vent system. If the water flow through any condenser is interrupted, the vapors from that condenser will pass to the vent condenser and be condensed, preventing loss.

There are two principal ways by which steam may be wasted: by leaks in piping and equipment and by excessive process demands. Since the first is a common maintenance problem needing no discussion, only the second will be discussed here.

Almost all process steam is used for vaporizing hexane from the extracted oil and spent flakes. Therefore a logical way to reduce steam consumption is to pump less hexane; that is, reduce the solvent ratio. To the superintendent selecting a new plant, this means choosing an efficient extractor, one making the best use of the solvent supplied it. To the superintendent operating an existing plant, this means substituting, insofar as possible, thin flakes and high extraction temperatures for high solvent ratio. Ordinarily the system with the lowest solvent ratio will have the lowest steam demand.

The steam consumption in many of the older plants also can be diminished by reducing the amount of blowing or direct steam used for final stripping of both oil and meal. In most of the older plants there is no accurate measurement of these two flows and, as a result, an excess is frequently used.

Water requirement in general follows steam requirement rather closely. Many plants using a large amount of steam will also use a large amount of water, and any reduction in steam usage can be followed by a reduction in water usage, provided proper attention is given to discharge water temperatures.

5. *Operating safely.* The plant which is well maintained, which has a minimum of leaks, and in which the housekeeping is good, automatically tends to be a safe plant.

Mention has already been made of the importance of the vent system in minimizing solvent loss. Where flammable solvents are used, this same vent system is of considerable importance from the safety standpoint. If the system is designed with each vent large enough to carry all the vapors from the equipment it serves to the vent recovery system, the tendency to lose solvent inside the plant is greatly diminished. As a result, there is little possibility of building up significant concentrations of vapor in the extraction area.

Choice of proper electrical equipment and controls also can have an important bearing on safety where flammable solvents are used. Almost every major fire in the solvent extraction industry in this country has been caused first by a build-up of flammable vapors and second by an electrical spark. Spark-proof motors and controls should be used not only in the extraction area but also in any adjacent area where there is a possibility of vapors concentrating. The electrical control room should either be spark-proof or should be situated so as to prevent entry of flammable vapors. This can be accomplished either by sealing the room and drawing air from a safe point, or by locating the room at a point where contamination is not possible. With the vent system completely engineered to prevent discharge of hexane except at a preselected point and the possibility of sparks prevented wherever hexane might conceivably collect, the risk due to fire and explosion is extremely slight.

It should be made clear that explosion and fire are not the only hazards in solvent plants. Probably more injuries and lost time have resulted from the usual industrial accidents than from fires.

In the designing of these plants economic pressure is always present. There is always temptation to reduce cost by omitting such so-called niceties as access ladders, working platforms, and guards. Resisting this temptation is the particular responsibility of the superintendent. He has a responsible position, and his opinions are well respected by his management. He should insist that proper safety features are included in the design. The small added cost for such safety features will be justified many times over by prevention of down time of equipment and lost time of experienced operators.

[Received January 2, 1951]

Studies of the Spectral Characteristics of Alkali-Isomerized Autoxidized Fatty Acids[1,2,3]

ORVILLE S. PRIVETT and W. O. LUNDBERG, The Hormel Institute, University of Minnesota, Austin, Minnesota

THE presence of small amounts of nonconjugated trienoic and tetraenoic fatty acids in certain oils, detected by spectrophotometric methods but not detectable by chemical methods, has been questioned (2, 4). Hilditch and Shrivastava (2) were unable to confirm spectrophotometric analyses of linolenic acid in a number of common seed oils by a refined chemical procedure and suggested that the slight conjugated triene absorption developed during the alkali isomerization might be caused by any one of a number of extraneous factors. Swain and Brice (4) showed that small amounts of conjugated triene and tetraene formed during the alkali-isomerization of autoxidized linoleic and linolenic acids, respectively. They suggested that the conjugation produced in the products of autoxidation during the alkali-isomerization could be estimated by a spectrophotometric examination of the sample after heating in neutral ethylene glycol. However a careful examination of their results indicates that the procedure does not afford a quantitative means for estimating the spurious conjugation formed during the alkali-isomerization treatment.

TABLE I
Alkali-Isomerization—Spectrophotometric Analysis of Methyl Linoleate and Methyl Linolenate Autoxidized at 0°C.

