zene, with very little apparent change in the colloidal properties of the system. It is well known that oil-soluble petroleum sulfonates may contain on the order of 5% of carboxylate soaps. These examples might be viewed as cooperative micelle formation rather than solubilization. The phenomenon is analogous however to the mechanism proposed by Harkins and others for the solubilization of long-chain alcohols in aqueous micelles (20, 30). It is probable that in non-aqueous systems nearly all solubilization (except for water and similar small polar molecules) involves such cooperative micelle formation.

The field of solubilization by micelles of oil-soluble soaps has been little studied and will repay a larger amount of research attention that it has yet received.

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Report of the Spectroscopy Committee, 1954-1955

THE SPECTROSCOPY COMMITTEE in its report for 1952–1953 [Journal, *30*, 352 (1953)] concluded that "reasonably reproducible results, using A.O.C.S. Tentative Method Cd 7-48, revised May 1951, can be obtained in the hands of experienced operators."

In the report for 1953-1954, at the spring meeting in San Antonio, the committee confirmed this statement but concluded that "while the method gave satisfactory results within its scope, this scope was too restrictive." Many types of samples cannot be analyzed by the tentative method, several others are analyzed by unnecessarily complicated procedures. No further collaborative work is required to test the method, but further work is desirable to investigate possible means of extending its scope. Further investigation, with the view to simplifying the procedure in the analysis of specific types of samples, is also needed.

Present Work

Accordingly during the past year your committee has conducted a series of collaborative tests to determine whether

1. the method can be simplified in the analysis of samples which do not contain constituents more unsaturated than linoleic acid. Specifically can the method be revised to restrict measurements and calculations to the dienoic region in the analysis of cottonseed oil, peanut oil, sesame oil, and similar vegetable oils? The present A.O.C.S. method Cd 7-48 permits only elimination of measurements in the tetraene region.
2. a satisfactory modification can be devised which will permit the measurement of polyunsaturated nonconjugated constituents in the presence of large quantities of conjugated polyunsaturated constituents. Specifically can the linoleic acid content of tung oil be determined by any modification of the method? The present A.O.C.S. method Cd 7-48 is limited to materials containing only traces of preformed conjugation.
3. the method can be extended to include the determination of pentaenoic acids with the use of 21% alkali reagent. Is this reagent preferable for the determination of arachidonic acid? What recommendations can be made regarding the selection of % alkali in the reagent? The present A.O.C.S. method Cd 7-48 permits only the use of 6.6% alkali and does not provide for the analysis of pentaenoic acids.

Results of these collaborative tests are summarized briefly in Tables I, II, III, and IV.

Conclusions

At a session held during the meeting of the American Oil Chemists' Society in Minneapolis last fall the committee studied and discussed these results and agreed on the following conclusions:

1. The present tentative A.O.C.S. method Cd 7-48 can be simplified. A fat or oil containing no unsaturated constituents greater than diene (for example, cottonseed oil, peanut oil, sesame oil, etc.), or any sample subsequently shown during the analysis (by absence of specified absorption bands in the triene or more highly unsaturated regions) to contain no constituents more unsaturated than diene, can be analyzed by measurements in the dienoic region: 233 mμ only. Similarly a sample known to contain no unsaturated constituents more highly unsaturated than triene (soybean oil, linseed oil, etc.), or shown to exhibit no absorption bands in regions of conjugated unsaturation higher than trienoic, need be measured in the dienoic and trienoic regions only.
2. The scope of the tentative method Cd 7-48 can be increased to include the determination of pentaenoic acids by means of the 21% alkali reagent. This reagent is preferable for the determination of arachidonic acid. The present 6.6% alkali reagent was considered first choice for the determination of linolenic and linoleic acids. However, when application of this choice would require preparation of both reagents for complete analysis of a sample, the 21% KOH procedure may be used as a second choice for linoleic and linolenic acids, or the 6.6% KOH procedure may be used as a second choice for arachidonic acid. Pentaenoic acids must be determined with the 21% KOH procedure. For example, a sample containing all four acids may be analyzed with the 21% KOH reagent, using the second choice for the determination of linoleic and linolenic acids, or a sample containing linoleic, linolenic, and arachidonic acids may be analyzed with the 6.6% KOH procedure, using the second choice for the arachidonic acid determination.
3. The committee did not consider the collaborative tests to extend the method Cd 7-48 to include the determination of linoleic acid in the presence of large quantities of preformed conjugated acids, as in tung oil, to be sufficiently conclusive. Further testing of this type of sample was recommended. The problem of analyzing samples which contain major quantities of preformed conjugated fatty acids and smaller quantities of nonconjugated acids should receive individual attention in collaborative study with the view of proposing an official method for such analyses.

Projected Committee Work

At the present time the committee is engaged in a revision of Tentative Method Cd 7-48 to provide for the more simplified analyses where justified, to increase the scope to include the determination of pentaenoic acids, and to establish criteria to govern the choice of % alkali in the reagent.

A series of tung oil samples is being prepared for submission to all committee members for collaborative study of a proposed method to determine both the preformed conjugated constituents (alpha- and beta-eleostearic acids) and nonconjugated polyunsaturated constituents (linoleic acid).

