Thermal Analysis: An Alternative Method of Measuring Oil Stability

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ABSTRACT

Preliminary results using three different thermal analysis techniques to evaluate the relative oxidative stabilities of five vegetable oil samples yielded good correlations with the predicted stabilities by the active oxygen method. The thermal analysis techniques offer the advantages of good quality control time, being less empirical, and requiring limited equipment and operator expertise. In addition, these techniques should be useful in evaluating oil-processed finished products as well as the oils themselves.

Oxidative stability is an important quality control parameter for the manufacturers and users of many different types of commercial materials, including edible fats and oils. For this reason, a number of methods have been developed for evaluating the long range stabilities of these fatty samples, the majority of which are based on subjecting the sample to conditions that attempt to accelerate the normal oxidation process. Most commonly, elevated temperature is used.

In the fats and oils industry, the method of evaluation still most commonly used is the AOCS certified active oxygen method (AOM) (1). This particular method measures the time (in hr) required for a sample of fat or oil to attain a predetermined peroxide value under the specified conditions of the test. The length of this period of time is then assumed to be an index of the sample's resistance to rancidity. Specifically, one is talking about holding the samples isothermally at 97.8 C ± 0.2 C until a peroxide value of 100 mEq is obtained. (Other peroxide values may be considered the rancidity point depending on the sample studied or the specification established by the tester [2].) Basically, the active oxygen method works fairly well (the relative standard deviation is ca. 13%). However, it does suffer from several major disadvantages. First, the procedure involved is highly empirical, and close attention to details is required if reproducible results are expected. This makes it very hard to compare results from two different runs by two different technicians. Secondly, even though, because of the elevated temperature, the AOM is faster than quality control by normal aging methods, it still leaves a lot to be desired, since most "normal lifetime" samples would take days via AOM. Hence, other methods are currently being evaluated as possible replacements for the AOM.

One such method which has gained wide popularity recently is the ASTM oxygen bomb test (3). This procedure, which has been used successfully for years by the lubricating oils and greases industry, is based on the following:

A sample of the material to be tested is placed in a glass container which is inserted into a stainless steel bomb. The bomb is sealed and pressurized with O_2 to a specified pressure. The whole bomb is then immersed in a bath of boiling water. A pressure recorder is used to plot a continuous curve of oxygen pressure versus time. The length of time in minutes from the time the pressure reaches an initial plateau at the temperature of the bath until a sharp drop in the pressure within the vessel occurs (due to rapid oxygen uptake as oxidation occurs) is taken as a measure of the stability to oxidation of the sample. Since it was found that most fats and oils do not yield a well defined pressure drop, an arbitrary endpoint based on comparative pressure drops is generally used (2).

This method offers several advantages over the AOM. It's faster—ca. 1.5 times—for, even though it is run at essentially the same temperature as AOM, the increased pressures of the reactive gas (O_2) involved act to speed up the reaction. It's more reproducible, and it can be used to evaluate not only the fats and oils themselves but also samples which have been processed in the fats and oils, e.g., potato chips. Work has been done correlating it with tests such as the Schaal Oven Test (2). The ASTM bomb test, however, still involves considerable time.

Most researchers in fat and oil chemistry consider that fats break down in a chain type of reaction, first forming hydroperoxides, then peroxides, and finally aldehydes, ketones, and acids. Most authorities also agree that a multiplicity of these reactions are occurring simultaneously. Thus, there are a series of parameters by which the overall degradation process can be detected. These include peroxide formation, oxygen absorption, aldehyde and ketone formation (smell), wt gain associated with oxygen uptake, and finally the heat of the reaction involved. The AOM measures the beginning of the breakdown reaction (peroxide formation), while the ASTM bomb method measures the peak in oxygen uptake during the entire breakdown procedure. Since the two procedures do measure the onset of rancidity via two different stages in the overall degradation process, absolute correlation (correlation coefficient = 1.0) is extremely difficult to obtain. While this complicates absolute comparisons of the methods, it does not mean that either given procedure cannot be effectively used in evaluating relative sample stabilities. (NOTE: This argument holds when comparing any of the methods discussed.) Thermal analysis techniques gain their handhold on the overall degradation process through the latter two aforementioned parameters, namely, the wt gain associated with oxygen uptake and the heat associated with the degradation processes.

