

TABLE IV
 Solubility of the Metal Soaps (g./1000 g. of Solvent)

Soap	CCl ₄	Benzene	Absolute ethanol	Methanol	Ethyl acetate	Isopropyl alcohol	Acetone	Petroleum ether
Fe ⁺⁺⁺ (W).....	0.17	0.29	0.47	0.39	0.23	0.41	0.27	0.30
Cr ⁺⁺⁺ (W).....	0.37	0.50	0.43	0.38	0.33	0.41	0.37	0.35
Cu ⁺⁺ (W).....	0.39	0.33	0.28	0.24	0.23	0.22	0.20	0.18
Pb ⁺⁺ (W).....	0.28	0.24	0.21	0.59	0.14	0.15	0.16	0.13
Mg ⁺⁺ (W).....	0.13	0.19	0.40	0.25	0.14	0.18	0.18	0.17
Ni ⁺⁺ (W).....	0.11	0.19	0.39	0.67	0.23	0.23	0.21	0.19
Mn ⁺⁺ (W).....	0.10	0.17	0.27	0.35	0.15	0.17	0.16	0.17
Co ⁺⁺ (W).....	0.24	0.27	0.31	0.48	0.16	0.19	0.21	0.17
Ba ⁺⁺ (W).....	0.36	0.15	0.19	0.32	0.13	0.12	0.14	0.16
Ba ⁺⁺ (H).....	0.14	0.20	0.17	0.21	0.19	0.21	0.15	0.22
Ba ⁺⁺ (NHI).....	0.08	0.04	0.07	0.13	0.09	0.07	0.06	0.05
Ba ⁺⁺ (NHII).....	0.06	0.19	0.18	0.63	0.13	0.11	0.10	0.10
Cd ⁺⁺ (W).....	0.15	0.23	0.27	0.33	0.23	0.25	0.23	0.24
Cd ⁺⁺ (H).....	0.17	0.20	0.24	0.28	0.23	0.50	0.30	0.23
Cd ⁺⁺ (NHI).....	0.22	0.65	0.12	0.12	0.07	0.08	0.06	0.05
Cd ⁺⁺ (NHII).....	0.16	0.12	0.58	0.53	0.12	0.25	0.11	0.13

(W)—Soap made from whole acid fraction (Table I); (H)—Soap made from hydroxy acid fraction (Table I); (NHI)—Soap made from non-hydroxy acid fraction I (Table I); (NHII)—Soap made from non-hydroxy acid fraction II (Table I).

chromic from chrome alum; and cadmium from cadmium acetate.

Determination of Metal Content. With the exception of barium, cadmium, nickel, and cobalt soaps, metal content was determined by ignition to oxides. Barium and cadmium content was determined by ashing as sulfate in a platinum crucible. Nickel was determined as the dimethylglyoxime complex. Cobalt was determined with α -nitroso- β -naphthol.

The metal content of the individual soaps of the whole acid fraction is given in Table II. Table III lists similar data for the barium and cadmium soaps of the partitioned acid fractions.

Solubility Determination. Two hundred fifty ml. of solvent and approximately 0.2 g. of metal soap were added to a 500 ml. flask, the flask was stoppered and shaken vigorously in a constant temperature bath for 4 hr. At the end of this period the contents of the flask were poured into two 100 ml. graduate cylinders. The cylinders were then stoppered and allowed to stand in the constant temperature bath until all the solids had settled and the supernatant liquid was clear. A portion of the supernatant liquid (96 ml.) was withdrawn from the graduates with a specially designed automatic pipette (7) into a tared beaker. The beaker and solution was weighed. The solvent was evaporated. The beaker and residue were dried to constant weight and weighed. The solubility of the soap per 1000 g. of solvent was calculated from these data. The solubility data is summarized in Table IV.

