TABLE XII

Surfactants Used in Textile Applications
(Millions of pounds of active agent)

Anionics		
Alkylarylsulfonates	6.0	
Sulfated esters and ethers	4.0	
Fatty alcohol sulfates	2.5	
Sulfonated amides	2.5	
Sulfosuccinates and secondary alkyl sulfates	1.0	
Others	0.5	
Total		16.5
Nonionics		
Alkylphenol ethers	7.0	
Fatty alcohol ethers	2.0	
Alkylolamides	1.5	
Tall oil and fatty acid esters	1.5	
Others	0.5	
Total		12.5
Cationics		4.0
Grand Total		33.0

be obtained from a new product are worth less than the cost of evaluating the surfactants. Nevertheless extensive surfactant testing is being carried out in many of the larger mills. Some of the factors which will cause further shifts in the selection of surfactants are: the steadily decreasing price of the nonionics, the increasing proportion of fabric that receives special finishing operations, the increase in the production of nylon and other synthetics, the decrease in the production of acetates, the displacement of cotton by synthetic fibers in tire yarn, and the displacement of kier boiling by the open boil-out.

Other definite trends are the rapid displacement of soap by synthetics in scouring after dyeing and printing, the displacement of sulfonated oils by cationics in finishing, and the rapid increase of nonionic usage.

There is one further point to be noted by research chemists in preparing surfactants for the textile industry. Although this industry consumes very large quantities of chemicals, it is not primarily one of the chemical processing industries. It is a mechanical industry, concerned with the conversion of materials of one physical form to another. The chemicals are used as auxiliaries to facilitate these mechanical operations. They may be used to lubricate the fiber to make it spin better or to color the fabric to make it more attractive or to coat the fabric to change its handling properties, but the basic operations are still mechanical. The investment in money and know-how in these mechanical operations is tremendous. It does no good therefore to develop a surfactant that is excellent under some theoretical set of conditions. The surfactant is the tail of the dog. It must be designed to work best under the conditions that exist.

Acknowledgment

The success of a paper of this type is largely dependent on the assistance of associates to provide the information. Special credit must be extended to Luther B. Arnold of the Vikon Company and to George Gantz of General Aniline and Film Company. Several other private communications were also of important help, including those with

Joseph Benischeck, Fred Whitaker Company, Philadelphia, Pa.
Wm. Bertholet, 3rd, Laurel Soap Company, Philadelphia, Pa.
Carl Blumenstein, Seydel-Wooley, Atlanta, Ga.
Wm. Ebersold, James Lees' Sons, Bridgeport, Pa.
James Egee, Philadelphia Dye Works, Philadelphia, Pa.
H. Ehrhardt, Botany Mills, Passaic, N. J.
Wm. Healy, General Aniline and Film, New York, N. Y.
J. M. Hoerner, Armour and Company, Chicago, Ill.
J. M. Jester, Amalgamated Chemical, Philadelphia, Pa.
Lloyd Koons, Scholler Brothers, Philadelphia, Pa.
E. A. Leonard, Alexander Smith Inc., Yonkers, N. Y.
Harold Naidus, American Polymer, Peabody, Mass.
Joseph Oliver, Stodghill, Atlanta, Ga.
Dan Terry, Bon Ami, New York, N. Y.
G. E. Thurmond, American Enka, Asheville, N. C.

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[Received October 19, 1954]

Chemical Determination of Unsaturation of Fats and Derivatives

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THIS PAPER is a summary progress report on the chemical determination of unsaturation of fats and derivatives. Special emphasis is placed on recent studies and the current status. The determination of unsaturation of vegetable oils has been studied for a very long time. The importance of unsaturation in determining the characteristics of oils and fats is well recognized. For example, vegetable oils are sometimes characterized as nondrying when the iodine value is below 120, semi-drying when between 120 and 160, and drying when above 160. Their use and value depends to a large extent upon their unsaturation.

The usual procedure for determining the degree of unsaturation is to measure the amount of halogen that may be added to the double bond. The chemistry involved is very simple. Two halogens, not necessarily the same, attach themselves to the two carbons involved in the unsaturation. These halogens may be chlorine, bromine, or iodine. The general procedure is to add an excess of the halogen and determine the amount used by measuring the amount of halogen left after the reaction. The trick is to arrange conditions so that quantitative addition takes place without the substitution for one of the hydrogens.

