

Analysis of Fats and Oils

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ABSTRACT

Analytical information on fats and oils is required for trading, quality control, nutritional labeling and forensics. Development of analytical procedures was one of the historical reasons for the organization of the Society of Cotton Products Analysts; it continues as a major effort of the successor organization, the American Oil Chemists' Society, through its Uniform Methods Committee and final publication of methods in the Society's "Official and Tentative Methods." A review of the current status of methods development will be followed by a glimpse of methodological research currently underway.

Oilseed commodity trading, quality control in processing, storage stability, nutritional labeling of food and feed products, and forensics in domestic and export markets are some of the areas in which industry requires analytical information. Development of analytical procedures was one of the historical reasons in 1909 for the organization of the Society of Cotton Products Analysts, whose successor is the American Oil Chemists' Society. Discussions were held in the spring of that year as to how results from various laboratories could be reconciled. By 1915 the Smalley Committee had been organized, and check samples with which to compare results and methods were made available to all chemists in the cotton mills.

Development of analytical procedures remains a major effort of the American Oil Chemists' Society. Through its journals, first *Oil and Soap*, and more recently the *Journal of the American Oil Chemists' Society*, newly discovered methods are described. Procedures that have wide use and applicability will find their way into the Society's "Official and Tentative Methods," a two volume loose-leaf publication that has become a "bible" to analytical chemists in fats and oils throughout the world. It contains at present some 311 individual methods for the analysis, divided into Vegetable Oil Source Materials [58], Commercial Fats and Oils [74], Soaps and Synthetic Detergents [117], and Industrial Oils and Derivatives [62].

A few sentences about the writing and editing of the Official Methods is in order. As its loose-leaf format suggests, it is a dynamic book with old or less satisfactory or unused methods being dropped and new procedures continually being added. The mechanism for this change is the Uniform Methods Committee whose chairman sits ex officio on the Governing Board of the American Oil Chemists' Society. The Committee consists, in addition to the chairman, of eight members including the editor of the Methods book. The Committee's responsibility is to receive suggestions from any member of the Society for improvement of old methods or establishment of new. Through its system of technical committees, analytical procedures are studied and tested. If recommended by a two-thirds affirmative vote, procedures are sent to the Uniform Methods Committee for a similar vote and acceptance as a "Tentative Method." All methods remain tentative for at least 1 year before being adopted as "Official." Further on in this paper a review will be given as to what new analytical procedures are in the technical subcommittees, on the horizon, or even a "glint in the analyst's eye."

Passing reference has been made to the Smalley Committee, which carefully prepares and circulates samples for analysis to various analytical laboratories. On the basis of

performance of the laboratories in analyzing these samples, the Smalley Committee and the Examination Board make awards for excellence and grant referee certificates to commercial laboratories in the name of qualified representatives who are members of the American Oil Chemists' Society. Some 79 chemists, including a representation from Japan and Canada, presently hold referee certificates in categories of cottonseed, soybeans, peanuts, cottonseed oil and other cup-refined oils, soybean oil and other neutral oil-loss oils, tallow and grease, protein concentrates, and cellulose yields. Laboratories holding certificates use the Official Methods of the AOCS wherever applicable. For further reading on Referee Chemists and Official Methods, a recent publication in the Society's journal is suggested (1).

Analyses of fats and oils are required for a number of purposes other than the obvious needs of commodity trading. In every oil production plant, there are analytical requirements for quality control. Refiners of oils need, for example, the free fatty acid content of oils when received and at the stages of alkali refining, bleaching, hydrogenation, and deodorization. Soap content, color, and phosphorous are examples of other analyses that are required. On final edible oil products, oxidation stability, fatty acid composition, solid fat index, and peroxide value may be needed for quality control.

A recent thrust has been that of nutritional labeling. A listing of calories, protein, carbohydrate, polyunsaturate and saturate fat, cholesterol, and vitamins may appear on the labels. Of even greater concern for the producer may be the analysis for trace constituents required by governmental regulations. All of these trends bring to the surface the increased needs of the fats and oils industry for analytical information.

Forensic chemistry is frequently required in the analytical laboratory. Adulteration of oils and identity of oils are of great concern at times. Oil pumped into an improperly cleaned ship's hold may contaminate a current oil shipment. "What is the contaminating oil?" and "How much?" is asked. In Italy each year a prize is given for work on the identity of olive oil, in part to maintain its position. Adventitious contamination of oil is an everpresent concern of oil chemists. Contaminants may range from trace metals to pesticide residues.

Specialty fats, confectionary, coatings, and hard butters all have their individual analytical requirements and specifications in terms of chemical and physical properties, plasticity and melting point range, which must be measured and maintained. These needs and the omnipresent diversity of other oil products and applications are the continuing challenges to the analytical chemist in the oil industry.

New methods proposed as Tentative Methods are first considered as described above in the technical subcommittees and, if one would prophesy what future methods are to emerge, he would do well to learn what methods are under study in the subcommittees. In a report of its chairman to members of the Uniform Methods Committee dated Dec. 27, 1977, Dr. William Link summarizes the work underway:

In the Dibasic Acids Subcommittee, a method for the determination of monomer in dimer products is being screened.