From an inspection of the data given in Table IV, no hard and fast rule for solubility of the metal soaps

can be established. For the most part, in any given solvent, the soaps of the trivalent metals were more soluble than those of the divalent metals. Generally, the soaps have the greatest solubility in methanol and the least solubility in carbon tetrachloride. In no instance did the solubility of any soap exceed 1 g. per 1000 g. of solvent.

Partitioning did not seem to be much of a factor in solubility. The cadmium and barium soaps of the whole acid fraction and the hydroxy acid concentrate had about equal solubility characteristics. However, chain length appears to have a greater effect than hydroxyl content. The corresponding soaps of the non-hydroxy acid fraction having a low acid number were less soluble than the whole acid fraction soaps. Those of the high acid number fraction were more soluble than the whole acid fraction soaps.

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Report of the Spectroscopy Committee, 1960-61

FOLLOWING usual custom, the Spectroscopy Committee met only once during the past year. The meeting was held during the American Oil Chemists' Society 52nd Annual Convention at the Sheraton-Jefferson Hotel, St. Louis, Mo., May 1-3, 1961. Fifteen members and guests attended the session held Monday, May 1.

A.O.C.S. Tentative Method "Isolated Trans Isomers—Infrared Spectrophotometric Method"

Announcement was made that the Uniform Methods Committee has approved the method for "Isolated *Trans* Isomers—Infrared Spectrophotometric Method," recommended by the Spectroscopy Committee. The method accepted by the Uniform Methods Committee as a tentative method of the Society is essentially that published in our report for the year

1958-1959 (1), as revised following a discussion of the problem of the direct determination of long-chain fatty acids (2). The tentative method includes provision for direct determination of *trans* isomers in long-chain fatty acids if the *trans* content is 15% or greater. If less than 15%, the method provides for conversion of the fatty acid to the methyl ester (2). The method will appear as a tentative method of the Society in the next revision of A.O.C.S. Book of Methods.

New Subcommittee to Investigate Methods for Preparing Methyl Esters from Long-Chain Fatty Acids

The provision in the revised tentative method "Isolated *Trans* Isomers—Infrared Spectrophotometric Procedure" requiring that samples of fatty acids

containing less than 15% isolated *trans* be converted to their methyl esters before analysis, made necessary a provision for the conversion of the fatty acid to its methyl ester. The Spectroscopy Committee after considerable discussion voted unanimously for a modification of the diazomethane method described by Schlenk and Gellerman (3) for esterification of fatty acids on a small scale (2). However, there has been considerable difference of opinion as to how long-chain fatty acids could be best converted to their methyl esters, particularly for the purposes of spectrophotometric analyses or for gas-liquid phase chromatography. The Uniform Methods Committee recommended to President Bates the creation of a committee or a subcommittee of an existing committee to be assigned the task of investigating methods for this conversion and recommending a specific procedure for adoption by the Society. Bates subsequently authorized formation of a subcommittee of the Spectroscopy Committee to handle this task and J. R. Chipault agreed to be chairman. A complete subcommittee has now been formed; its members are as follows:

J. R. Chipault chairman	William E. Link
James Benedict	Francis E. Luddy
Seymore Goldwasser	Robert T. O'Connor
Ralph E. Kelly	W. Sidney Singleton
	R. C. Walker

Dr. Chipault presided over that portion of the above mentioned meeting of the Spectroscopy Committee which dealt with the authorization and planning of the subcommittee. The first activity of the subcommittee will be collaborative work leading to the establishment of a more satisfactory method for converting fatty acids to their methyl esters primarily for the purpose of spectroscopic and gas-liquid phase chromatographic analysis. Among methods which will be studied are: (a) acid esterification, (b) diazomethane, (c) boron trifluoride, and (d) dimethoxypropane, along with any other methods suggested by or to the subcommittee. A later activity of the subcommittee may probably be preparation of methyl esters from triglyceride by *trans* esterification using one of the three methods; (a) with alkoxides, (b) with hydrochloric acid, (c) with sulfuric acid, or by any method recommended by or to members of the subcommittee. Collaborative work is planned on the first phase to start early in our activities for the year 1961-62.

