Modifications of the Swift Stability Test

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Experience in this Laboratory with the active oxygen method, commonly referred to as the Swift stability test, described by King, Roschen, and Irwin (1), has shown that the following changes in the apparatus and procedure are advantageous. All-glass aeration tubes were substituted for the rubber-stoppered test tubes; provision was made to prevent entrained moisture in the air-distributing system from clogging the capillary orifices; the procedure for the stability test, including the determination of the peroxide values, was modified so that only one aeration tube is required for each test instead of three.

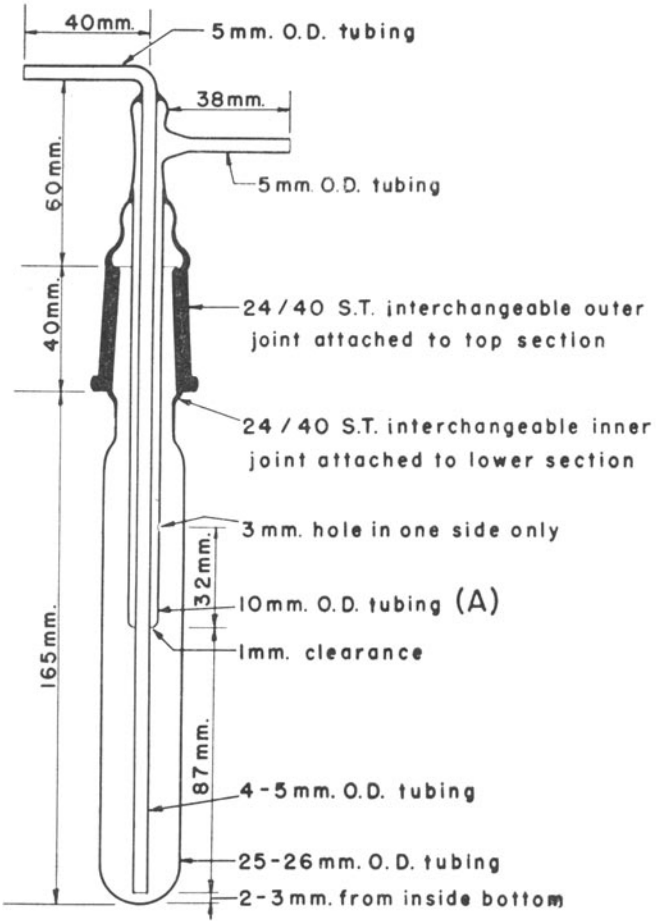

FIG. 1. Aeration tube.

A—Device to prevent foam from being carried out of tube.

Aeration tube. The aeration tube[1] illustrated and described in Figure 1 has been found to be satisfactory and serviceable. Breakage has been negligible. The tube (A) containing a 3-mm. hole in the side wall serves effectively to prevent foam from being carried through by the air stream with attendant loss of sample. This device also adds support to the long air-inlet tubing. A similar arrangement for breaking foam has previously been described (1). The all-glass aeration tubes have several advantages over the rubber-stoppered test tubes. Thorough cleaning of all parts is facilitated since the entire tube can be immersed in cleaning fluids; possible contamination of the sample by rubber particles is avoided; greater reproducibility of rate of air flow is achieved because the air-inlet tube is always immersed in the sample to the same depth.

Air-distributing system. Some irregularities in the rate of air flow to the aeration tubes in the Swift stability apparatus have been caused by entrainment of condensed moisture. At times this condensate collected at the capillary orifices and stopped the flow of air to the aeration tubes. This trouble has been effectively eliminated by insertion in the aeration train of a cold-water condenser (J) and an extra air-distributing bottle (I), shown in Figure 2. Differences in moisture content of the air passing to the samples, caused by fluctuations in the temperature of the solution in bottle (E), can be minimized by controlling the condenser fluid at a suitably low temperature. Tap water at 15° C. was found satisfactory.

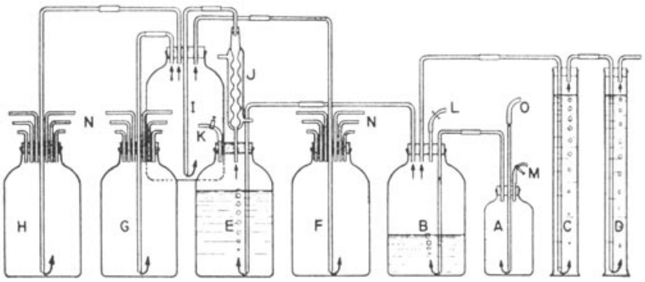

FIG. 2. Diagram of air-distributing system.

