# Susceptibility of Fats to Oxidative Rancidity†

## A Method of Measuring the Rate of Formation of Oxidative Decomposition Products in Fats and Oils

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THE intense research which is being applied to shortening material by both the producer and the user has emphasized the need of better methods for testing its various functional qualities. The susceptibility of fat to oxidative rancidity is one of the most important factors in evaluating a shortening for many uses. There is, therefore, need of a quick reliable method for determining the relative susceptibility of various fats to rancidity.

Such a method should give quickly, an accurate indication of the stability of a fat under ordinary conditions. Any method in which rancidity is developed rapidly requires the application of rigorous conditions, hence it is to be expected that any such method will not give absolute comparisons between different kinds of fats for all conditions. It is possible, however, that such a method may give reliable comparisons between samples of fat from the same general source, and some indication of the relative keeping qualities of samples from different sources if the method provides an accurate means of measuring the rancidity developed.

Several accelerated rancidity tests have been proposed. The best known of these are:

1. The oxygen absorption method.
2. The Bailey method.
3. Incubation followed by organoleptic inspection.

The oxygen[1] absorption test is especially subject to criticism in comparing fats from different sources, because the rate of oxygen absorption is not always comparable with the rate at which volatile oxidative decomposition products are formed. It is these oxidative decomposition products which render the fat unusable. For example, semi-drying oils consume large amounts of oxygen in the formation of gums, and condensation products with very little formation of the undesirable odor of rancidity.

The Bailey[2] method makes use of Schiff's reagent to measure the amount of volatile aldehydes, produced under controlled conditions. The objection to this method lies in the fact that the Schiff's reagent, in which the volatile products of rancidity are condensed, is very unstable and difficult to maintain in a colorless condition. There is some difficulty also in measuring accurately the amount of color developed.

Probably the simplest and most reliable method heretofore developed is the incubation test in which the fat is kept in an oven at an elevated temperature and inspected for odor and flavor at regular intervals. In this test rancidity usually develops at some time between two and forty days, depending upon the stability of the particular sample under test. There are, however, two objections to this method for ordinary use.

1. The time required to get results is entirely too long for many practical purposes.
2. The criterion is that of odor and taste, and therefore subject to a very decided personal element of possible error in judging the point of inception of rancidity.

The Kreis[3] test may be used as an auxiliary indication of the amount of rancidity developed at various stages of the incubation period. The Kreis test fails completely, however, when fats from different sources are compared.

The method herein described was designed to measure the relative rate of formation of volatile oxidative decomposition products of fats held under a specified set of conditions. It is

† Presented before American Oil Chemists' Society.

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[1] G. R. Greenbank and G. E. Holm, Ind. and Eng. Chem. *17*, 625 (1925).

[2] H. S. Bailey and H. C. Ebert, Cotton Oil Press I, No. 8, P 35.

[3] Robert Kerr, Ind. and Eng. Chem. *10*, 471 (1918).

*Apparatus for the*
**MEASUREMENT OF VOLATILE OXIDATION PRODUCTS OF FATS AND OILS**