The degree of unsaturation is expressed as the grams of iodine added to 100 g. of material, or the equivalent centigrams of iodine per gram of sample. This brings up one point of controversy among the oil chemists. Should this constant be called iodine value or iodine number? The older literature seems to prefer iodine number while more recently iodine value is obtaining wide usage. A.O.C.S. methods use iodine value while American Society for Testing Materials uses iodine number. The writer prefers iodine value, which will be used throughout this paper.

The unsaturation in vegetable oils may be conjugated or nonconjugated. The measurement of the nonconjugated oils by chemical means is far simpler and will be dealt with first. Typical oils of this nature are linseed, soybean, safflower, and cottonseed. It is fortunate that all the common vegetable oils have their unsaturation a number of carbons away from the carboxyl group. It might be mentioned in passing that when the double bonds are close to the carboxyl group, they react hardly at all with the various halogen reagents. For example, Ponzio and Gastaldi (34) observe that with the common iodine value reagents (Hübl, Wijs, and Hanus) practically no halogen absorption took place in a fatty acid with a double bond adjacent to the carboxyl group. Also as might be expected, maleic anhydride does not react with the common halogen reagents.

Nonconjugated Unsaturation

About a hundred years ago the degree of unsaturation of vegetable oils was quantitatively measured by halogen reaction. The original method involved reacting dry bromine with the oil, and the constant was called the bromine absorption value. These original methods were rather inaccurate because of substitution. In 1884 Hübl (14) introduced a quantitative method for determining unsaturation by the use of iodine absorption. This soon displaced the bromine value, and unsaturation is now stated in terms of iodine absorption whether iodine is the actual reagent or not.

TABLE I

Principal Iodine Value Methods

Name	Introduced	Reagent	Reaction time
Hübl	1884	$I_2 + HgCl_2$	18 hr.
Wijs	1898	I Cl	30-60 min.
Hanus	1901	I Br	30-60 min.
Rosenmund-Kuhnhenn	1923	Pyridine sulfate dibromide	5 min.
Kaufmann	1926	$Br_2 + NaBr$	2 hr.

Eckey (1954)

Table I shows the common methods successfully used for determining iodine value of oils. The original Hübl Method was quite satisfactory and obtained wide usage. In fact, it is still used to a small extent, and the method may be found in most books dealing with oil technology. Its principal disadvantage is its long reaction time and the unstability of the reagent.

Shortly after the Hübl Method became accepted, Wijs (44) suggested the use of iodine monochloride. This had the advantage of a more stable reagent and gave apparently more consistent results. After about 50 years of controversy it is now the most commonly accepted method for determining iodine value. When modern procedures for isolating the pure components of vegetable oils were developed, it was observed that near theoretical values were obtained by use of the Wijs Method. For example, Kass (16, 17) obtained 90.1 for elaidic acid (theo. 89.9), linoleic acid 181.0 (theo. 181.0), and ethyl linolenate 247.1 (theo. 248.8). Matthews (26) also obtained a Wijs value of 181.0 for linoleic acid and 269.9 (theo. 273.5) for linolenic acid. Brown and Frankel (5) obtained a Wijs iodine value of 180.9 from a linoleic acid prepared from the tetrabromide. The reagent, while considerably more stable than Hübl's, is sensitive to light, and various investigators state that it should be replaced when more than 30 days old. However Norris and Buswell (30) report that, with a slight excess of iodine over chlorine, it may be stored in the dark for at least 505 days.

A few years later than Wijs' suggestion, Hanus (10) introduced iodine monobromide. The claimed advantage over Wijs was principally in the stability of the reagent. This method likewise received wide acceptance. However it was noted that somewhat lower iodine values were obtained for the highly unsaturated nonconjugated oils. At first it was believed this represented the truer values, but now most authorities concede that it is a result of a less reactive reagent not completely saturating the double bonds unless a large excess is used.

About a quarter of a century later Rosenmund and Kuhnhenn (36) suggested pyridine sulfate dibromide. The chief advantage to this method was a short reaction time. Lips (25) observed that the iodine values determined with pyridine sulfate dibromide tended to increase with the reaction time and amount of excess reagent. Also about this time Kaufmann (19) recommended a reagent prepared by dissolving bromine in methanol saturated with sodium bromide. This determination takes a little longer but is stated to be less affected by light. Neither of these two methods has obtained wide acceptance.