At the fall meeting of the Spectroscopy Committee in Minneapolis it was decided that sufficient interest is being maintained in methods for the determination of *trans*-isomers of the fatty acid constituents to necessitate some collaborative study of this method for adoption as an A.O.C.S. procedure. Accordingly preliminary plans are being made to test collaboratively the determination of percentage *trans*-isomers in the presence of *cis*-isomers in samples containing saturated, monounsaturated, and nonconjugated polyunsaturated fatty acids. Attempts are being made to obtain both primary and secondary standards for comparison of instruments to be used in this collaborative study.

Attempts will be made to finish the first two items on the projected committee work promptly. The exact program to be followed then must, of course, be left to the 1955-56 Spectroscopy Committee.

Robert T. O'Connor, chairman
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Samuel F. Herb
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Results of Collaborative Work of Spectroscopy Committee, A.O.C.S., 1954

I. Cottonseed Oil Methods No. C-1 and C-2

Collaborator No.	Method No. C-1				Method No. C-2	
	Conjugated Diene	Conjugated Triene	Linooleic Acid	Linolenic Acid	Conjugated Diene	Linoleic Acid
	%	%	%	%	%	%
1	0.31	0.09[a]	50.0[a]	0.00[a]	0.31	50.1[a]
2	0.32[b]	0.09[a]	50.9[a, b]	0.32[a, c]	0.32[b]	51.0[a, b]
3	0.32	0.09[a]	49.5[a]	0.38[a]	0.32	49.6[a]
4	0.34	0.06[a]	49.3[a, b]	0.05[a]	0.34	49.4[a,b]
5	0.34	0.09[a]	47.5[a, d]	0.41[a, c]	0.34	47.9[a, d]
6	0.33[b]	0.09[a]	48.8[a, b]	0.00[a, b]	0.33[b]	49.0[a, b]
7	0.32	0.00[a]	47.1[a, b]	0.00[a, b]	0.32	47.2[a]
8	0.32	0.09	49.0	0.40	0.32	49.2
Avg.	0.32	0.08	49.0	0.20	0.32	49.2

[a] One or more of the slit widths involved in measurements from which these values were calculated were not within the range 0.8 to 0.9 mm. required by Tentative Method Cd 7-48 for measurements in the triene region.

[b] One or more of the absorbancies involved in this calculation were not within the range of 0.2 to 0.8 required by Tentative Method Cd 7-48.

[c] Value calculated by chairman.

[d] Value recalculated by chairman.

II. Linseed Oil Methods No. L-1 and L-21

Collaborator No.	Method No. L-1				Method No. L-21	
	Conjugated Diene	Conjugated Triene	Linoleic Acid	Linolenic Acid	Linoleic Acid	Linolenic Acid
	%	%	%	%	%	%
1	0.21	0.003[a]	13.6[a]	51.5[a]	14.4[a]	50.8[a]
2	0.21	0.002[a]	12.9[a]	52.3[a]	11.1[a]	53.1[a]
3	0.21	0.002[a, b]	12.2[a, b]	52.6[a, b]	14.4[a, b]	50.4[a, b]
4	0.26	0.002[a,b,c]	11.1[a, b]	49.1[a, b]	12.0[a, b]	47.0[a, b]
5	0.22	0.003[a, b]	11.6[a, b]	52.7[a, b]	14.0[a, b]	52.2[a, b]
6	0.21[b]	0.000[a]	10.7[a, b]	50.2[a, b]	15.8[a, b]	48.5[a, b]
7	0.23	0.002[a]	14.2[a]	54.8[a]	17.9[a]	47.9[a]
8	0.20	0.000	12.7	52.3	13.1	52.4
Avg.	0.22	0.002	12.4	51.9	14.0	50.3

[a] One or more of the slit widths involved in measurements from which these values were calculated were not within the range 0.8 to 0.9 mm. required by Tentative Method Cd 7-48 for measurements in the triene region.

[b] One or more of the absorbancies involved in this calculation were not within the range of 0.2 to 0.8 required by Tentative Method Cd 7-48.

[c] Value calculated by chairman.

Objective: Tentative Method Cd 7-48 provides for a simplification of procedure and calculation for sam-

III. Animal Fat Concentrate No. A-21

Collaborator No.	Method No. A-21						
	Conjugated Diene	Conjugated Triene	Conjugated Tetraene	Linoleic Acid	Linolenic Acid	Arachidonic Acid	Pentaenoic Acids
	%	%	%	%	%	%	%
1	2.08	0.04[a]	0.00	4.6[a]	7.9[a]	21.2	2.0
2	2.12	0.03[a]	0.00[c]	6.4[a, b]	8.4[a, b]	22.2	2.3
3	2.17[b]	0.05[a]	0.00[a, b]	7.3[a, b]	3.3[a, b, d]	26.2[b]	2.5[b]
4	2.31	0.01[a]	0.00[b]	5.1[a]	4.0[a]	25.6	2.5
5	2.32	0.50[a, b, e]	0.00[c]	4.6[a]	11.8[a]	23.5	2.2
6	......	......	......	6.7[a, b]	4.4[a, b]	25.3[b]	2.6
7	1.95[b]	0.03[a, b, d]	0.00[b, d]	8.9[a, b, d]	16.2[a, b, d]	14.9[d]	1.3[d]
8	2.06	0.04	0.00	7.1	9.0	21.1	1.5
Avg.	2.14	0.03	0.00	6.3	8.1	22.5	2.1

[a] Indicates that one or more of the slit widths involved in measurements from which these values were calculated were not within the range 0.8 to 0.9 mm. required by Tentative Method Cd 7-48 for measurements in the triene region.