A—Device to control pressure of incoming air.
B—Bottle containing water for washing air.
C, D—Water columns. Air in space above water in B is kept under constant pressure sufficient to bypass air through C and D at a steady rate.
E—Bottle containing acid permanganate or acid dichromate solution. The air from E passes through condenser J into bottle I, thence into bottles F, G, and H, which distribute the air to the tubes N, which lead to the aeration tubes.
M—Screw clamp to regulate flow of air.
O—Connection to source of air pressure.
K, L—Pinchcocks to release pressure when shutting off apparatus.

Stability test. In the procedure described by King, Roschen, and Irwin, three tubes, each containing 20 cc. of sample, are required for one stability test. An alternate procedure, which requires only one tube for each test, permits stability tests to be carried out simultaneously on 18 samples on one standard size Swift stability apparatus. This procedure is described as follows. The aeration tubes, each containing 20 cc.

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[1] The assistance of H. J. John, chief glassblower, Eastern Regional Research Laboratory, in designing and constructing these aeration tubes is gratefully acknowledged.

of sample, are first brought to a temperature of 208° F. by immersion in hot water, and then placed in the bath at the same time and connected to the air-distributing system. The rate of air flow to each tube is adjusted to 2.33 ml. per second by means of a flowmeter, as described by King et al. (1). At regular time intervals, the samples are examined, and as soon as any "off" odors are detected, small samples,[2] preferably 0.2 gm., are removed for peroxide determinations. The tests are continued until the samples are definitely rancid, during which time peroxide values for at least three time intervals are obtained. The stability is then estimated in the usual manner from the peroxide-time curves and reported to the nearest half hour. For most lards, organoleptic rancidity can be detected at a peroxide concentration of 10 to 15 millimols per kilogram of sample.

The removal of small samples for peroxide determinations causes a slight increase in the rate of air flow. This, however, affects neither the rate of peroxide accumulation nor the resultant stability of the fat to an extent greater than the range of accuracy claimed for this type of test. The stability of a number of lards was determined by this one-tube procedure and also by the three-tube method of King, Roschen, and Irwin. These determinations were run simultaneously and in the same apparatus. The peroxide values for the one-tube procedure were determined on 0.2-gm. samples using 1 cc. of saturated potassium iodide solution exposed to air for one minute. The results are shown in Figure 3.

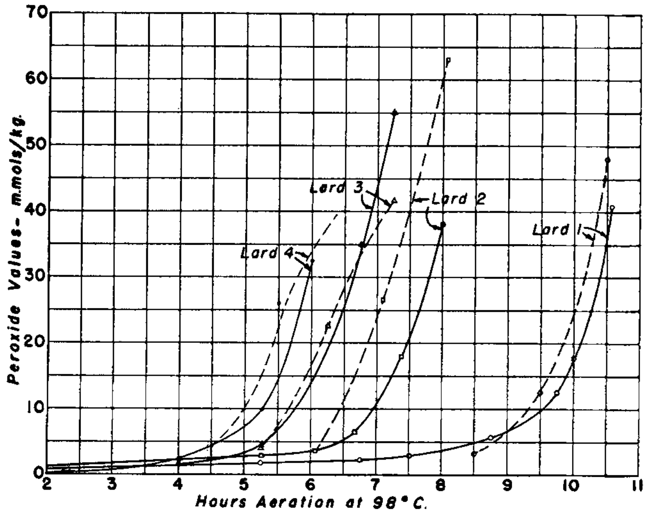

FIG. 3. Peroxide accumulation curves obtained by the one-tube and three-tube procedures in the Swift stability test.

Broken lines = 3-tube method, using 5-g. samples for peroxide values.

Solid lines = 1-tube method, using 0.2-g. samples for peroxide values.

If the commonly accepted peroxide value of 10 millimols is taken as the rancid point, the agreement in stability values obtained by the two methods is within the half-hour tolerance usually claimed for the Swift stability test. The one-tube method gave slightly higher stability values in each instance, probably owing to the fact that in this method the aeration tubes were disconnected from the air-distributing system for several minutes each time samples were removed for peroxide values.