Collaborative Testing—Preparation of Secondary Standards

Secondary standards required to calibrate infrared spectrophotometers for the determination of isolated *trans* isomers in methyl esters or triglycerides have been available from the Society through the Chairman of the Spectroscopy Committee (1, 2). These standards have continued to be useful. Thirty sets have been furnished during the past year. They will continue to be available. Samples of all secondary standards will be available through the Society. Questions regarding them should be addressed to the Chairman of the Spectroscopy Committee, American Oil Chemists' Society, P. O. Box 19687, New Orleans 19, Louisiana. The provision in the revised procedure that the isolated *trans* contents of long-chain fatty acids containing more than 15% *trans* isomer may be analyzed directly will require secondary standards for determinations of *trans* isomer content of fatty

acids. These secondary standards are now being prepared by the Spectroscopy Committee and will be available early this year.

Collaborative Testing—Near Infrared Method

At the meeting of the Spectroscopy Committee in Dallas in 1960, it was decided that the next collaborative effort of the Committee would be a test of one or more of the following methods by means of near infrared: (a) epoxy value, (b) hydroxyl, and (c) *cis*-isomers. By letter ballot all members were asked to vote on their choice of one or two (but not more than two) of these methods which should be collaboratively studied first. From our ten-member committee, eight votes were received, seven indicating two methods and one only 1. The results were: hydroxyl number, 8; epoxy value, 3; *cis* determination, 4. As hydroxyl number was the unanimous choice of all members voting and considerably ahead of the other two methods, it was decided to initiate collaborative testing on procedures for hydroxyl as soon as appropriate primary standards could be obtained. During the past year effort has been made to obtain suitable standards. We now have available primary standards for the determination of hydroxyl value in long-chain alcohols and hydroxy acids. Collaborative study of these determinations by means of near infrared is planned for the early work of the Committee during the coming year.

Collection of Spectra of Fatty Acid Materials For the Coblenz Society

As announced in the previous reports of the Spectroscopy Committee (1) (2), the Coblenz Society of Infrared Spectroscopists has initiated a system of collection and dissemination of infrared spectra and have several "collectors" throughout the country. Arrangements have been made whereby the single group of spectra of a particular type, as for example, spectra of interest to the fat and oil industry, can be submitted to the Coblenz Society and subsequently, copies of this spectra may be purchased by any interested individual. In this manner spectra of pure fatty acid and fatty acid derivatives could be made available to any member of the A.O.C.S. At their meeting in St. Louis, the Spectroscopy Committee was fortunate in having as a guest Clare E. Smith, Chairman of the Coblenz Society Committee for the Collection and Dissemination of Infrared Spectra. Dr. Smith explained the Coblenz plan for collecting spectra in one particular area of interest and publishing as a single block which could be purchased by members interested in that particular area without the necessity of buying all of the Coblenz published spectra. Essential to this plan is the necessity of getting enough spectra of pure compounds submitted to the Society in order to enable them to publish a supplement of sufficient size in which all of the spectra would contain fatty acid compounds. The Spectroscopy Committee again repeats its plea that all members throughout the A.O.C.S. participate in this activity. Spectra to be submitted to the Coblenz Society may be sent to the Chairman of the Spectroscopy Committee and any details of the plan, requirements for the spectra to be submitted or how spectra may be purchased, can be obtained from him.

New Members

During the year three changes have been made in the membership of the Spectroscopy Committee.