For those not familiar with thermal analysis, a slight digression is in order. Thermal analysis is a generic term for a series of techniques which in general measure some physical or chemical change in a material as a function of temperature. This change, whether it be a change in sample wt, sample length, specific heat, etc., is monitored by a transducer which converts the measured change into an electrical signal. This signal is subsequently amplified and fed into some type of output device, generally an X-Y recorder where it is plotted on the Y-axis versus temperature (or time with isothermal operation) on the X-axis. Thermal analysis techniques originated primarily as a tool for the polymer research chemist. However, in recent years, with the advent of robust, versatile, easy to operate, and relatively inexpensive commercial instruments, thermal analysis has expanded its scope to become an important quality control tool as well as a research tool, and has expanded its areas of application to include inorganics, etc. With edible fats and oils under discussion here, the two thermal analysis techniques of interest are differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC measures the heat flow into and out of a sample as a function of temperature and hence can be used
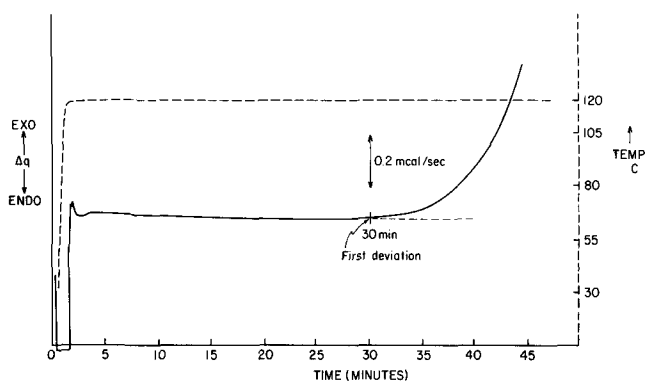
FIG. 1. Isothermal calorimetric measurement of vegetable oil stability. Sample size, 5.10 mg; atmosphere, 500 psig O_2; 120 C.

FIG. 3. Isothermal thermogravimetric measurement of vegetable oil oxidative stability. Sample size, 5.18 mg; atmosphere, O_2 at 50 cc/min; 137 C.
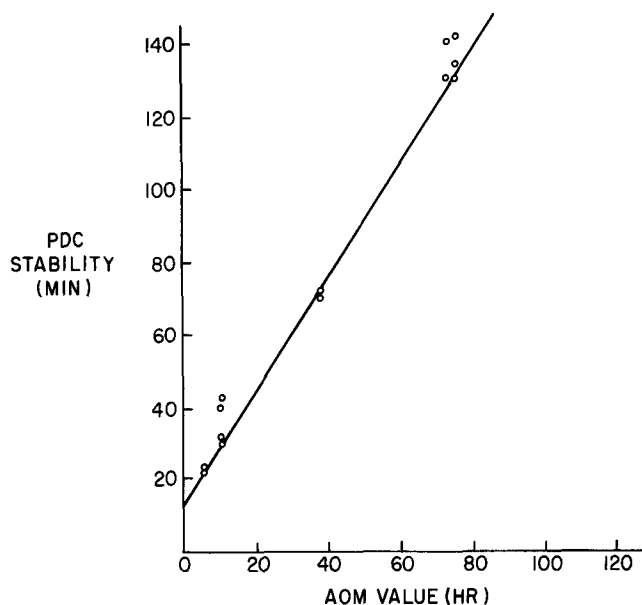

FIG. 2. Isothermal calorimetric method (120 C, 500 psig O_2) vs. active oxygen method (AOM) for five vegetable oil samples. PDC = pressure differential calorimetry.

to measure the keeping times of some commercial fats. His determinations were made at 155 C and under 20 cc/min of O_2 purge. The time to the extrapolated onset of the oxidation exotherm was taken as the measure of the stability of the sample. The results were good: samples which required 14 days via AOM, for example, were evaluated in <4 hr by DC; correlation coefficient with AOM was 0.974. Simultaneous peroxide determination on the DC run samples showed that the oxidation process had, in general, proceeded further before detection by DC than with the AOM procedure. This goes back to the absolute correlation problem mentioned earlier, and Cross concluded that the closer the DC determination temperature was to the AOM temperature, the better the correlation would be.

