Comparisons: measuring oxidative stability

The edible oil industry has long sought a rapid analytical test to quantitatively predict the susceptibility of an oil to autooxidative breakdown. Historically, the Active Oxygen Method (AOM, AOCS method Cd 12-57), also known as the Swift Test, is the most widely used test for obtaining oxidation stability data. First introduced to the fat industry in 1933 (1), the method was defined by exact operating conditions: purified air is bubbled through a fat sample held in a heated oil bath at 97.8°C and, at certain time intervals, aliquots are sampled for the determination of peroxide values (PV). The PVs are plotted against time, and time required to reach a PV of 100 is reported as the AOM time. However, this method suffers many drawbacks in terms of operation and application. Modified versions of the AOM, which do not adhere to the exact conditions of the original method, creating wide variability in reported “AOM” times, were developed. As a result, alternative methods have been devised to replace the AOM as an accelerated method for studying oil oxidation stability.

Some alternative methods are straightforward, such as the Schaal or oven test method where about 100 g of oil sample is kept at 65°C in a drying cabinet and examined periodically.

(2). Analysis includes both PV and sensory determination, with the first signs of rancidity and PV change deemed the induction period. Most newer methods designed to measure an oil’s resistance to oxidation are rather sophisticated and require complex instrumentation. Included in this group are methods based on oxygen adsorption and the formation of volatile oxidation products.

Three methods based on oxygen consumption are commonly employed: gravimetric (3), oil headspace oxygen concentration measurement (4) and pressure change in the contained oil headspace (5). The third method is based on the theory of the Oxygen bomb (Sylvester test, FIRA-Astell Apparatus, ASTM Bomb). A new instrument based on this theory, the Oxidograp, was recently displayed at the 1993 AOCS Annual Meeting and Exposition; it consists of a thermostat, a heated aluminum block containing holes for reaction flasks, a magnetic stirrer and a transducer, which converts pressure changes in the oil’s headspace to electronic output (6).

Gas chromatographic (GC) methods for oxidative stability determination can be rather complex, with instrumentation typically including a headspace sampler interfaced with a gas chromatograph and a mass spectrometer. The oxidation stability measurements are made by oxidizing the oil by some means (usually at an elevated temperature) and by following the development of oxidation volatile over time. While the above-mentioned methods for determining oxidation stability have specific and general applications of their own, the purpose of this article is to discuss yet another method for indexing the oxidation stability of fats and oils, the conductimetric method.

Development, operation
Some years ago, Brinkman Instruments introduced the Rancimat, while more recently Omnion began marketing the Oil Stability Instrument (OSI). Both instruments are based on the conductimetric method Hadorn and Zürcher (7) developed for fat and oil analysis. This method also has been referred to as the Modified Swift Test. Hadorn and Zürcher (7) arrived at the conductimetric method by studying different ways of measuring the stability of fats and oils. The induction period of oils at 110°C was measured three ways: development of PV over time, generation of organic acids (secondary oxidation products) as measured by conductimetry and formation of conjugated dienes as measured by ultraviolet spectrophotometry. All three curves were nearly parallel and resulted in the same induction time. The simplest of these three methods was found to be conductivity measurement, thus the development of the conductimetric method. Oxidation stability of various oils has been studied using the conductimetric method (8–11), with excellent

**Figure 1. Diagram of conductimetric method**

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correlations (0.90–0.999) reported between the Rancimat and AOM, and the OSI and AOM at various temperatures. The increased use of these instruments as an AOM alternative necessitated the AOCS to initiate a collaborative study to investigate the conductimetric method as an official alternative to the AOM. The OSI method is scheduled to become the official method in 1996.

During 1991, an AOCS collaborative study was conducted to establish relative error statistics, confidence limits and effective sample stability ranges for the different types of conductimetric method analysis instruments available: ten Brinkman Rancimats (nine automatic, one manual), four OSI units and one home-built unit. The study was restricted to vegetable-type oils. Two temperatures were studied: 110 and 130°C. The overall coefficient of variation in the study was 11.3%, with 110°C recommended as their operation temperature of choice. As a result of this study, the AOCS has adopted the conductimetric method as an official alternative method to the AOM.

