

# Oil Stability: A DSC Alternative for the Active Oxygen Method

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## Abstract

A differential scanning calorimeter was used to measure the keeping time of commercial fats. The method described is rapid and simple. The stability of oils which would require 14 days in the AOM (AOCS) procedure can be determined in less than 4 hr by the differential scanning calorimeter technique. Although a good correlation was found with keeping times determined by the AOM method, the spread in AOM hours calculated from the calorimetric data was too great to suggest replacement of the AOM method by this new one.

## Introduction

In the determination of oil stability by the AOM method (1) the peroxide value vs. time curve shows two main characteristics. They are the relatively long period in which there is only a slight increase in peroxide value and the rapid increase in peroxide value which occurs near the end point. The increased heat of reaction during this period of rapid change can be detected by the differential scanning calorimeter (DSC). The high sensitivity of the DSC makes it useful in studying heat effects with small samples.

In this study the oxidation of edible oils at constant temperature in an oxygen atmosphere was followed by the determination of peroxide value, light absorption at 233  $m\mu$  and heat effects in the DSC. It has been shown that both the peroxide value and optical density at 233  $m\mu$  begin to increase rapidly at the same time as the DSC curve shows a sharp directional change.

## Experimental Procedures

The ultra violet measurements were made on a Beckman DK 2 spectrophotometer. Peroxide values were determined on a semi-micro scale by the method described by Dahle and Holman (2). The AOM hours reported are the average of two determinations in each case done according to the official method. A Perkin-Elmer DSC-1 scanning calorimeter was used throughout this work.

The sample (10-15 mg) was weighed into an

aluminum DSC cup and placed in the cup holder at 127 C and left uncovered. The temperature 127 C was chosen arbitrarily as being low enough not to interfere with the subsequent reaction and in addition is equivalent to the 400 K calibration of the Perkin-Elmer temperature indicator. The reference side held a similar cup containing Fluorolube LG 160. At constant temperature, there is a difference of heat input to the reference and sample sides of the DSC which is determined by the different emissivities of the two compartments. The effect of different emissivities can be balanced electronically resulting in a straight zero-slope line being drawn by the recorder over a period of time at any constant temperature. When there is a sufficient heat effect due to reactions in the oil sample the pen trace changes direction. Oxygen was passed through the sample enclosure at 20 cc/min and the temperature was raised rapidly to the reaction temperature which was either 155 C or 170 C. At the same time, the recorder was started. Following the initial temperature upset, the recorder pen traced a straight zero-slope line till a detectable reaction occurred, at which time there was a change in direction of the recorder trace indicative of an exothermic reaction. The time from starting the recorder to the intersection of the two extrapolated straight line portions of the curve was designated the break time.

Reproducibility of break time was poor when the DSC was run lower than 155 C. At 155 C variation of sample break time was approximately  $\frac{1}{2}$  min in 12 min. For samples exhibiting break time of 1 hr there was still a variation of  $\frac{1}{2}$  min on duplicate sampling.

After the break time of each oil sample was determined, fresh samples were inserted in the reaction chamber and were removed at various times throughout the period up to and beyond the break time. These samples were analyzed for peroxide value and diene conjugation. The DSC break time was determined for several commercial lard, shortening and frying fats at 155 C and an attempt was made to correlate the values with AOM hours.

## Determination of Peroxide Value

Approximately 10-20 mg of oil were weighed accurately and placed in the DSC. After the ap-

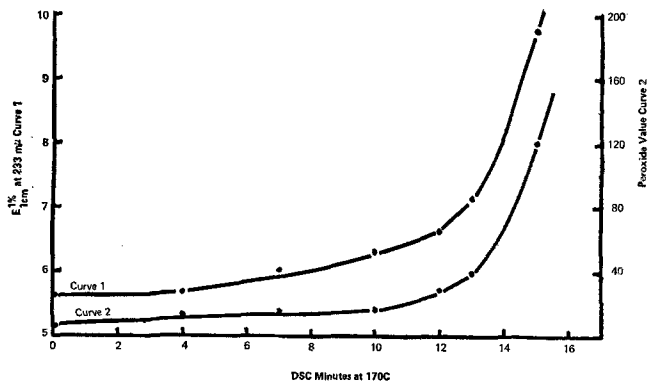


FIG. 1. Light absorption at 233  $m\mu$  and peroxide value vs. residence time in the DSC.

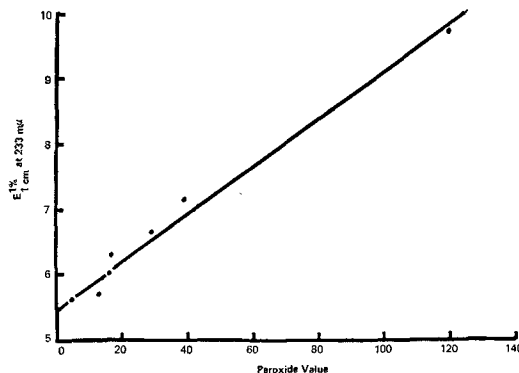


FIG. 2. Light absorption at 233  $m\mu$  vs. peroxide value.