Peroxide value	Iodine value (Wijs)	"Saturated"	"Oleic"	"Linoleic"	"Linolenic"	"Arachidonic"	Conjugated diene	Conjugated triene	Amount autoxidized[a]
Methyl Linoleate									
m.e./kg.		%	%	%	%	%	%	%	%
0	172.2	0	0	99.86	0	0	.084	.009	0
158	171.7	0	0	98.45	0	0	1.5	0	2.6
620	168.1	Trace	0	94.51	.063	.022	4.73	0	10.3
965	165.45	3.8	0	86.68	.108	.022	9.39	0	16.1
1470	161.5	6.72	0	78.21	.97	.032	14.07	0	24.5
Methyl Linolenate									
0	260.0	0	0	0	100.2	0	0.176	0	0
168	254.6	0	0	0	97.68	1.295	1.31	0	2.8
415	250.8	0	0	0	95.42	4.21	2.89	0	6.9
800	243.7	0	0	0	88.39	6.65	5.26	0	17.0
1320	241.0	0	0	0	82.84	11.89	8.40	0.165	22.0
2300	213.8	0	0	0	66.89	17.83	15.71	0.711	38.3

Percentage of conjugated tetraene 0 in all cases.
[a] Calculated from peroxide value.

In this investigation the nature and extent of the changes produced by autoxidation on the spectral characteristics following alkali-isomerization were studied with methyl linoleate and methyl linolenate. The segregation of the oxidized and unoxidized portions of autoxidized fatty acid esters by countercurrent methods of extraction was also investigated, and a simple procedure for a quantitative separation was devised. By segregation of the unoxidized fat and subsequent analysis of the fatty acids by the usual spectrophotometric method it was possible to analyze fats that have undergone some autoxidation.

Spectral Characteristics of Autoxidized Methyl Linoleate and Methyl Linolenate

Methyl linoleate and linolenate were prepared by debromination and esterification with methyl alcohol of the purified tetra- and hexabromostearic acids, respectively.

Small samples (5 grams) of the methyl linoleate and linolenate were weighed into a series of 50-ml. Erlenmeyer flasks and stored in the dark at 0°C. At appropriate intervals an Erlenmeyer of each series was removed and the sample examined for peroxide content by an iodometric method in which air was excluded at all critical phases of the determination. The percentage of conjugated constituents (1) and the iodine value (Wijs) were determined immediately, and then each sample was hydrolyzed.

For the hydrolysis the remainder of each sample was dissolved in 30 ml. of redistilled 95% alcohol and flushed thoroughly with purified nitrogen. Then 5 ml. of 50% aqueous KOH was added and the mixture boiled vigorously under reflux for 10 minutes. About 35 ml. of distilled water was added to the soap solution and the nonsaponifiable fraction extracted with three 50-ml. portions of Skellysolve F. The soaps were then acidified with 50% HCl and the resulting fatty acids extracted with purified Skellysolve F. The Skellysolve F solution of the fatty acids was washed with distilled water until free of HCl as shown by tests with methyl orange indicator. Finally, after treating the solution with anhydrous sodium sulfate to remove the last traces of water, the fatty acids were recovered by evaporating the solvent under reduced pressure.

The solutions were maintained as much as possible under a nitrogen atmosphere during the entire procedure, including the saponification, in order to avoid further autoxidation. The analysis of the fatty acids was carried out according to the method of Brice and coworkers (1) except for minor modifications in the calculation of the percentage of linoleic acid. The calculation in this case was based on a specific absorption coefficient of 86.2 found for pure linoleic acid at 232 mμ. The results of the analyses are reported in Table I.

Autoxidized methyl linoleate assayed in part as "saturated acids," as "linolenic acid," and as "arachidonic acid" depending upon the degree of autoxidation. The values for linoleic acid (unoxidized) also appeared to be invalid as indicated by the percentage autoxidized as calculated from the peroxide value. If anything, the amount of unoxidized linoleate is slightly less than indicated by the peroxide values whereas the values for "linoleic acid" given by the spectrophotometric method are greater in all cases. This is not surprising since unconjugated linoleate hydroperoxides might be expected to appear partly as "linoleic acid" in the analysis.