Kilgore and Wheeler (2), using apparatus similar to that used in the Swift stability test, made a detailed investigation of the effect of varying air flow upon the stability of a number of vegetable oils. They found that the rate of air flow can be varied within wide limits, the range being 2.5 to 10 liters per hour, without impairing the accuracy of the method.

Determination of peroxide values. The method described by Wheeler (3) was found adaptable for the determination of peroxide values in small samples such as those used in the stability test described above. The following procedure gave reproducible results. An accurately weighed 0.2-gm. sample of fat is dissolved in 20 cc. of a mixture of glacial acetic acid and chloroform (3:2 by volume) and 1 cc. of a saturated solution of potassium iodide added. The mixture is agitated by giving a rotary motion to the flask. This reaction with potassium iodide should be carried out either in a dimly lighted room or in a darkened cabinet.[3] Exactly one minute after the addition of the potassium iodide, 100 cc. of freshly distilled water is added. The liberated iodine is titrated with 0.002N thiosulfate solution, about 2 cc. of 1 percent starch solution being used as indicator. If good quality reagents are used under proper conditions, the control blank on the reagents will be zero.

The effect of air in the flask during the reaction with potassium iodide (1 cc.) is shown by the results in Table 1. The peroxide values determined under nitrogen appear to reach nearly a maximum in 5 to 10 minutes reaction time. Comparable values were obtained in 1 minute reaction time for 0.2-gm. samples and in 2 minutes for 0.5-gm. samples, when the determination was carried out in air. The determinations under nitrogen were carried out in 250-cc. Erlenmeyer flasks fitted with ground-glass stoppers. Immediately after the addition of the potassium iodide solution the air in the flask was displaced by leading a stream of nitrogen into the space above the liquid for 30 seconds. The flask was then stoppered for the remainder of the reaction time. Control blanks on the reagents in all cases were zero.

TABLE 1

Effect of Reaction Time on Peroxide Value of Rancid Lard Determined in Air and in Nitrogen

Sample	Reaction Time, Min.	Weight of Sample, gms.	Peroxide Values	
			In Air m. mols	In Nitrogen m. mols
Lard A	1	0.2	27.5	25.1
Lard A	2	0.2	28.6	25.6
Lard A	5	0.2	30.5	27.0
Lard A	10	0.2	32.3	27.5
Lard A	2	0.5	27.0	......
Lard B	2	0.5	24.7	23.1
Lard B	5	0.5	26.3	24.1
Lard B	10	0.5	28.4	24.3

The method of determining peroxide values described by King, Roschen, and Irwin (1) and that described in this paper may be regarded as variations of Wheeler's method (3). Variations in amounts of sample and reagents and in time of reaction with potassium iodide produced appreciable differences in

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[2] The samples for peroxide determinations can be conveniently removed from the aeration tubes by using the air-inlet tubes (Figure 1) in much the same manner that one would use a pipette, and placed in small test tubes for weighing on an analytical balance.

[3] Blanks on the reagents gave appreciable titrations and were variable when determinations were carried out in diffuse light, especially light from a south window.

TABLE 2

Effects of Size of Sample, Amount of Reagent, and Reaction Time with Potassium Iodide in Air on the Peroxide Value of Oxidized Lard

Sample	Weight of Sample, gms.	Solvent, cc.	Saturated KI Solution, cc.	Reaction Time, Min.	Peroxide Value, m. mols
Lard C	0.2	20	0.5	1	7.4
Lard C	0.2	20	1.0	1	8.3
Lard C	0.2	10	0.5	1	7.8
Lard C	0.2	10	0.5	2	8.1
Lard C	0.5	20	1.0	2	8.2
Lard C	5.0*	50	1.0	1	6.5
Lard C	5.0**	30	0.5	2	6.2
Lard D	0.5	20	1.0	2	28.2
Lard D	1.0	20	1.0	2	26.4
Lard E	0.5	20	1.0	2	22.9
Lard E	1.0	20	1.0	2	21.2
Lard E	2.0	20	1.0	2	19.9
Lard F	0.5	20	1.0	2	29.6
Lard F	5.0**	30	0.5	2	26.2
Lard G	0.2	20	1.0	1	38.3
Lard G	5.0**	30	0.5	2	32.4
Lard H	0.5	20	1.0	2	70.1
Lard H	5.0**	30	0.5	2	63.7
Lard I	0.2	20	1.0	1	4.1
Lard I	0.5	20	1.0	2	4.0
Lard I	5.0*	50	1.0	1	3.3
Lard I	5.0**	30	0.5	2	3.3

* Wheeler's method (3).
** Wheeler's method as used by King, Roschen, and Irwin (1).

peroxide values, as shown in Table 2. These differences are shown to be of minor significance, however, when the peroxide values are plotted against time to estimate the stability, especially when the tests were carried out at elevated temperature and with aeration.