TABLE I  
AOM and DSC Keeping Times of Commercial Fats

Sample	AOM-hours	DSC-minutes at 155 C
1 <sup>a</sup>	100	43
2 <sup>a</sup>	78	27
3 <sup>b</sup>	71½	10
4 <sup>b</sup>	88	12
5 <sup>b</sup>	46	10
6 <sup>c</sup>	119	42
7 <sup>c</sup>	158	62
8 <sup>d</sup>	171	85
9 <sup>d</sup>	132	35
10 <sup>d</sup>	141	86
11 <sup>d</sup>	131	45
12 <sup>e</sup>	208	108
13 <sup>e</sup>	206	180
14 <sup>e</sup>	248	155
15 <sup>e</sup>	168	117
16 <sup>e</sup>	198	128
17 <sup>e</sup>	327	202
18 <sup>e</sup>	355	234

<sup>a</sup> Shortening.

<sup>b</sup> Lard.

<sup>c</sup> All-vegetable shortening.

<sup>d</sup> Frying fat.

<sup>e</sup> All-vegetable frying fat.

appropriate reaction time, they were removed from the apparatus and the peroxide value was determined by the method of Dahle and Holman. The peroxide values obtained by this method tended to be about 10 units higher than those obtained by the standard AOCS procedure but this tendency was not consistent. Peroxide values were plotted against residence time of the sample in the DSC (Fig. 1, curve 1).

#### Diene Conjugation

Spectral grade isooctane was used to make the proper dilutions of 10–20 mg samples taken in the same manner as those for peroxide determination. The u.v. curve was drawn in the region of 233  $m\mu$  on a DK 2 spectrophotometer using 1 cm liquid cells. The calculated  $E_{1\text{cm}}^{1\%}$  values were plotted against DSC residence time (Fig. 1, curve 2).

### Results and Discussion

Measurements of peroxide value and diene conjugation taken at several times up to and past the DSC break time were plotted as in Figure 1. This figure shows the results obtained for a normal shortening formulation which was run at 170 C in the DSC. At this temperature the break time was found to be 11½ min. Other samples of shortenings and frying fats were examined in the same way. All showed identical behavior with break times ranging from 6 to 33 min. The two curves of Figure 1 exhibit a remarkable similarity to an AOM peroxide value curve in which there is a long period over which only a slight increase in peroxide value is observed (the induction period) followed by a rapid rise of peroxide. The time at which both the curves of Figure 1 start to rise rapidly corresponds closely to the break time in the DSC curve. A plot of  $E_{1\text{cm}}^{1\%}$  vs. peroxide value (Fig. 2) gave a linear relation. This agrees with the results reported by Dahle et al. (3) for the autoxidation of polyunsaturated esters.

From these results it appears that the DSC curve breaks when the rate of hydroperoxide formation be-

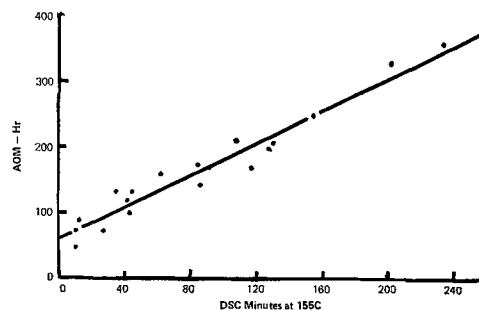


Fig. 3. AOM hours vs. DSC break time.

comes sufficiently great to be detected. In order to obtain a correlation with AOM keeping times the DSC should be run at the same temperature as the AOM method. The minimum practical temperature which could be employed for the DSC work was found to be 155 C. This might be expected to interfere with a possible correlation with AOM results since the AOM method is performed at 100 C.

The work of Knight et al. (4) as early as 1951 showed the enormous effect that temperature exerted on the course of the oxidation reactions. It is certain that there are many reactions taking place at the same time and that individual reactions are affected differently by temperature, catalyst and other factors. Nevertheless, an attempt was made to correlate DSC results with those of the official AOM method of determining oil stability. The DSC-AOM data obtained for 18 samples of lard, shortening and frying fat are given in Table I and are graphically represented in Figure 3. Sample 7 was kept at 3 C for two months and the DSC run was repeated. The break time was then 64 min compared with 62 min originally. The DSC times given in Table I are for single determinations. Application of statistical analysis to the data gave a correlation coefficient,  $r$ , of 0.974 which indicates that there is a good correlation between the AOM hours and DSC time. At a DSC time of 85 min, the upper and lower limits of the calculated AOM times are 206 and 121 hr, respectively, at the 95% confidence level. Similarly, at a DSC time of 40 min the upper and lower limits are 156 and 69 hr, and at a DSC time of 120 min they are 250 and 164 hr. Although it is unlikely, the large spread in AOM hours determined from DSC results at any particular DSC time may, in fact, be due to variability of the AOM method itself. To ascertain whether or not this is the case considerably more work must be done.

#### ACKNOWLEDGMENT

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