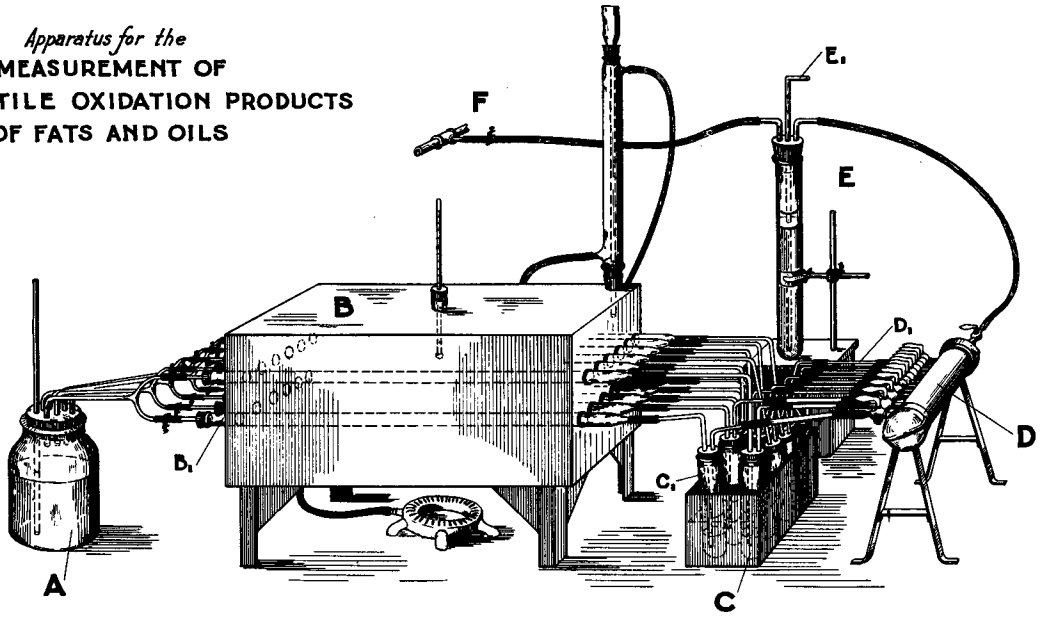


Figure 1

a modification of the methods of Bailey and of Issoglio. Since all of the volatile products probably contribute to the odor given off by a rancid fat, the measure of these products should be also a measure of the degree of spoilage of the fat in question. This measurement is performed by titrating, against acid permanganate, the products carried away in a given time interval by a constant stream of air passing over the fat. The fat being dispersed on filter paper and maintained at a specified elevated temperature. The stream of air is drawn over the fat and then through a standard solution of acid permanganate, which is maintained at a temperature of 25° C. to condense any decomposition product picked up from the fat. This solution is then titrated against oxalic acid to determine how much has been used by the decomposition products condensed in it. The titration of the distillation products of rancid fats with permanganate was formerly proposed by Issoglio[4].

## Description of Apparatus

FIGURE 1. A—Wash bottle containing acid permanganate solution through which the air is drawn before passing over the fat. This washing operation is for the purpose of removing from the air any impurities which might catalyze the oxidation of the fat. Individual tubes lead from this wash bottle to the glass tubes ($B_1$) where they are connected by tight-fitting rubber stoppers. Means must be provided in these connections for closing off any tube not in use, or which is temporarily open for the replacement of condensation tubes.

B—The tubular oven is a metal box 19½″ x 14″ x 8″ with two openings in the top and containing a number of tubular holes extending full length from end to end. These tubes are also made of metal and soldered water-tight throughout. The openings in the top are to accommodate a thermometer and reflux condenser. The oven is filled with water and kept at boiling temperature throughout the test. $B_1$ is a glass tube containing a pleated filter paper upon which the weighed fat is dispersed. This tube is 20 mm., inside diameter except for a few centimeters at one end where it has been constricted to a diameter of about 4 mm. so that it may be connected to the glass tube ($C_1$) by rubber connection. This tube ($B_1$) extends entirely through the metal tubular oven and the filter paper is so placed that it is near the center of the oven.

C—Water Bath, maintaining equalized temperature of permanganate solution in the condensation tube. A temperature of 25° to 30° C. has been found satisfactory for this bath.

[4] G. Issoglio, Ann. Chim. Applica *1916* 1-18.

$C_1$ is a large test tube (diameter 1 inch) containing 10 cc. of 0.01 N potassium permanganate solution made acid with 1 cc. of approximately 5 N sulphuric acid. Air is allowed to bubble through this solution after passing over the fat, so that any volatile material picked up from the fat is condensed in this tube.

D—A manifolding device consisting of a 2-inch iron pipe inset with a number of openings connected with petcocks. This device serves for the purpose of connecting a number of test samples with precisely the same vacuum. $D_1$ is a capillary glass tube which throttles the flow of air and thereby allows a very accurate control of the volume of air passing over any test sample. This tube is connected between the manifolding vacuum device and the condensation tube. By using capillaries of the same bore and the same length, it is a relatively simple matter to obtain the same volume of air over each of a number of samples. A capillary tube of ½ mm. bore and 10 cm. length gives satisfactory results.