Numerous studies have been made comparing the various methods, and backers of each method can be found. For example, Barbour (2) compared the Wijs, Hanus, Rosenmund-Kuhnhenn, and Kaufmann methods and concluded for edible fats that the Kaufmann Method was outstanding since the reagent is much superior to the Wijs in stability and to the Hanus in ease and convenience in preparation. Like other observers, he noted that the Wijs gave the highest values, the Rosenmund-Kuhnhenn the lowest, with the Hanus intermediate. Earle and Milner (6) observed that, on a given sample of soybean oil, Wijs gave 134.1, Kaufmann 132.6, and Hanus 131.4. A study of a considerable amount of data indicates to the writer that the Wijs Method gives the most accurate results for nonconjugated fats and their derivatives.

Both the Hanus and Wijs Methods are accepted as official by the Association of Official Agricultural Chemists. The Wijs Method is the official method of A.S.T.M. as well as of our organization. Actually we have two Wijs iodine value methods, Cd 1-25 "applicable to all normal fats and oils not containing conjugated systems" and Ka 9-51 under the analysis of drying oils "applicable to all natural and synthetic oils and their fatty acids." There are some minor differences in these two methods which will probably be ironed out.

There is still interest in the possibility of using the elements—iodine, bromine, and chlorine—for iodine value determination. Thus the Margosches Method uses a solution of iodine in ethanol. However a slightly elevated temperature is necessary for the reaction. Winkler (45) has proposed the direct titration with a solution of bromine in acetic acid, catalyzed by mercuric chloride as a rapid method for fats and oils. Reutenauer and Regent (35) have suggested a chlorine titration with mercuric acetate catalyst, again stressing the rapidity. The values obtained checked fairly well with the Wijs Method except that they were considerably high for castor oil, probably due to reaction with the hydroxy.

The use of a mercuric acetate catalyst has been suggested for all of the reagents composed of halogen compounds. Both Hoffman and Green (13) and Hiscox (11) observed that when mercuric acetate was added to the Wijs reagent, the reaction was completed in 3 to 5 min. The values obtained were in good agreement with the standard Wijs Method. Norris and Buswell (29) added mercuric acetate to the Hanus solution and obtained identical values with the nonconjugated oils with the exception of castor. Rowe (37) used mercuric acetate with the Rosenmund-Kuhnhenn Method and stated that better results were obtained for tall oil. The values reported for various samples of tall oil ranged from 237 to 287. The catalytic methods should have some usefulness where speed of single determinations is desirable, such as in studying a process involving changing degree of unsaturation. However in this case the change in physical constants, such as refractive index, should be considered. While the results of the various investigators appear good, it is not believed the rapid catalytic methods are as reliable as the standard Wijs procedure for the usual type of nonconjugated oils.

The degree of unsaturation has been measured by temperature rise when an oil is mixed with concentrated sulfuric acid (Maumené Value). This method is apparently only semiquantitative. Hypochlorous acid has been used by Basu (3) as well as Goswami and Basu (9). This method is stated to be a "simplified procedure." However the writer's opinion, based on some experience on hypochlorous acid reactions, is that this method holds little promise.

Conjugated Unsaturation

While we have a generally accepted and accurate procedure for measuring nonconjugated unsaturation of fatty materials, this is not true for the conjugated types. However there is some reason for optimism in view of methods that are now in the development stage of acceptance. There are several methods, that in the hands of individual investigators, have yielded good results for tung, dehydrated castor, and similar oils. These methods are being studied by various committees with the hope that at least one of them may be acceptable and adopted. After some of the background has been explained, the current status of these methods will be discussed.

As the various iodine value methods previously referred to were developed, they were also naturally tried on the conjugated oils. It was soon noted that they gave considerably lower results. While an effort was made to modify the various methods to make them adoptable for conjugated materials, the unmodified methods were utilized and specifications drawn up to conform with the empirical and low values observed. For example, the A.S.T.M. specification for tung oil states that it should have a minimum Wijs value of 163 while actually the total unsaturation is approximately 230. Likewise the A.S.T.M. specification by the Wijs Method for unbodied dehydrated castor oil ranges from 125 to 145. Actually the total unsaturation is approximately 155. This is an unsatisfactory state of affairs.