In the case of methyl linolenate greatest changes produced by autoxidation were in the spectral region of 310 to 322 mμ. In these experiments the fatty acids of the autoxidized linolenate assayed as high as 17.83% "arachidonic acid." The magnitude of the values for "arachidonic acid" depended upon the degree of autoxidation of the linolenate. Also, as seen in Table I, a considerable amount of conjugated diene was formed during the autoxidation of methyl linolenate. Values for conjugated diene from this source, in certain cases at least, would cause errors in the calculation of the percentage of linoleic acid should any of that acid be present.

Quantitative Extraction of the Oxidized Fraction from Autoxidized Fats and Fatty Acid Esters

It was found that the oxidized fraction of autoxidized fatty acid esters of monohydric alcohols could be quantitatively separated by countercurrent extraction using aqueous ethanol as the hypophase and Skellysolve F as the epiphase. The solvents were prepared by mixing equal quantities of absolute ethyl alcohol and Skellysolve F in a large separatory funnel and forming two phases by adding 7 ml. of distilled water for each 40 ml. of absolute alcohol. The hypophase thus formed consisted of 13% to 13.5% water.

The extraction was carried out in stages in order to follow the course of the extraction. The first stage consisted of extracting 200 ml. of the Skellysolve phase, containing the sample (approximately 10 g.), with as many 100-ml. portions of the aqueous alcoholic phase as was required to remove all of the autoxidized fraction from the Skellysolve phase. In the second stage all of the 100-ml. portions of alcoholic phase were extracted successively with a new single 200-ml. portion of the Skellysolve phase. At this point a large portion of the unoxidized ester was distributed in the Skellysolve fractions, and most of the autoxidized ester was in the alcoholic fractions, but a small amount of autoxidized ester remained in the last 200-ml. Skellysolve fraction. The second stage was therefore completed by extracting this Skellysolve phase with two additional 100-ml. portions of fresh alcoholic phase. All succeeding stages were carried out in the same manner as the second stage. Finally, when essentially no more unoxidized material could be recovered by additional stages, all the Skellysolve F fractions were combined and the unoxidized ester recovered by removal of the solvent under reduced pressure. The non-volatile oxygenated products could also be recovered quantitatively and free from unoxidized ester by combining the alcoholic fractions and removing the solvent. The results of successive stages in the extraction of the oxidation products of autoxidized methyl linoleate and methyl linolenate are shown in Table II.

TABLE II

The Countercurrent Separation of the Unoxidized Fraction of Methyl Linoleate, Methyl Linolenate Autoxidized at 0°C., and Methyl Esters of Lard Autoxidized at 35°C.

Stage	Number of plates	Amount recovered as unoxidized ester		Peroxide value	Per cent unoxidized ester calculated from peroxide value
		grams	%	m.e./kg.	
Methyl Linoleate					
Initial	0	9.4327	....	894	85.1
1	7	4.656	49.36	6	99.9
2	9	2.177	22.44	5	99.9
3	11	0.813	8.62	4	99.9
4	13	0.314	3.33	3	99.9
5	15	0.132	1.39	3	99.9
Totals	55	8.032	85.14	5	99.9
Methyl Linolenate					
Initial	0	7.5138	....	523	91.3
1	6	4.264	56.75	Trace	99.9
2	8	1.742	23.18	Trace	99.9
3	10	.598	7.95	8	99.8
4	12	.213	2.83	12	99.8
Totals	36	6.819	90.71	Trace	99.9
Methyl Esters of Autoxidized Lard					
Initial	0	10.233	....	835	86.1
1	7	5.230	51.11	6	99.9
2	9	2.019	19.73	0	99.9
3	11	0.677	6.61	5	99.9
4	13	0.238	2.32	7	99.9
5	15	0.095	0.93	8	99.9
Totals	55	8.259	80.70	6	99.9

A total of five stages and 55 plates were required for the extraction of the autoxidized linoleate fraction. The amount of unoxidized ester recovered represented 85.14% of the original autoxidized sample. This was in excellent agreement with the percentage of unoxidized ester in the original as calculated from the peroxide value (85.1), and indicated complete recovery of the unoxidized fraction. The recovered fraction was also relatively free of autoxidation products, as indicated by the low peroxide value.