The Fatty Nitrogen Subcommittee is working on the determination of quaternaries with sodium tetraphenyl boron.

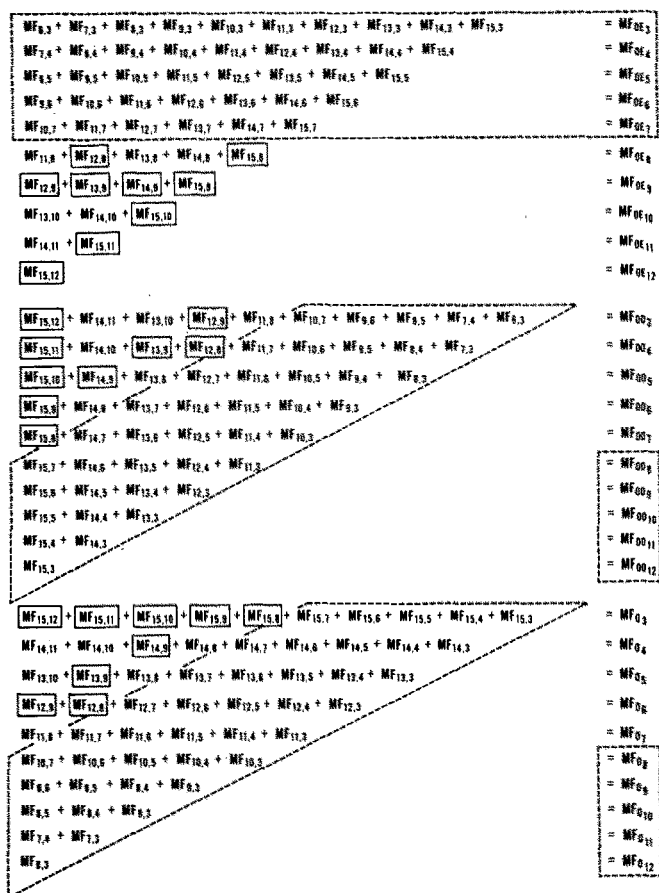


FIG. 1. Scheme for analysis of hydrogenated fats and oils (Refs. 2-5).

A recommended practice, Ca 17-76 "Activity of Hydrogenation Catalysts," has been issued by the Hydrogenated Oils Subcommittee, and this Committee has provided the AOCS office with 50 samples of standard catalyst. This subcommittee is also recommending a computer program for determining catalyst selectivity and an alternate means of calculating results of Ca 17-76 (above) as recommended practices; it is also considering a Tentative Method a procedure for overall characterization of a hydrogenated oil.

The Atomic Absorption Subcommittee is completing a study of the graphite furnace technique.

In the Chromatography Subcommittee, revision and updating of Ca 1-62, "Fatty Composition by Gas Chromatography," is underway. Screening of GLC proce-

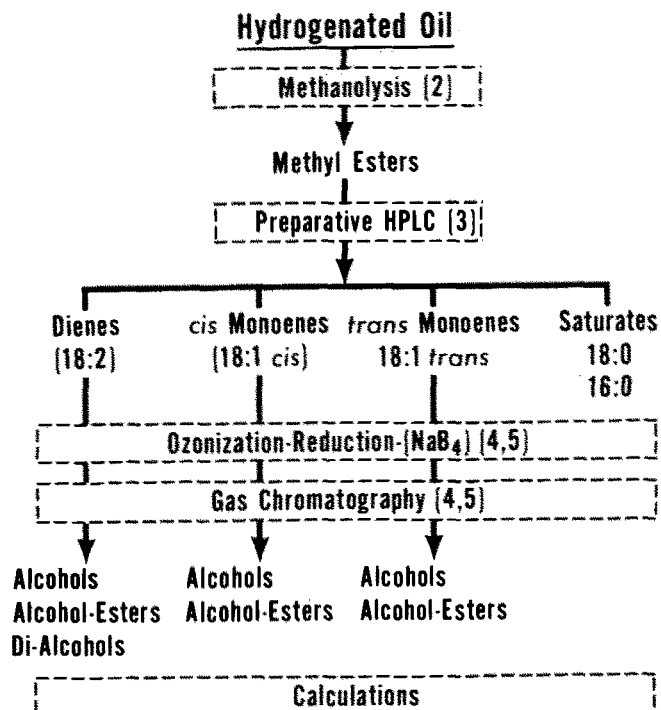


FIG. 2. Linear simultaneous equations relating composition of octadecadienoate isomer mixture to composition of alcohol, alcohol ester, and dialcohol fragments from ozonolysis. The area not included within dotted lines includes dienes that may be expected in hydrogenated oils. The diene isomers enclosed in rectangles assume that residual double bonds either do not move from their naturally occurring positions or that one of the two bonds moves only once.

dures for analysis of *cis* and *trans* isomers, for sterols in fats and oils and for short chain fatty acids is being carried on by task groups.