As an example of the difficulty in using empirical methods, recently there resulted considerable confusion with the iodine value of dehydrated castor oil. In a laudable effort to make the Wijs iodine value methods between A.S.T.M. and A.O.C.S. more uniform, some changes were made in required sample weights of the A.S.T.M. Method. After adopting these, it was found that, when applied to dehydrated castor oil, iodine values were appreciably lower than observed with the previous A.S.T.M. Wijs Method. Since the iodine values appear in numerous specifications as well as appear to be related to quality in some people's minds, artificial lowering of the iodine value of dehydrated castor oil did not make the producers happy. The values obtained by the two different methods are shown in Table II. It is readily observed that the lower sample weight of the older standard method gave appreciably higher iodine values as might have been predicted. This situation was corrected in A.S.T.M. by recommending that the lower sample weights be used when testing for dehydrated castor oil. The higher sample weights are still in effect in the A.O.C.S. method.

TABLE II

DCO Iodine Value

Viscosity	D-555-47		D-555-51T	
	G. weight	Value	G. weight	Value
G-H	0.11-0.13	131.8	0.21-0.23	126.3
G-H	0.11-0.13	133.6	0.21-0.23	127.3
G-H	0.11-0.13	133.7	0.21-0.23	127.3
Z-2	0.11-0.13	110.3	0.25-0.27	103.3
Z-2	0.11-0.13	115.4	0.25-0.27	110.2
Z-2	0.11-0.13	115.9	0.25-0.27	110.0
Z-4	0.11-0.13	115.5	0.25-0.27	109.5
Z-4	0.11-0.13	109.4	0.25-0.27	101.9
Z-4	0.11-0.13	114.8	0.25-0.27	109.2

A.S.T.M. Committee

Ho *et al.* (12) have made a thorough study of the effect of variables in the Wijs iodine value determination of tung oil. They obtained wide differences by varying the reagent's strength, temperature, time, and so forth. The difficulty of obtaining consistent results is understandable. Forbes and Neville (8) made a somewhat similar study with both tung and dehydrated castor oil. They likewise obtained large differences in values by varying the conditions. Neither approached the theoretical value. It had been early observed that the Hanus reagent gives higher values than the Wijs reagent for tung oil. Von Mikusch and Frazier (38) observed that, by using about 400% Hanus reagent, tung had an iodine value of 205 and dehydrated castor of 155. These are in the correct order of magnitude. This method has become known as the Woburn Method. It is used to some extent but has not received wide application.

The original Rosenmund-Kuhnhenn Method gave somewhat lower results than the regular Wijs for conjugated materials. However Benham and Klee (4, 22) indicated that, by the addition of a mercuric salt catalyst, the determination could be shortened and consistent results also obtained on conjugated oils. Some of their values are shown in Table III. They seem to be a little high for dehydrated castor but about right for tung. Their results looked good to an A.S.T.M. Committee, which gave the method considerable study by cooperative testing. After several years it was concluded that the determinations were too variable for

TABLE III
Iodine Value

Oil	B. & K.	Wijs	Calc.
Soybean	129	133	(132)
Linseed	178	184	(185)
Castor	85	86	(86)
DCO	160	138	(155)
Oiticica	195	145	(220)
Tung	229	162	(232)

Benham and Klee (1950)

a standard method. These results were published (1), and the work was discontinued. Table IV shows some average results obtained by various members of the committee. The calculated results are those we believed to be about correct. The variations obtained are quite apparent. About the time this work was terminated, Planck *et al.* (33) published a paper commenting on the Benham and Klee modification. They showed that the effect of light was the cause of the trouble and suggested various precautions and modifications involving the order of reagent addition. Some of the results obtained are given in Table V.

TABLE IV
Iodine Value by B. and K. Method

Linseed	DCO	DCO acids	Tung
184 calc.	155 calc.	172 calc.	232 calc.
176	154	172	235
172	146	174	222
176	142	162	222
185	139	181	219
172	145	159	214
162	137	155	207

A.S.T.M. Committee

TABLE V
Iodine Values by Modified R.-K.