[b] Indicates that one or more of the absorbancies involved in this calculation were not within the range of 0.2 to 0.8 required by Tentative Method Cd 7-48.

[c] Value calculated by chairman.

[d] Value recalculated by chairman.

[e] Not included in average.

ples known to contain no arachidonic acid, *i.e.*, most vegetable and drying oils, by elimination of all values in the tetraene region, about 300 mμ. Can a further simplification of similar nature be made for oils known to contain no linolenic acid, *i.e.*, cottonseed, sesame, peanut oil, etc., by elimination of all values in the triene region, about 268 mμ?

In your opinion has this collaborative work satisfactorily demonstrated that such a simplification should be recommended and included in Method Cd 7-48?

Objective: Certain laboratories dealing primarily with animal fats, fish oils, etc., prefer to work with 21% alkali for determinations of arachidonic acid, pentaenoic acids, etc. Other laboratories, working primarily with vegetable and drying oils, consider the 6.6% alkali more convenient. Can Tentative Method Cd 7-48 provide 21% and 6.6% alkali as alternate methods for all samples, thus eliminating the requirement for some groups to work with both concentrations?

In your opinion does the collaborative work on Linseed Oil, reported here, justify this alternate method?

Objective: A method involving 21% alkali is proposed as superior for determination of arachidonic acid and essential for determinations of acids more unsaturated than arachidonic acid.

In your opinion should the 21% alkali be introduced into Tentative Method Cd 7-48 for all polyunsaturated acids more unsaturated than arachidonic?

Should determination of arachidonic acid be recommended with 6.6%, 21% alkali, or optional use of either?

IV. Tung Oil Methods No. T-1 and T-2

Collaborator No.	Method T-1				Method T-2
	Conjugated Diene	Conjugated Triene		Linoleic Acid	Linoleic Acid
		α-Eleostearic Acid	β-Eleostearic Acid		
	%	%	%	%	%
1	0.12	80.6	0.0[a]	6.4	7.0
2[b]	0.00	81.0	0.0	5.8	7.0
3[b]	1.22	77.0	2.4	4.2	6.4
4	0.00	81.2	10.4	4.0	4.4
5	......	......	......	......	......
6[b]	0.08	74.8	5.5	4.5	5.2
7[c]	2.32	41.1	35.7	2.2	3.0
8	0.16	79.3	0.0	6.2	7.4
Avg.	0.26	79.0	3.0	5.2	6.2

[a] Actually reported as a negative value.

[b] Indicates that one or more absorbancies used in the calculations were not obtained on a Beckman DU with maximum sensitivity.

[c] Not included in averages.

Objective: At the present time no official method exists for the determination of non-conjugated acids in the presence of large quantities of conjugated constituents. The linoleic acid content of tung oil studied is one example. Should Tentative Method Cd 7-48 be extended to include the method studied here? If so, should the simplified calculation of Method T-2 be used or is the more rigorous Method T-1 desirable?

Properties of the Methylene Group in 1,4-Dienes. I. Catalytic Polymerization of 1,4-Pentadiene[1]

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THE METHYLENE GROUP in the 1,4-diene system of linoleic and linolenic acids is a key structural feature in the chemical behavior of non-conjugated drying oils. The simplest compound containing this structure is 1,4-pentadiene. While this is not an exact model of the fatty acids, because of the terminal double bonds in 1,4-pentadiene, its chemical behavior should be closely analogous. The purpose of this work was to study catalytic isomerization and polymerization reactions of 1,4-pentadiene in relation to those reactions of drying oils.

According to the current theory of thermal polymerization (heat bodying), non-conjugated oils, such as linseed and soybean, initially isomerize on heating so that a fraction of the ethylenic groups are conjugated. Polymerization then proceeds by Diels-Alder addition between a 1,3-diene group in one acid radical and a double bond in another.

While many substances accelerate the thickening of fatty oils, the important catalysts, *i.e.* substances which do not permanently combine with the oil, are sulfur dioxide, quinones, and nickel. These compounds are also isomerization catalysts because they accelerate the conversion of 1,4-diene groups to conjugated structures. Among other isomerization catalysts, alkali metal hydroxides are best known. Typical catalysts of these types have now been investigated for their quantitative effects on 1,4-pentadiene.

Polymerization of 1,4-Pentadiene

Thermal and boron fluoride-catalyzed polymerizations of 1,4-pentadiene have been reported by Ahmad and Farmer (1), who showed that 1,4-pentadiene

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[1] Presented before the Organic Chemistry Division, American Chemical Society, Atlantic City, September, 1952.

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