Summary

An all-glass aeration tube and improved air-distributing apparatus are described for use in the Swift stability test or similar accelerated method of determining stability of fats.

A procedure is described in which only one tube is required for each test sample. By this procedure, it is possible to carry out as many stability tests simultaneously on one standard apparatus as on three such units by the usual three-tube method.

Observations on the use of adaptations of Wheeler's method of determining peroxide values are reported. The effects of air, time of reaction, size of sample, and quantities of reagents were investigated.

LITERATURE CITED

(1) King, A. E., Roschen, H. L., and Irwin, W. H. Oil and Soap *10,* 105 (1933).
(2) Kilgore, L. B., and Wheeler, D. H. Oil and Soap *12,* 178 (1935).
(3) Wheeler, D. H. Oil and Soap *9,* 89 (1932).

The Detergent Properties of Bactericidal Fatty Acid Derivatives

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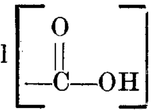
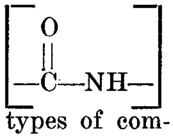
New types of quaternary ammonium derivatives have been recently introduced by Epstein and Harris (1) as bactericidal agents. From a chemical and physico-chemical standpoint, these new compounds may be characterized in the following manner: First, one relatively high molecular weight organic radical and three relatively low molecular weight organic radicals are attached to pentavalent nitrogen. Second, the organic portion of the molecule is the cation, i.e., charged positively; the inorganic portion attached to the pentavalent nitrogen is the anion, i.e., charged negatively. Third, the total mass of the lipophile groups in the cation are of such magnitude and so orientated in relation to the hydrophile groups, as to produce the proper lipophile and hydrophile balance* of the groups in the molecule, which according to Harris (2), endows the compound with interface modifying properties. Fourth, the high molecular weight radical, which is attached to the pentavalent nitrogen contain carboxyl  $\left[-\overset{\overset{\displaystyle O}{\|}}{C}-OH\right]$ and amide  $\left[-\overset{\overset{\displaystyle O}{\|}}{C}-NH-\right]$ linkages. The structures of these new types of compounds are shown in Table I.

The fatty acid esters of the pyridinium derivatives (compound No. 5, Table I), designated as E 607, were selected for our present investigation. A study was made to determine first, the effect of varying the number of carbon atoms in the fatty acid radical on the bactericidal value and detergency of the homologous compounds. Second, a study was made of the comparative detergent potency of the quaternary ammonium derivative containing carboxyl and amide groups in the molecule, and of quaternary ammonium compounds which do not contain carboxyl and amide linkages. Third, the detergent potency of the quaternary ammonium compounds was compared with that of soap and certain other alkaline detergents.

The homologous series of the E 607 compounds, N—(acyl esters of colamino formyl methyl) pyridinium chloride, was prepared from fatty acids of C_8, C_{10}, C_{12}, C_{14}, C_{16} and C_{18}, according to methods described by Katzman (3). The phenol coefficient of each of the homologous compounds was determined at 20°C. and 37°C. respectively, according to the official F.D.A. method (4), using Staphylococcus aureus and Eberthella typhosa as test organisms. The results are tabulated in Table II.

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* The nature of "balance" in interfacially active molecules and a method for measuring "balance" are described in the cited Harris patents. A further discussion of "balance" is to be found in the book and journal literature, particularly:

Clayton—"Theory of Emulsions," pg. 101—P. Blakiston's Son & Co., Philadelphia, Pa. (1935).

Hefter-Schonfeld—"Chemie und Technologie der Fette und Fettprodukte," vol. 2, pp. 755, 756—Verlag von Julius Springer, Vienna, (1937).

Snell—"Surface Active Agents"—Industrial and Engineering Chemistry, Vol. 35, No. 1, pp. 107-117 (1943)—this is a comprehensive review of the field and contains more than a dozen references to "balance."