	Value
Domestic Tung	232.0
Chinese Tung	228.5
100% Alpha E. A.	273.2 (Theo. 271.5)
98% Beta E. A.	274.3

Planck et al. (1953)

Since rather good results were obtained, the A.S.T.M. Drying Oil Committee decided to reopen the investigation. Mr. Spagnolo of National Lead volunteered to check the results with dehydrated castor and has recently obtained the values given in Table VI. We believe these results are quite encouraging and trust that it is the beginning of an accepted method for determining conjugated unsaturation by a halogen procedure.

About as soon as the catalytic hydrogenation of oils was discovered, quantitative methods for using this tool to measure unsaturation were developed. The equipment and procedure were quite complicated although good results were obtained. Kaufmann and Baltes (21) observed beta licanic acid to have a value of 260.0 (theoretical 260.6). Equally good results were obtained for nonconjugated derivatives. Mead (27), using a catalyst consisting of a palladium black on charcoal in a 15-ml. Warburg flask, obtained near theoretical results for various oils as well as maleic anhydride. Ogg and Cooper (31) reported hydrogen iodine value for maleic acid of 115.9 (theoretical 116.1) and 9,11-linoleic acid 140.8 (theoretical 140.2). In 1952 Pack *et al.* (32) suggested a simplified procedure for analytical hydrogenation. His apparatus could be easily constructed in the laboratory or by glass blowers for about $40. Some of the results they obtained are shown in Table VII. These results appeared interesting to the A.S.T.M. Committee that was becoming discouraged with the Benham and Klee modification of the Rosenmund-Kuhnhenn Method. They therefore undertook to study this method by cooperative testing. Some of the results obtained are given in Table VIII. Two members of the committee were unable to obtain reasonable results, and the committee as a whole had difficulty with both the blank determinations and checks with dehydrated castor oil. Several attempts to modify this method were not successful. However, since encouraging results were obtained, this study is still active.

TABLE VI
Iodine Values by Modified R.-K.

	Obs.	Calc.
Unbodied DCO	150	155
Bodied DCO	136	137
DCO Acids	166	172
Tung	235	232

Spagnolo (1954)

TABLE VII
Iodine Values

	Hydrogen	Wijs	Theoretical
Maleic Acid	217.6	(16)	218.8
96% Methyl Linoleate	166.9	166.5	(172.3)
Alpha E. A.	271.2	188.0	273.8 (271.5)
Beta E. A.	270.9	186.7	273.8 (271.5)
Chinese Tung	228.2	164.3	(232)
Domestic Tung	238.8	165.7	(232)

Pack et al. (1952)

TABLE VIII
Hydrogen Iodine Value

Soybean	DCO	Tung
136.3	146.0	229.0
135.2	151.3	225.0
135.1	156.9	228.1
134.9	140.1	226.9
139.2	148.4	226.0

A.S.T.M. Committee

Composition of Fat

The degree of conjugation of an oil has considerable effect on the rate of heat polymerization, hardness on drying, etc. It is therefore desirable to have a quantitative method for measuring the amount of conjugation present. Originally this was done by physical tests, such as the rate of heat bodying or gel time. Obviously a chemical method for measuring amount of conjugation could be obtained by using methods for the determination of total unsaturation and partial unsaturation. The difference would give an empirical indication of the degree of conjugation. This was best developed by von Mikusch and Frazier (39), using the Woburn iodine method.

