b) A band at 8.6 to 8.7 microns is observed in the spectra of the acids but not in that of the esters.

c) A band at 9.6 microns is exhibited by all ethyl esters but not by methyl esters, nor by saturated acids, thus affording an opportunity to distinguish between methyl and ethyl esters.

d) A band at 10.5-10.6 microns is seen in the spectra of the acids, but not in the spectra of the esters.

Summary

Infrared spectra from 1 to 12 microns have been obtained for 7 of the homologous series of monobasic, straight-chain, saturated fatty acids of even carbon atom content from C_6 to C_{18} and of their methyl and ethyl esters.

Infrared data are presented as plots of the percentage transmission against the wavelength in microns on a linear wavelength scale for each compound, and the exact wavelength positions of maxima of the 11 most prominent bands are tabulated.

Correlations of each of these bands with molecular structure are given.

Methods for distinguishing the acids from the esters and of differentiating an ethyl ester from a methyl ester by observation of infrared spectra are described.

An explanation, supported by earlier work with deuterium-substituted compounds, is given to account for the nonappearance, in the spectra of the fatty acids of any absorption attributable to either the free O—H group or the bonded O—H . . . O group.

Evidence has been accumulated which indicates an association of some sort of the esters and that this association probably involves the carbonyl and the methyl groups.

Data are presented to show which of the bands in the infrared spectra do and which do not follow Beer's law.

The tabulation of the absorption bands with their intensities and a correlation of each with molecular structure should be helpful to future studies of the applications of infrared spectra to fatty acid chemistry.

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Oxygen-Absorption Apparatus for Measuring Induction Periods of Fats[1]

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WORK in this laboratory on the separation of an antioxidant material from defatted rice bran has prompted the development of an apparatus for the automatic determination of the induction period of fats by the oxygen-absorption method. The usefulness of this method for indicating susceptibility of fats to oxidative rancidity has been established by previous investigators. It has been applied successfully to studies on the stabilization of fats by antioxidants (1, 2, 3). The method consists in maintaining a sample of the fat in an oxygen-filled glass chamber at a constant temperature until a predetermined amount of the gas is absorbed.

The present apparatus is distinguished by the use of a modified glass syringe, which responds to contraction in oxygen volume and opens an electrical circuit after the calculated amount of absorption. The entire apparatus is sufficiently compact that several can be operated in a single constant-temperature bath.

As illustrated in Figure 1, the unit consists primarily of the reaction flask (A) and the syringe (B) modified by replacing the tip with an inner standard-taper $^{19}/_{38}$ ground-glass joint (C). The flask is made from a 250-ml. Erlenmeyer by attaching an outer ground-glass joint with a lip (D) for holding a mercury seal (J); side arms (E) carrying 2-mm. stopcocks are attached to the flask about 1 cm. below the neck. The plunger of the syringe has an opening (F) so that plunger weights can be equalized by the addition of mercury or shot (H). The flask is made gas-tight by lubricating the stopcocks with a silicone stopcock grease and the hypodermic with a silicone oil having a viscosity of 150 centistokes. As an added precaution against leakage, a mercury seal is placed in the lip of the flask.

The electrical system comprises a lever-operated microswitch (G) and an ordinary electric clock modified so that the time of stopping during a 96-hour

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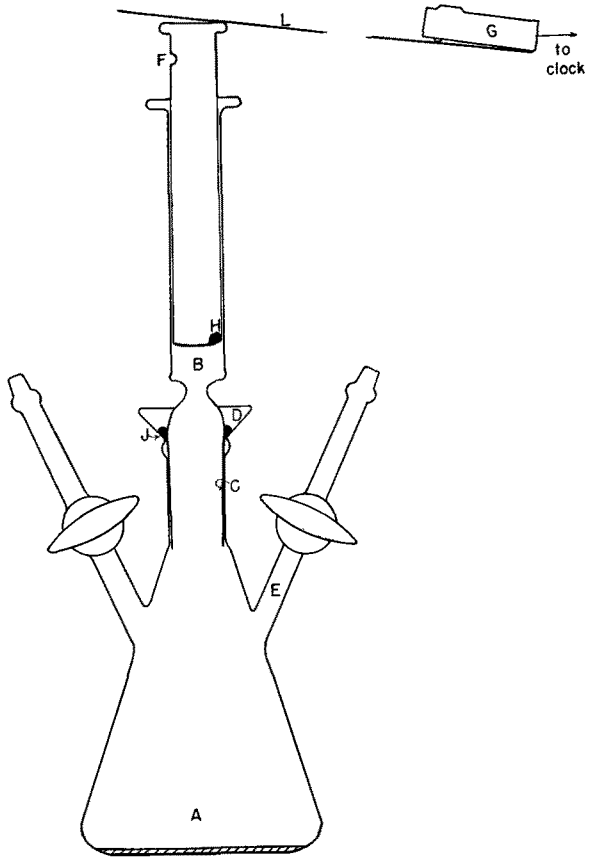