In the case of autoxidized methyl linolenate four stages with a total of 36 plates were sufficient for the quantitative separation of the unoxidized and oxidized fractions. Here again the value for the percentage of unoxidized material in the original, as represented by the recovered unoxidized ester, was in good agreement with the percentage of unoxidized material as calculated from the peroxide value. Again there was only a trace of peroxidic material in the recovered ester indicating that it was relatively free of autoxidation products.

In the case of glyceridic fats, such as lard, it was necessary to perform a preliminary interesterification before extracting the autoxidized fraction. This was effected by an adaptation of the procedure used by Kurz (3) in studies on the nature of the reactions in the interesterification of fats.

About 10 grams of fat dissolved in 100 ml. each of diethyl ether and methyl alcohol was refluxed gently (47°C.) in the presence of a catalyst (3 ml. of a 3% solution of KOH in methyl alcohol) for one hour. The reaction mixture was maintained at all times under an atmosphere of purified nitrogen. Most of the solvent was removed under reduced pressure and the resulting fatty acid esters were then subjected to countercurrent distribution by the aforementioned procedure.

The stage-to-stage results of the countercurrent extraction of a sample of autoxidized lard interesterified with methyl alcohol according to the above procedure are also shown in Table II.

In spite of the disparity between the percentage recovered as unoxidized ester (80.7) and the percentage unoxidized in the original sample calculated from the peroxide value (86.1), the small amount of unoxidized lard ester recovered in the last stage (0.93%) indicated that essentially all of the recoverable unoxidized fraction had been obtained. The difference is due at least in part to the fact that the peroxide value in this case is a less reliable indication of the amount of unoxidized ester since appreciable peroxide decomposition would occur in lard autoxidized to a peroxide value of 835 m.e./kg. at 35°C. Such oxygenated nonperoxidic products are known to be almost entirely removed in the alcohol fractions with the peroxides.

Spectral Analysis of Autoxidized Fats and Fatty Acid Esters Before and After Removal of the Products of Autoxidization

In the first experiment of the succeeding series (Table III) a sample of methyl linoleate autoxidized to a peroxide value of 894 m.e./kg. at 0°C. was divided into three portions. The first was analyzed directly by the method of Brice and Swain (2). The unoxidized material was separated from the second portion, as already described, and analyzed. The third portion was interesterified by the procedure described above, then treated to remove all oxidized material, and analyzed; the purpose in this case was to determine whether the interesterification conditions had any harmful effect on the separation procedure or on the subsequent analysis.

The table reveals that the values for "saturated" and "arachidonic" acids were eliminated by first removing the oxidized materials. Even though the peroxide value was reduced by about 40% in the interesterification treatment, there was no significant

TABLE III

Spectral Analysis of Pure and Mixed Fatty Acid Esters After Various Treatments

Description of sample	I.V. of acids (Wijs)	Saturated	Oleic	Linoleic	Linolenic	Arachidonic	Conjugated diene	Conjugated triene[a]
Methyl Linoleate								
		%	%	%	%	%	%	%
Original (unoxidized)	180.52	0	0	98.72	1.079	0	0.246	0.047
Autoxidized, P.V. 894 m.e./kg	175.08	3.07	0	89.1	0.809	0.111	6.91	0.027
Recovered unoxidized fraction	180.81	0	0	99.08	0.500	0	0.191	0
Recovered unoxidized fraction after esterification	180.82	0	0	99.24	0.385	0	0.226	0.006
Methyl Linolenate								
Original (unoxidized)	272.56	0	0	0	99.78	0	0.466	0
Autoxidized, P.V. 600 m.e./kg	264.86	0	0	0	92.34	4.74	2.940	0.014
Recovered unoxidized fraction	272.08	0	0	0	99.43	0	0.490	0
Methyl Oleate								
Autoxidized, P.V. 415 m.e./kg	87.89	2.52	97.19	0	0	0	0.287	0
Mixture of Autoxidized Linoleate, Autoxidized Linolenate, and Unoxidized Oleate								
Original, P.V. 500 m.e./kg	186.92	1.32	31.84	24.45	37.42	1.63	3.29	0.0197
Recovered unoxidized fraction	188.93	Trace	31.45	26.95	40.58	0	0.287	0
Calculated values of unoxidized fraction	188.46	Trace	31.5	28.2	40.3	0	......	......