Kaufmann and Baltes (20) first applied the Diels and Alder Reaction to the determination of conjugation of fatty oils. This reaction involves the addition of maleic anhydride to the conjugated double bonds. Under controlled temperature conditions it does not react appreciably with the nonconjugated unsaturation. The Kaufmann procedure involves the use of a sealed tube reaction. Ellis and Jones (7) developed a procedure similar in principle, but one which could be run in a regular flask on a steam bath. These methods gave a constant known as the diene value, which may be defined as the grams of iodine equivalent to the maleic anhydride used per 100 g. of sample. Jamieson (15) observed that elaeostearic acid gave a value by the Kaufmann procedure from 75 to 78 while the Ellis and Jones modification was 89.0 to 89.6; the theoretical value was 91.2. At present the Ellis and Jones modification is the more accepted procedure. Both committees in the A.O.C.S. and the A.S.T.M. have studied this method. Some of the results obtained are given in Table IX. The method has been adopted by the A.S.T.M. and is currently under consideration by the A.O.C.S. From the diene value the apparent percentage conjugation may be readily calculated. It is now agreed by all investigators that this percentage conjugation is considerably lower than the actual value of the dehydrated castor oil. This was confirmed by experiments conducted at the Spencer Kellogg and Sons Laboratories. A sample of dehydrated castor oil was calculated to have 17% conjugation by the regular chemical diene value method. After reaction with maleic anhydride under conditions of the method the residual diene conjugation was determined spectrophotometrically to be 11.7%. This indicates that the reaction between maleic anhydride and dehydrated castor oil was incomplete. The sum (17.0 + 11.7) agrees approximately with the values obtained by ultra-violet absorption techniques, which indicate the true conjugation to be in the order of 25% to 30%. The reason for the discrepancy between the chemical and spectral methods apparently lies in the different rate of activity of maleic anhydride with the *trans* and *cis* isomers. We must consider the chemical diene determination an empirical indication of the amount of conjugation. However, even with this limitation, it is a useful method.

TABLE IX

Chemical Diene Determination

	Obs. Values	Av. Value	% Conj.
DCO	17.3, 18.5, 14.9	16.9	19.5
Tung	62.0, 60.4, 65.1	62.5	72.2
Soya	0.7, 1.1	0.9	1.0
Linseed	1.6	1.6	1.8

A.O.C.S. and A.S.T.M. Committees

It has been known for some time that small amounts of iodine isomerize the *cis* double bonds to *trans*. Von Mikusch (40, 41) has shown that certain conjugated linoleic isomers which do not react appreciably with maleic anhydride give quantitative reaction after the iodine treatment. Nonreactive *cis-trans* conjugated isomers would probably transform to the reactive *trans-trans*. The name, "Pandienzahl" (Pandiene Value), was proposed by Von Mikusch for the Kaufmann-Baltes Diene Value when the iodine treatment is used. Only a trace of iodine is necessary, 1 ml. of a 0.1% solution of iodine in acetone. The Pandiene Value for *trans* linoleic isomers has been found to be the same as the Diene Value (42, 43). Thus, by determining both values, it becomes possible to obtain added information on the isomer distribution.

The hexabromide method was used early to determine the amount of linolenic acid in mixed fatty acids from vegetable oils. It is performed by completely brominating the fatty acids and precipitating the insoluble hexabromide from ethyl ether. Unfortunately only a portion of the hexabromide precipitates under conditions of the test. This proportion is known, and thus the total hexabromide or linolenic acid may be calculated.

The tetrabromide value is obtained by measuring the petroleum naphtha insoluble after removal of the ether insoluble hexabromide. Again the precipitation is only partial. For instance, Brown and Frankel (5) observed a 90% precipitate of tetrabromide from linoleic acid when the theoretical should be 214%. Mathews (26) obtained 102.9%. However, even with these difficulties, the tetra and hexabromide method has been of considerable value in the past in establishing the amount of linoleic and linolenic acid contained in nonconjugated oils.

Kaufmann (18) back in 1926 observed that thiocyanogen $(SCN)_2$ could be used somewhat similarly to halogens in adding to the double bond. He originally thought one equivalent would add to oleic and linoleic and two equivalents to linolenic. This along with the iodine value permitted a calculation of the fatty acid components of the common nonconjugated oils. However it was soon found that it was not quite that simple, thiocyanogen did not add in such a regular manner to the fatty acid components. A large amount of work was then undertaken by various investigators to determine the actual amount of thiocyanogen it would add under specific conditions to the nonconjugated components. Lambou (23) has published a very good review of this work along with data to indicate the amount actually added. She (24) also studied the method for preparing lead thiocyanogen reagent. These studies finally resulted in a standardized procedure which has been adopted by both the A.O.C.S. and the Association of Official Agricultural Chemists. Table X gives the accepted values for thiocyanogen addition expressed in iodine value and compared to the Wijs iodine value. Using these values in simultaneous equations, the various compounds of an oil may be calculated. Narayan (28) this year has published a nomograph for making this calculation easier. The thiocyanogen method is difficult and time-consuming. It is fortunate for the modern chemist that it now is being replaced by light absorption methods.

