11B, or 15 were reported.

Sample No. 2. No deduction was made on color where 13, 11A, 11B, or 15 were reported.

Sample No. 3. A tolerance of ±0.5% was used in grading the free fatty acid.

A complete and detailed report was sent to all collaborators.

J. L. TRAUTH	C. D. LEAVITT
DAN L. HENRY	K. FINK
J. E. MARONEY	W. C. AULT, chairman

The Glyceride Structure of Natural Fats. I. A Technique for the Quantitative Determination of Glyceride Types in Natural Fats

A. R. S. KARTHA, Maharaja's College, Ernakulam, India [1,2]

SYSTEMATIC investigation of the natural fats was first undertaken by Hilditch and colleagues. Among their many noteworthy contributions was an oxidative method for the quantitative determination of GS_3[3] (1). A modification of this procedure forms the basis for the present method of determination of the four glyceride types, GS_3, GS_2U, GSU_2, and GU_3.

There have been several attempts to separate and estimate the GS_2U, GSU_2, and GU_3 components of natural fats (3, 4, 5, 6, 7, 8). None of these has been entirely successful.

During attempts at separating the products of fat oxidation according to the Hilditch method, by preferential extraction with bicarbonate (8), Kartha (2a) found that the azelaoglycerides formed in the reaction were partly destroyed by hydrolysis. He then developed the acetic acid-acetone-permanganate method of oxidation and the azelaoglycerides-separation method which will be described in this paper. These procedures are the basis of the method for quantitative estimation of the glyceride types, which will also be presented.

Sources of Error in the Acetone-Permanganate Method for Estimation of GS_3

Oxidation of GS_2U, GSU_2, and GU_3 according to the Hilditch method produces GS_2A GSA_2, and GA_3, respectively. Among the other products of the reaction are carbon dioxide, water, and potassium hydroxide. Some of the carbon dioxide doubtlessly combines with the potassium hydroxide to produce potassium carbonate.

There is evidence for the belief that there is an appreciable loss of azelaoglycerides by hydrolysis during the oxidation process. The hydrolysis is caused by the carbonate solutions produced in the reaction. It is also likely that the azelaoglycerides undergo hydrolysis during the process of separation with aqueous carbonate solutions.

The following experiments are the basis for these conclusions:

1. A sample of GU_3 prepared by synthesis was oxidized according to the Hilditch method, using 12 g. of $KMnO_4$ per gram of fat and a total oxidation time of 10-11 hours. The oxidation products were isolated by extraction with ether, and the volatile acids were removed by steam distillation as suggested by Stainsby (9). The yields of GA_3 were only 0.35-0.45 g. per gram of fat. The theoretical yield is 0.68 g. per gram of fat. The difference is attributed mostly to partial hydrolysis of the GA_3 during oxidation; part of the products were lost because of their comparative solubility in water and insolubility in ether. The great loss can hardly be due entirely to hydrolysis during steam distillation since there is no indication in the work of Stainsby that this would occur.
2. *Garcinia Indica* and *Vateria Indica* fats, which contain about 60% of saturated acids and only traces of GS_3, were oxidized according to the Hilditch method. The products in ethereal solution were washed with an excess of dilute bicarbonate solution. The residues, which varied in quantity and should consist of GS_2A, showed saponification values of 240-260, which are much less than the theoretical value for GS_2A. This fact indicates that GS_2A was lost during the oxidation procedure or during the extraction process, or both, probably by hydrolysis to GS_2OH and by solution in the bicarbonate.
3. A GS_3-GS_2U mixture containing 66.6% of GS_2U was prepared by crystallization of peanut oil, hydrogenated to an iodine value of 45, from acetone at 30-32°C. A sample was oxidized according to the Hilditch method with 9-10 g. of $KMnO_4$ per gram of fat. The reaction period was 10 hours. The oxidation products were collected in ether, and the ether was removed by distillation. The residue was dissolved in cold, dilute carbonate solution. An excess of carbonate was avoided so no hydrolysis should have resulted from this treatment. Evidence of this will be presented in experiments 1 and 2 (see also conclusion 3 following these experiments) under the heading, Procedure for Acid-Acetone-Permanganate Oxidation of Unsaturated Fats.

The GS_2A was precipitated as the magnesium salt by addition of ammonium chloride and finally an excess of magnesium sulfate solution. The GS_3 separated with the magnesium-GS_2A salt, and both were removed by filtration. The filtrate contained no higher acids, showing that the magnesium-GS_2A salt is insoluble in water. The total fatty matter recovered from the magnesium salts was 86.9% of the original fat; the theoretical amount is 92.9%. The quantity of GS_2A found was 80.5% of the GS_2U originally present; the theoretical value is 89.5%. The saturated fatty acids were isolated from the GS_2A-GS_3 fraction and agreed in quantity with the quantity present in the original fat. No hydrolysis should have resulted from the brief, mild carbonate treatment; therefore the loss of azelaoglycerides is most reasonably attributed to hydrolysis during oxidation.

The hydrolysis of azelaoglycerides can affect the GS_3 determination according to the method of Hilditch since hydrolysis of GS_2A and GSA_2 produces

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[2] Edited and revised by R. J. Vander Wal, Armour and Company, Chicago, Ill.

[3] The following symbols will be used in the text:

G = Glyceryl radical.

S = Saturated acid group or saturated acids according to context.

U = Unsaturated acid group or unsaturated acids according to context.

A = Azelaic acid group.