[a] Amount of conjugated tetraene was negligible in all cases.

change from the analytical values obtained without the interesterification procedure. Similar results were obtained for autoxidized methyl linolenate; erroneous values were corrected by first removing the autoxidized fraction. Autoxidized methyl oleate, on the other hand, did not form any chromophores during the alkali-isomerization treatment that would interfere with the spectrophotometric analysis of other fatty acids.

In order to test further the accuracy of the procedure for the estimation of the fatty acid composition of the unoxidized fraction of fats that have undergone some autoxidation, an experiment was conducted on a known mixture of oxidized and unoxidized fatty acid esters. The mixture consisted of 4.669 grams of unoxidized methyl oleate (approximately 99% pure), 5.2153 grams of methyl linoleate (peroxide value 894) and 7.0537 grams of methyl linolenate (peroxide value 600). The autoxidized methyl linoleate and linolenate used in these experiments were obtained from samples stored in covered Erlenmeyer flasks in the dark at 0° C. Under these conditions the peroxide value served as a good indication of the proportion autoxidized in each constituent. The results of the spectral analysis of this mixture from which the autoxidized fraction was removed were in good agreement with the calculated values whereas values on the original mixture were obviously in error (Table III).

Two samples of autoxidized lard and a sample of autoxidized methyl esters of corn oil fatty acids were also analyzed before and after removal of the autoxidized fraction (Table IV). The differences in analytical values caused by the presence of autoxidation products in the first sample of lard (P.V. 77 m.e./kg.) were only slight but nevertheless were evident in the values for linoleic, arachidonic, and linolenic acids. When the autoxidation was allowed to proceed to a much higher level (P.V. 835), all of the analytical values were different from those obtained when the oxidized materials had been removed.

The presence of autoxidized products in the mixed esters of corn oil also caused errors of considerable magnitude in the values for the individual constituent fatty acids (Table IV).

Discussion

In the analysis of fatty acid composition of autoxidized fats by spectrophotometric methods it is evident that errors are produced by the products of autoxidation of linoleates, linolenates, and presumably of arachidonates. It is also apparent that the detection of small amounts of "arachidonic acid" in many instances may be due to the production of spurious tetraene conjugation from autoxidized linolenic acid during the alkali-isomerization.

Although a spurious triene conjugation may be produced from autoxidized linoleates on alkali-isom-

TABLE IV

Spectral Analysis of Lard and a Natural Mixture of Fatty Acid Esters[a] After Various Treatments

Description of sample	I.V. of acids (Wijs)	Saturated	Oleic	Linoleic	Linolenic	Arachidonic	Conjugated diene	Conjugated triene[b]
Lard								
		%	%	%	%	%	%	%
Original	68.56	38.06	49.12	12.07	0.260	0.381	0.202	0
Autoxidized, P.V. 77 m.e./kg	66.82	39.66	47.35	12.20	0.240	0.323	0.266	0
Recovered unoxidized fraction of above sample after interesterification	66.40	39.39	48.63	11.43	0.255	0.277	0.20	0
Autoxidized, P.V. 835 m.e./kg	55.0	44.51	50.0	3.46	0.110	0	2.085	0.0068
Recovered unoxidized fraction of above sample after interesterification	52.02	46.51	49.16	4.20	0	0	0.134	0
Mixed Esters								
Original	120.77	25.35	16.0	57.86	0.583	0	0.172	0.036
Autoxidized P.V. 2020 m.e./kg	102.69	30.60	26.36	28.48	0.768	0.142	13.55	0.105
Recovered unoxidized fraction of above sample after interesterification	99.20	29.0	32.45	38.17	0.122	0	0.263	0

[a] A distilled fraction of the mixed methyl esters of corn oil.
[b] Amount of conjugated tetraene was nil in all cases.

erization, it is questionable whether the small amount of nonconjugated trienoic acid reported in tobacco seed oil and other similar oils (1) is due to simple oxygenated products of autoxidation. This is suggested in view of the fact that the nonconjugated triene is not completely eliminated by countercurrent extraction of the autoxidized fraction in the case of autoxidized corn oil esters. It is possible however, that some of this conjugated triene absorption may result from the alkali isomerization of other products of autoxidation which cannot be separated from the unoxidized fraction by the procedure outlined.