TABLE X

Composition Determination

Fatty Acid	I.V.	T.V.
Saturated	0	0
Oleic	89.9	89.3
Linoleic	181.1	96.7
Linolenic	273.7	167.1

Conclusions

This discussion has indicated that the chemical determination of unsaturation of fats and derivatives depends on the type of unsaturation, whether conjugated or nonconjugated. This may be indicated by a chemical diene value if the ultra-violet absorption equipment is not available. If the oil is nonconjugated, the standard Wijs Method should give accurate and precise values. If it is desirable to speed up the determination, this can be done by the use of catalysts although the accuracy would probably suffer. In the case of conjugated oils a widely accepted method is still not available although the hydrogenation procedure is valuable as a research tool and the modified Rosenmund-Kuhnhenn Method described by Planck and associates at the Southern Regional Laboratory seems to offer definite possibilities. As for determination of composition the old, much used thiocyanogen, hexabromide, and tetrabromide procedures are giving ground to the more modern spectral methods.

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[Received November 8, 1954]

Letter to the Editor

Recently Cama, Chakrabarty, Hilditch, and Meara (1, 2) have published evidence in opposition to Kartha's criticism of the crystallization procedures for estimation of glyceride types in natural fats (3, 4, 5). The writer has made a careful study of the article by Cama *et al.* and has communicated with Dr. Kartha concerning it. There appear to be some items which are open to question.

1. Cama and colleagues record the results of the analysis, by the "crystallization" method, of several fat mixtures of supposedly known composition. The authors say that the accordance between observed and calculated values is generally good, but they express uncertainty over the composition of some of the ingredients because of the possibility that oxidative changes have occurred. In this writer's opinion there is reason, in addition, to question the calculated compositions of all the fat mixtures; consequently the accuracy with which the glyceride types were determined is in doubt. This uncertainty arises from the fact that the very same "crystallization" method used in the analysis of the mixture was employed in the analysis of the various ingredients thereof. Any errors inherent in this crystallization technique would appear in both the analysis of the ingredients and that of the mixture, and the latter analysis could therefore be erroneous even though the observed and calculated values were in perfect agreement. If the proportions of the various glyceride types were not accurately determined when the ingredients were analyzed, the same or similar errors could appear when the mixtures were analyzed because the analytical procedure was the same. Therefore even good correlation cannot in this case be taken as evidence that the "crystallization" method is accurate.

2. Cama *et al.* have collected data from the literature showing the proportions of GS_3 in samples of several natural fats, determined by both the "oxidation" and "crystallization" procedures. On the basis of these data and on the assumption that the oxidation method gives correct values, they have concluded that GS_3 can accurately be determined by the crystallization method.

Kartha (3, 4) has cast some doubt on the reliability of the particular oxidation method employed for determination of GS_3 in the work cited by Cama. If the procedure is unreliable, it cannot be employed as the whole method or any part of a method used as a criterion of the accuracy of the crystallization method.

Of the 14 fats cited by Cama *et al.* nine were analyzed by a "crystallization" procedure which includes an oxidation step. Errors inherent in the "oxidation" procedure will therefore appear in the "crystallization" procedure, and the two cannot with confidence be placed in contrast.

Of the remainder of the fats three, namely, stillingia tallow, cocoa butter, and palm oil (Belgian Congo), were each analyzed by a "crystallization" procedure including no oxidation step. Two, coconut oil and palm kernel oil, were probably analyzed in a similar manner, but this is uncertain because the reference is to unpublished data.

In every case, save one in which the proportions of GS_3 were the same by either method, analysis by the "oxidation" procedure resulted in a higher value for the content of GS_3 than that obtained by the crystallization method. When the values are corrected to compensate for the differences in the S content of the whole fat, the divergence is even greater.

This relationship is in complete accord with Kartha's statement (4) that determination of GS_3 by the oxidation method used in these instances may result in error and that the error will be positive. The evidence advanced by Cama *et al.* therefore tends to prove that the "oxidation" procedure is subject to error and does not prove that either of the "crystallization" procedures is accurate. The writer readily concedes that low temperature fractionation followed