Study of *trans* unsaturation procedures is also underway in the Nuclear Magnetic Resonance Subcommittee.

The Mass Spectrometry Subcommittee held a full day symposium in New York in 1977 and is considering formulation of an AOCS mass spectral library.

A final collaborative effort by the Instrumental Melting Point Subcommittee should result in submission of a written method to the Uniform Methods Committee.

Other active technical committees are concerned with commercial fats and oils, seed and meal analysis, soap and synthetic detergents, and biochemical methods and standards.

By the time this manuscript is published, many of the

TABLE I
Compositions of Monoenes in Diet Fats

Diet fat % 18:1	Double bond position															
	4	5	6	7	8	9	10	11	12	13	14	15	16			
1. 65.55 <i>cis</i>						64.6	0.8	0.2								
2. 44.76 <i>cis</i>						39.2	1.5	1.2	1.2							
21.89 <i>trans</i>	0.2	0.3	0.4	1.1	2.8	3.9	4.7	3.9	2.5	1.6	0.4	0.1				
3. 19.26 <i>cis</i>		0.2	0.3	0.8	2.1	6.9	3.2	2.6	1.8	0.8	0.5	0.2				
45.81 <i>trans</i>		0.4	1.1	2.6	5.9	9.8	9.3	7.7	5.5	2.8	1.0					
4. 42.23 <i>cis</i>						41.7	0.5									
1.25 <i>trans</i>	0.02	0.01	0.01	0.05	0.17	0.33	0.27	0.19	0.13	0.06	0.01	0.01				
5. 19.79 <i>cis</i>				0.1	0.3	1.0	12.7	2.0	1.7	0.2	0.2					
23.79 <i>trans</i>		0.1	0.3	0.8	2.8	5.0	5.4	4.5	2.9	1.7	0.3	0.05	0.05			
6. 22.50 <i>cis</i>						22.3	0.05	0.14								
1.89 <i>trans</i>	0.02	0.02	0.08	0.12	0.20	0.44	0.30	0.28	0.21	0.14	0.06	0.01	0.01			
7. 39.47 <i>cis</i>					0.04	37.8	0.95	0.67								
13.23 <i>trans</i>	0.16	0.08	0.11	0.37	1.35	3.07	2.96	2.52	1.57	0.82	0.12	0.03	0.07			

TABLE II
Calculation of Isomeric Octadecadienoates^a

Sample	Isomer								
	8,12	8,15	9,12	9,13	9,14	9,15	10,15	11,15	12,15
A			67.31	0.11	0.67	3.58	0.90	0.39	27.04
B			43.79			31.64			24.57
C	5.12		83.79	4.32	2.83	3.45	0.50		
D		6.63	18.28	1.35	20.81	21.59	20.60	0.41	9.79

^aSample A is a 9,12-12,15 (70%, 30%) mixture as determined by capillary gas chromatography; B is a 9,12-9,15-12,15 (44%, 29%, 27%) mixture similarly determined; C is diene from shortening; D is from hydrogenated linolenate.

recommendations and actions indicated above may have been made.

There is a need for an overall characterization of a hydrogenated oil. This area of methodology is cited above and is being considered by the Hydrogenated Oils Subcommittee. While admittedly far beyond the stage of a "glint in the analyst's eye," it will serve to illustrate methodology at a pre-subcommittee stage.

As an example of methodology development, a request for positional and geometric isomers was made of our Northern Regional Research Center to characterize hydrogenated oils that were to be used for atherosclerosis experiments in swine at the University of Wisconsin. The schematic of Figure 1 gives the procedure used to determine positional and geometric isomers in the monoenoic acid fractions. The complete analysis is given in Table I for positional and geometric isomers of octadecenoic acids for the seven fats used in the feeding studies (6).

Analytical methodology, such as the above (4) for determining the position and configuration of double bonds in mixtures of monoenoic fatty acids found in hydrogenated fats, may be conceded to be generally available and adequate (7). In the dienoic fatty acids, comparable methodology is essentially absent.

Recently a procedure has been described (5) that provides information on the positional dienoic isomers that may be expected in hydrogenated fats. As indicated in Figures 1 and 2, the calculation requires quantitative gas chromatographic data for dialcohols as well as for alcohols and alcohol-ester fragments of reductive ozonolysis. A series of linear simultaneous equations shown in Figure 2

account individual alcohols, individual dialcohols, and individual alcohol esters in terms of the proportion of dienoic isomers that contribute to the individual alcohol types. Although rigorous algebraic solutions are possible, an alternative computer program is used to give a "least squares best fit."

Data for a dienoic acids fraction of hydrogenated fat are given in Table II, along with the analysis of independently analyzed mixtures. From a perusal of these data, it would appear that a new approach to analyzing diene isomers in commercially hydrogenated fat products is now at hand. Thus, in their search for adequate methodology, the Hydrogenation Subcommittee may be a step closer to their goal of overall characterization of hydrogenated fats. Should the interest in the method justify and the Uniform Methods Committee approve, a new procedure might be added to the expanding "Official and Tentative Methods of the American Oil Chemists' Society."

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