E—A device for maintaining constant vacuum. The depth of the tube $E_1$ (which is open to the air) below the surface of water controls the pressure difference between the manifolding device and the atmosphere. We have regulated this depth to 29.5 c.m. which when we deduct for total of 13.5 c.m. column in wash bottle and condensation tube is just sufficient to produce 1 c.c./sec. air flow in our apparatus.

F—Vacuum line with screw clamp for regulating the flow of air so that the incoming air at $E_1$ is steady and not too vigorous.

## Procedure

THE tube $B_1$ is removed and properly cleaned with acid dichromate solution, after which it is thoroughly dried. A piece of filter paper 5 x 30 centimeters is creased three times lengthwise to form pleats of four layers. This paper is placed across a clean watch glass on a balance and two grams of the sample of fat weighed onto it. The fat should be distributed so that when melted it will be soaked up by the entire paper. The paper is then very carefully placed in the glass tube $B_1$ about 8 inches from the end, and thence into the oven, which is maintained at 100° C.

The condensing tube containing 10 cc. of 0.01 N potassium permanganate solution to which has been added 1 cc. of dilute sulfuric acid is set into the water bath (C) and connected into the system. When all connections are adjusted, the stream of air (1 cc. per second) is started through the tube by opening the screw clamp leading to the vacuum line. At the end of 20 minutes the condensing tube $C_1$ is replaced by a like one and the contents of the first titrated as follows:

11 cc. of 0.01 N oxalic acid are added and the tube heated in a boiling water bath until completely decolorized. It is then titrated, while still hot, to the appearance of a faint pink, with standard permanganate solution. These replacements and titrations are made at regular 20 minute intervals until the rate of decomposition in the fat is sufficient to use up 1 cc. of the 0.01 N permanganate solution in one 20-minute period. For samples of exceptional stability, the replacements are made hourly and the criterion taken as the time required to produce a rate of decomposition equal to 1 cc. of 0.01 N permanganate solution per hour.

The above figures were taken arbitrarily after it was found by inspecting a large number of samples that the odor of rancidity developed at about this point.

## Precautions

DUE to the extreme rapidity with which samples of fat are forced to become rancid under this test, there are some variables which need very careful control in order to assure accurate results.

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In the following tables are given some results showing titrations for duplicate tubes containing portions of the same sample of fat. The values represent the cubic centimeters of 0.01 N permanganate solution reduced between the time intervals indicated.

| Sample | 20′ | 40′ | 60′ | 80′ | 100′ | 120′ | 140′ | 160′ | 180′ | 200′ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | .0 cc | 0.1 cc | 0.3 cc | 0.3 cc | 1.2 cc | 1.6 cc | | | | | | |
| | 0.1 cc | 0.1 cc | 0.3 cc | 0.6 cc | 1.1 cc | 1.5 cc | | | | | | |
| | 1 hr. | 2 hr. | 3 hr. | 4 hr. | 5 hr. | 6 hr. | 0.5 cc | 0.6 cc | 0.8 cc | 1.4 cc | | |
| B | 0.2 cc | 0.2 cc | 0.2 cc | 0.2 cc | 0.3 cc | 0.5 cc | 0.4 cc | 0.6 cc | 0.9 cc | 1.5 cc | | |
| (oil) | 0.2 cc | 0.2 cc | 0.3 cc | 0.3 cc | 0.4 cc | 0.4 cc | 7 hr. | 8 hr. | 9 hr. | 10 hr. | 11 hr. | 12 hr. |
| C | 0.0 cc | 0.1 cc | 0.0 cc | 0.1 cc | 0.2 cc | 0.6 cc | 0.9 cc | 1.5 cc | | | | |
| | 0.2 cc | 0.1 cc | 0.1 cc | 0.1 cc | 0.2 cc | 0.4 cc | 0.9 cc | 1.6 cc | | | | |
| D | 0.2 cc | 0.1 cc | 0.1 cc | 0.0 cc | 0.3 cc | 0.4 cc | 0.5 cc | 1.2 cc | 2.0 cc | | | |
| | 0.3 cc | 0.0 cc | 0.0 cc | 0.0 cc | 0.2 cc | 0.5 cc | 0.9 cc | 1.1 cc | 1.8 cc | | | |