E. F. Herb from the Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture, has resigned as his work is not now in the field of Spectroscopy. He has been replaced by Paul Magidman from the same organization. Donald Wheeler, General Mills, Inc., has also resigned as his work is now no longer closely related to spectroscopy. He has been replaced by Seymore Goldwasser, Lever Brothers Company. In addition, we have added one new member, David Firestone from the Food and Drug Administration of the Department of Health, Education, and Welfare. Dr. Firestone is a referee for official methods of the Association of Official Agricultural Chemists. His appointment to the Spectroscopy Committee of the A.O.C.S. will be another step in standardizing official methods of the two societies. We welcome Dr. Firestone, Dr. Magidman, and Dr. Goldwasser to the Committee. We regret the necessity for Drs. Herb and Wheeler to leave us, but we look forward to the opportunity to consult with them as they join the illustrious members of our alumni.

Acknowledgments

The Spectroscopy Committee is ever aware that, particularly in the collaborative testing program, it is indebted to several individuals for assistance in making spectral measurements, compiling data, and offering suggestions.

The chairman, in particular, wishes to acknowledge the considerable assistance of Elizabeth R. McCall in compiling results of polls of the members and in distributing the secondary standards for the A.O.C.S. tentative method "Isolated *Trans* Isomers—Infrared Spectrophotometric Method."

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J. R. Chipault	William E. Link
Robert O. Crisler	Paul Magidman
David Firestone	B. N. Rockwood
Seymore Goldwasser	Hans Wolff
Robert T. O'Connor, chairman	

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The Chemistry of the 2-Thiobarbituric Acid Test for the Determination of Oxidative Rancidity in Foods.

I. Some Important Side Reactions^{1,2}

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Evidence is presented by UV, visible, and IR spectra as well as by paper and column chromatography of variously treated TBA-acid reagents that the structure of TBA is altered upon acid-heat treatment. A more pronounced but similar effect results from the treatment of the TBA with hydrogen peroxide. Some of the degradation products of TBA absorb at the same wavelength as the TBA-malonaldehyde complex, as do many compounds which are reported in the literature to react with TBA. The significance of these findings in respect to the quantitative aspects of the test for the determination of rancidity in food products is discussed.

THE 2-thiobarbituric acid (TBA) test is widely used for measuring oxidative changes in foods containing unsaturated fatty acids. The red pigment produced after reacting TBA directly with oxidized foods or their distillates has been identified to be a condensation product of one molecule of malonaldehyde with two molecules of TBA (22). As malonaldehyde is believed to be derived from some decomposition product of the oxidized unsaturated fatty acids, spectrophotometric measurement of the TBA-malonaldehyde complex gives what is thought to be a quantitative measure of fat oxidation (18, 19, 21-23, 30).

In recent years various methods have been developed for performing the TBA test on food products. These methods can be classified under two categories. a) A solution of TBA in a strong acid is added to the

food product, and the whole mixture is heated for periods of 10-35 min. in a water bath to obtain maximum color development. The red pigment is then extracted with a suitable solvent and measured in a spectrophotometer. b) The food product is first steam-distilled with acid, and the TBA-acid solution is added to a portion of the distillate, which is then heated for 35 min. for maximum color development. The red pigment is measured directly in a spectrophotometer.

The two methods are similar in that they both employ heating of the food at a low pH (0.9-1.5). This step is claimed to be essential for the liberation of malonaldehyde from some precursor as well as for the condensation of malonaldehyde with TBA (1-3, 10-12, 18-23, 26, 29, 30).

Their differences however are many. The distillation method appears to have advantages in that prolonged heating of the food product is avoided, thus keeping to a minimum any further oxidative or decomposition changes during the test. Furthermore only the volatile constituents of the food are distilled over, thus avoiding any reaction of the TBA with nonvolatiles of the food which may react with it. Finally the acid of the TBA reagent is diluted as the reagent is added to the distillate in equal amounts before the heating begins.

All methods for performing the TBA test invariably employ the addition of TBA dissolved in acid. TBA is an amide, thus acid-heat treatment can be expected to hydrolyze TBA to thiourea and malonic acid. The same treatment may also hydrate the -C-SH group of the TBA molecule, thus yielding

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² Presented at the 52nd annual meeting, American Oil Chemists' Society, St. Louis, Mo., May 3, 1961.

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