FIG. 1. Apparatus for measuring induction periods of fats.

period will be indicated. The lever (L) is of 1/64-inch sheet brass about 8 mm. wide and 16 cm. long. The plunger head of the syringe contacts this lever about 12 cm. from the microswitch. The clock is equipped with a weight (1-cm. piece of capillary tubing) attached to the shaft of the hour hand by means of a fine nylon thread. As the hour hand revolves, the weight rises, travelling a definite distance for every 12-hour period. These distances are inscribed on a brass strip mounted beneath the clock and serve as elapsed time indicators.

Procedure

Six grams of the fat or oil to be tested is placed in the flask. This amount, which previously has been found (1) to be of suitable size for the conditions used, forms a thin layer on the bottom. The flask is fitted with the syringe and, with both stopcocks open, is immersed to the neck in a water bath at 75°C. The lever arm is raised or lowered so that the top of the plunger will contact it and cause the switch to close when the base is opposite a convenient graduation mark on the barrel, for example, at 3 ml. A vigorous stream of oxygen is run into the flask through one of the sidearms for 5 minutes. Then, by manipulation of the stopcocks, pressure inside the flask is adjusted against the spring pressure until the plunger has been raised 2 ml. above the predetermined shut-off level—that is, to the 5-ml. mark in the instance cited. This operation also closes the electrical circuit and starts the timing. At the end of the induction period, when oxygen absorption becomes quite rapid, the plunger sinks past the shut-off and opens the circuit, which stops the clock. This 2-ml. contraction in volume under the spring pressure corresponds to absorption of 4 ml. of oxygen by the fat. The peroxide number as determined by the Wheeler method (4) usually is found to be between 45 and 60 for lard samples treated under these conditions. When determinations of this value are desired, the flasks should be removed from the bath immediately after the clock stops. Other peroxide ranges can easily be used by adjusting the volume of oxygen absorbed.

The above-described conditions for operating this equipment are such that an increase in barometric pressure of at least 14 mm. would have to take place before the plunger would be depressed sufficiently to open the circuit and give a false endpoint. A change of this magnitude is not ordinarily encountered during a test, but if it were suspected, it would only be necessary to reset the plunger and observe whether rapid absorption failed to occur. Moreover the sample would show an abnormally low peroxide value. In this event the test should be repeated on a fresh sample.

It is necessary to pay particular attention to cleanliness of glassware to obtain consistent results. Imperceptible traces of metals and possibly other foreign materials catalyze the absorption reaction. In general, a cleaning procedure that utilizes an organic solvent wash followed by treatment with alkali, acid, and steam will yield flasks that are suitably clean.

Typical results that are obtainable with replicate samples in the apparatus are presented in Table I.

TABLE I

Induction Periods of Lard and Protected Lards as Measured by Oxygen Absorption at 75°

Material	Induction period (hours)
Unprotected lard A[1]	23.7
	22.9
	22.9
	23.4
Commercial shortening[2]	536.0
	544.0
	541.0
Unprotected lard B	37.2
	35.4
Lard B + 0.05% butylated hydroxyanisole	416.0
	409.0
Lard B + 0.05% NDGA	642.0
	665.0
Lard B + 0.05% propyl gallate	938.0
	834.0

[1] These samples were preliminary; induction periods were recorded at 2-ml. oxygen absorption and showed peroxide numbers (millimoles/Kg. fat) of 8, 9, 9, and 9. Induction periods of all other samples are for 4-ml. absorption.

[2] Contained lard, hydrogenated vegetable oil, and propyl gallate.

One replicate sample of commercial shortening not reported showed an abnormally low value for no apparent reason. This variation occasionally does occur, and accordingly samples should always be determined in duplicate. The usual operation of the apparatus yields results which have a precision of 5%.

The apparatus described has already proved useful in obtaining the relative potency of antioxidant materials obtained from natural sources, which will be the subject of a later paper.

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