1. *Cleaning of reaction tubes.* The reaction tube which contains the fat dispersed on filter paper, accumulates during the course of a test, small quantities of rancid fat closely absorbed to its surface. If this trace of fat is not completely removed it accelerates the course of rancidity of the next succeeding sample to such an extent that results are not at all reliable. These tubes can be cleaned sufficiently to give reproducible results, however, by filling and allowing to stand over night with strong acid bichromate cleaning solution. The last trace of cleaning solution must be removed completely with distilled water.

2. *The filter paper* has such intimate contact with the fat over a relatively large surface that the slightest trace of impurity leads to inaccurate results. It is necessary, therefore, to crease several sheets of filter paper at one time and discard the outside ones which have come in contact with the fingers. The type of filter paper used should be the same at all times, and should be the purest grade obtainable. It is important that extreme care be used to prevent contamination in handling the paper after it is creased while weighing the sample of fat and inserting the paper in the reaction tube.

3. The rate of flow of air over the sample of fat has two opposite effects on the rate of the development of rancidity. It furnishes agitation of the air which keeps uniform concentration of oxygen at the reacting interface. This also carries away a portion of the volatile oxidation products which are known to have an accelerating effect on the course of rancidity if not removed. Both of these factors may be standardized, however, by fixing the rate of flow of air and also the contact of this flowing air with the filter paper surface. It has been found that if two of the folds in the creased filter paper become adhered at one end or the flat surface of the filter paper is pressed against the glass so that the air does not have free circulation around all sides of the filter paper, the results will not check.

4. There is a very slight reduction in pressure in the reaction tube, due to the column of permanganate solution through which the air is washed. It is essential that all of the air be washed through the same bottle, so that there will be no difference in the air furnished the various tubes. For this reason it is essential to have a pinch clamp between the permanganate wash bottle and the reaction tube, so that any tube may be shut off while it is temporarily disconnected or out of use. If it is not shut off when disconnected, the air will be drawn through this tube in the reverse direction and then through the other reaction tubes, thus contaminating them all.

5. It is necessary to regulate the flow of air through the reaction tubes for reasons previously mentioned. If the diameter of the capillary tube and the difference in pressure are known, the length of the capillary can be calculated to give any desired rate of flow. Poiseuille's formula,

$$L = \frac{n\ r^4\ t}{8\ N\ V}$$

in which L is length of capillary tube, V is the volume of air, N is the viscosity of air (.000184), R is the radius of capillary tube. T the time in seconds, and P is the pressure in millimeters of mercury. The pressure difference can be obtained by measuring the column of water in the pressure regulating device, and deducting that in the wash bottle and condensation tube. This can be regulated to any desired amount.

6. It sometimes happens that water is vaporized from the permanganate condensing tubes and recondenses in the capillary tubes, thus temporarily closing them. When this happens the air will cease to bubble through the condensation tube so that it is readily noted. In this case the capillary tube should be removed and washed out with alcohol. If it has been stopped only a few minutes, there will be no noticeable difference in the result.

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A new type of evaporator unit for refrigeration work, recently introduced, employs a recently developed, light rustless alloy of aluminum known as "aluminol." The aluminol units may be used either for direct expansion or brine circulation systems. The use of aluminol instead of the usual cast iron or steel pipe coils is said to offer several important advantages. The weight of the aluminol unit is less than one quarter that of a cast iron or steel unit of equal radiating surface; besides which, the higher heat-transfer efficiency of the new alloy permits lower cost per square foot of surface and a more compact evaporator assembly which assures more B. T. U. transfer per cubic foot of installation space than is possible with other types of radiation. Being rustless, aluminol needs no metal coating, galvanizing, etc. to protect it against moisture.