The use of pressure differential calorimetry (PDC) offers some help in that respect. The only available commercial pressure DSC cell (5), the Du Pont pressure DSC cell, consists of a standard DSC cell in a pressure-proof housing. This pressure DSC cell covers essentially the same temperature range as the standard cell but adds the capability of working at increased pressures up to 1000 psig. The ability to work at increased pressures gives the fats and oils user two additional advantages. First, the increased pressure helps suppress any volatilization of the sample which may occur at the temperature used. Secondly, the increased partial pressure of the reactive gas (in this case O_2) facilitates more rapid reaction. Hence, a shorter analysis time can be achieved, or a lower determination temperature can be used. This is what was done in our work using cottonseed and soybean oil samples. A typical scan is shown in Figure 1. The first deviation from the baseline was used as the measure of the onset of oxidation. Typical results are summarized in Table I and are depicted graphically in Figure 2. The correlation coefficient was again >0.95. The relative standard deviation of PDC values was ca. 10%. Notice: these quality control values were obtained in a

to obtain both temperatures of transitions or reactions and the amount of heat involved (ΔH) in these processes. Its handhold on the oxidation process would be through the exotherm associated with the degradations in the fat or oil. TGA measures the change in wt of the sample as a function of temperature, and hence its handhold on the oxidation process would be through the wt gain of the sample resulting from oxygen uptake during the decomposition.

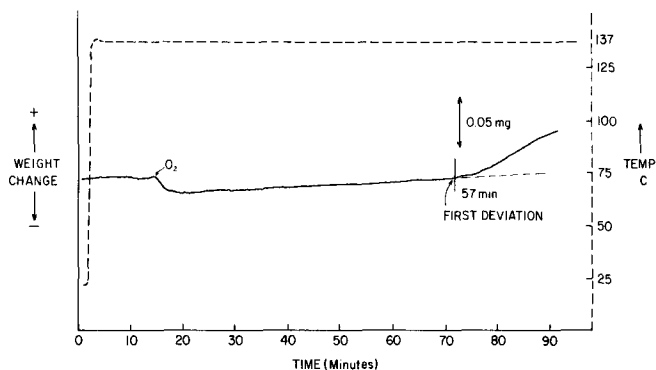C.K. Cross (4) at Canadian Packers Limited used normal differential calorimetry (DC), DSC in an isothermal mode,

TABLE I

Oxidative Stability of Vegetable Oils:
Comparison of Active Oxygen Method and Thermal Methods[a]

	AOM (hr)	PDC (min at 120 C)	TGA (min at 137 C)	TGA (dynamic C)
	5.5	22,23,23,24	14.5, 15,15,15	158,157,160
	10.5	30,30,32,40,43	17.5,18,20,21,18	161,162
	38	70,72	37,38,41,42	169,172,170
	73	130,140	64,65,70,70	176,179
	75	130,134,142	57,58,58,60,60	179,183
	>150	260	196	-
Relative SD	13%	10%	<7%	-

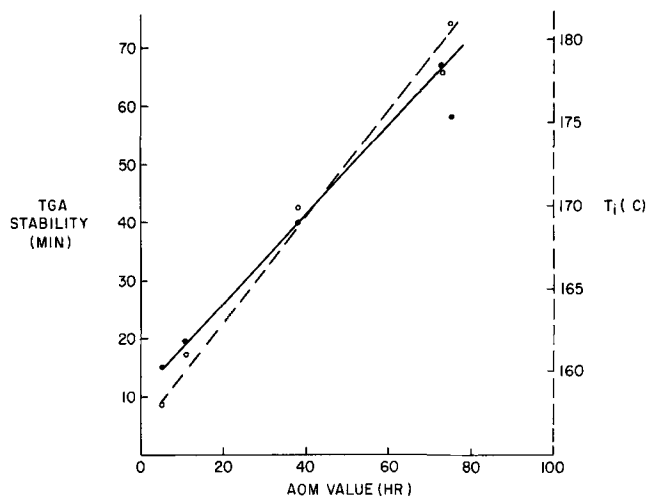[a]AOM = active oxygen method, PDC = pressure differential calorimetry, TGA = thermogravimetric analysis.