Nevertheless the major interferences in the spectrophotometric determination of fatty acids caused by the presence of the products of autoxidation can be eliminated by countercurrent extraction of the oxygenated fraction. The method of extraction is simple and applicable to glyceridic fats by performing a preliminary interesterification with methyl alcohol. Thus, by means of this method of separation, the scope of the spectrophotometric method of fatty acid analysis is extended to include fats that have undergone some autoxidation.

Summary

The nature and extent of the interferences by autoxidized fatty acids in the application of spectrophotometric methods of fatty acid analysis are described.

A simplified countercurrent extraction procedure for the quantitative removal of the oxygenated fraction of autoxidized fatty acid esters was developed. By means of a preliminary interesterification process it was found possible to apply the extraction procedure in the analysis of autoxidized glyceridic fats.

REFERENCES

1. Brice, B. A., Swain, Margaret L., Schaeffer, B. B., and Ault, W. C., Oil & Soap, *22*, 219 (1945).
2. Hilditch, T. P., and Shrivastava, R. K., The Analyst, *72*, 527 (1947).
3. Kurz, H., Fette u. Seifen, *44*, 144 (1937).
4. Swain, Margaret L., and Brice, B. A., J. Am. Oil Chem. Soc., *26*, 273 (1949).

Detergency Properties of Sodium Carboxymethyl Cellulose-Soap-Builder Systems

T. H. VAUGHN and M. G. KRAMER, Research and Development Division, Wyandotte Chemicals Corporation, Wyandotte, Mich.

AN OUTGROWTH of the general acceptance of sodium carboxymethyl cellulose for improvement of detergency properties of synthetic detergent compositions has been the investigation of its effect on the detergency properties of systems containing soap instead of synthetic detergents. To mention one such investigation, Bayley *et al.* (1) have reported on the effect of sodium carboxymethyl cellulose (CMC) on the suspending power of soap and soap-builder solutions. It is the purpose of this paper to present data on the effect of sodium carboxymethyl cellulose on both soil removal and whiteness retention properties of two soap-alkaline builder systems. This work may generally be considered a supplement to previously published work from these laboratories involving synthetic detergent-alkaline builder-CMC systems (2).

The principles, precision, and details of the detergency test methods used in this work have recently been published (3).

Materials

The analyses and other identifying characteristics of the test materials used in this work were as follows:

> Soap. A commercial grade, powdered 92% high titer (42°C.) soap.
> Carbose D[1] Lot No. C-3788-F. A technical grade of sodium carboxymethyl cellulose. This sample of carbose differs in analyses and detergency properties from the lots of carbose used in previously reported work (2). Hence the data presented, while quantitative and comparable for the systems under study, are not directly comparable with the previous data.
> Soda Ash. A commercial grade containing a minimum of 99.5% Na₂CO₃.

> *Modified Soda.*[2] A detergent grade meeting ASTM specifications with an average Na₂CO₃-NaHCO₃ ratio of 1:1.39 by weight.

Detergency in the Systems Soap-CMC-Alkaline Salts

Carbon soil removal and whiteness retention characteristics were determined on systems containing soap, CMC, and either soda ash or modified soda. Carbon soil removal and whiteness retention tests were conducted in distilled water at 140°F. and all data were calculated relative to soap as a standard having an assigned value of 100%.

The relative proportion of each component of each system was varied between the limits of 0 to 100% as the total concentration in the test solution was maintained at 0.25%. Triangular coordinate graphs of the detergency values of each three-component system were plotted, using 180 datum points of which a minimum of 36 were determined and the remainder obtained by interpolation. The interpolated values were obtained from curves drawn through points which were plotted, using as the abscissa the composition of a binary system or that of a ternary system in which the concentration of one component was kept constant, and as the ordinate the determined carbon soil removal or whiteness retention value. For ease of comparison only iso-detergency lines at various levels are presented, and discussion will be confined primarily to soap-CMC and soap-builder-CMC systems.

Although the effect of carbose has been studied over the range of 0 to 100%, economic considerations limit the use of CMC to relatively low concentrations, and it is these areas of the diagrams that are of major interest in detergent applications.

---

[1] Carbose D ®, produced by Wyandotte Chemicals Corporation, Wyandotte, Mich.

[2] Yellow Hoop, ®, produced by Wyandotte Chemicals Corporation, Wyandotte, Mich.