FIG. 4. Isothermal thermogravimetric method (137 C, 50 cc/min O_2) and temperature-programmed thermogravimetric method (5 C/min from 65 C, 50 cc/min O_2) vs. active oxygen method (AOM) for five vegetable oil samples.
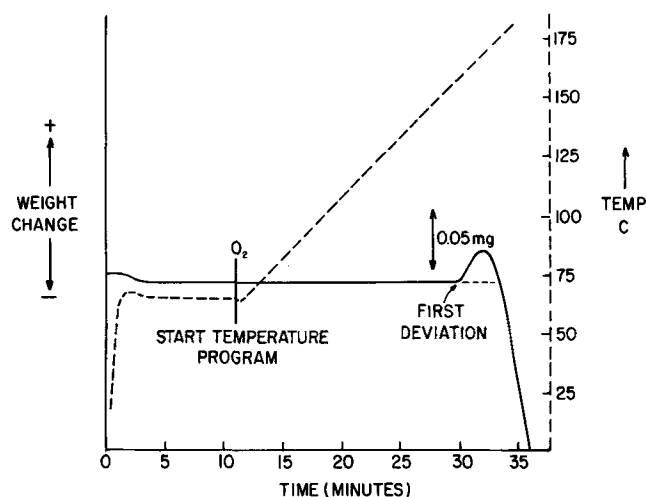

FIG. 5. Temperature-programmed thermogravimetric measurement of vegetable oil oxidative stability. Sample size, 25 mg; atmosphere, O_2 at 50 cc/min; isothermal at 65 C, program 5 C/min.

reasonable time frame at 120 C. One additional point of interest is the use of a thermocouple located close to the sample. This thermocouple, along with the second pen on the Du Pont 990 recorder, is used to monitor the sample temperature throughout the course of the experiment. Work by Knight et al. (6) has shown the enormous effect of temperature on oxidation reactions. Therefore, the ability to monitor temperature throughout the course of the experiment is important to make sure that the initial approach to the desired temperature is rapid with no overshoot and, once attained, is maintained.

One of the oldest techniques for evaluating rancidity was to heat the sample in an oven and remove it periodically to test for wt gain. This is essentially what is done in the isothermal TGA determination. However, the modern TGA system, with its microbalance in a controlled temperature environment, enables the user to monitor continuously changes in the sample wt while the sample is held isothermally in a pure oxygen environment. Moreover, any changes are permanently recorded as they occur. In the study in our laboratory, the same samples studied via PDC were run in the TGA at 137 C (higher temperature was requried than in PDC since the reactive gas was at ambient pressure; the Du Pont 951 TGA can be converted, if desired, to operate at higher pressures [7]), and the time to the start of wt gain was used as a measure of stability (Fig. 3). Typical results are shown in Table I and are depicted graphically in Figure 4. The relative standard deviation was <10%. TGA values obtained for the 75 hr AOM sample were reproducible; the reason for their deviation from an otherwise linear correlation is not known. Again, location of a thermocouple close to the sample—facilitated by the patented horizontal design of the Du Pont 951 TGA balance—assured the good temperature control so vital for an accurate determination.

Nieschlag and his coworkers (8) studied crambe oil samples using a dynamic rather than an isothermal TGA procedure. Three different parameters associated with the resultant wt gain scan were tried for evaluating the stability of the material. They were T_i (initiation temperature of wt gain), T_t (temperature of maximum wt gain), and ΔW (the total wt gained). It was their conclusion that T_i provided the best means of differentiation. The same type of study was done in our laboratory with the previously used vegetable oil samples. A typical scan is shown in Figure 5. Typical results are shown in Table I, and the correlation obtained with the AOM values is depicted in Figure 4. Here, particularly, the two-pen recorder—sample thermocouple capability of the Du Pont 990—951 TGA system is vital, because it is sample temperature at the wt gain onset (T_i)—not time—which is the measured parameter. These initial results would seem to indicate that this dynamic procedure could be used in evaluating these vegetable oil samples. However, not enough repetitive scans were done to determine the deviation associated with the procedure. (Nieschlag found ca. ±2 C.) The dynamic procedure has the obvious advantage of speed over the isothermal techniques. However, as a word of caution, in the samples studied here, which spanned an AOM range of 5-75 hr, there was only a 20 C temperature span for T_i. Therefore, care must be taken to ensure good accuracy.

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