The OSI and Rancimat are automated instruments based on the same conductimetric measurement method (Figure 1). A stream of purified air is

![Image of curves generated via conductimetric method (Rancimat or OSI); curves represent oils of differing oxidative stability. Tick marks indicate induction periods (automatically determined).](image)

**Figure 2.** Representation of curves generated via conductimetric method (Rancimat or OSI); curves represent oils of differing oxidative stability. Tick marks indicate induction periods (automatically determined).
passed through a sample of oil held in a thermostatted block. Holes in the block allow sample tubes to fit snugly. The air distribution system does not preheat the air prior to being bubbled through the oil. The incoming dry air can be regulated to vary the flow rate through the oil or fat sample. After bubbling through the oil, the effluent air is directed via tubing into a tube containing deionized water (DI). The effluent air contains volatile organic acids from oil oxidation, which increases the conductivity of the water (8). The conductivity of the water is monitored with a conductivity probe, and measurements are collected and stored continuously by data acquisition software. The length of time before the production of organic acids is assumed to be a measure of the induction period. The software that analyzes the data and chooses the induction period time is a design feature that differentiates the OSI and Rancimat. Typical output of the two instruments is shown in Figure 2.

Applications

The Rancimat and OSI can be used in applications where the AOM traditionally has been used: for determining trade standard of finished oil or in the quality control laboratory at production point. Use of the conductimetric method as an indicator of oil quality oxidative stability has been described (12–14). When incorporated into an analytical testing scheme, the method can automatically deliver rapid oxidation stability data. Analyst time does not need to be spent periodically sampling and performing PV determinations. The reduced number of PVs that need to be determined allows an analytical lab to lower solvent waste amounts, currently a concern to all who use chemicals. Finally, the use of the AOM alternatives gives the QC lab a more precise and reproducible method to use (14).

Recently, due to consumer demand for more “natural” products, the food industry has shifted away from using chemically derived antioxidants and oxidation quenching systems to ones obtained naturally. Extracts from rosemary, oregano and sage leaves, among other spices, are being investigated for their use as a potential antioxidant in foods. Use of the conductimetric method to determine the effectiveness of an antioxidant in an oil system has been widely applied (15–18). However, questions arise as to the accuracy of the conductimetric method when used with volatile antioxidants. Investigations have indicated that volatile antioxidants are ineffective at typical OSI and Rancimat operating temperatures (6,19,20). For this reason, instrumenta-
The OSI has also been used to study the oxidation stability of potato chips (28). Commercially obtained potato chips were evaluated at three temperatures, both the intact food and the extracted lipid. Potato chip analysis by the OSI was accomplished as outlined above with the Rancimat. The OSI induction times of extracted lipids and intact chip are presented in Table 1. As expected, these values decrease as the block temperature increases.

Results obtained by OSI analysis of the pulverized potato chips differed from those reported by Barrera-Arellano and Esteves (27) with potato chips analyzed by the Rancimat. Operating under normal conditions, the potato chip analysis produced a rapid increase in conductivity (Figure 3) upon the start of an OSI run. In a relatively short time, compared with the entire run, the conductivity reading reached a value that automatically shut down the OSI channel collecting data from the potato chip.

Figure 3. Conductivity graph obtained from a pulverized potato chip run on an OSI at 100°C, without purging. Instrument automatically shuts off once a high conductivity value is reached.

Table 1
OSI induction times of extracted lipid from potato chips and intact potato chips

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt (g)</th>
<th>85°C</th>
<th>100°C</th>
<th>115°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potato chip lipid⁶</td>
<td>6.6</td>
<td>47.4</td>
<td>16.8</td>
<td>5.6</td>
</tr>
<tr>
<td>Potato chip²</td>
<td>20.0</td>
<td>60.9</td>
<td>21.6</td>
<td>7.9</td>
</tr>
</tbody>
</table>

⁶ Means of three replications

⁷ Oil amounts listed are the amount in 20 g snack food.

⁸ 3-h hold time on 100°C samples; 1-h hold time on 115°C samples

Lipid oxidation is rather difficult to measure in complex food systems, but researchers have utilized a variety of techniques to accomplish this task. The most popular snack food analyzed has been the potato chip. Some of the common methods used for the analysis of snack food oxidation stability include: (a) measurement of the rate of oxygen uptake, (b) measurement of hexanal, pentanal and pentane, (c) peroxide value and (d) sensory evaluation (22–26). In general, conclusions indicated GC methods were good predictors of sensory evaluation.

Barrera-Arellano and Esteves (27) used potato chips as a lipid food analyzed with a Rancimat. These investigators fried potato chips, and then performed elevated temperature storage stability tests by both the Rancimat method and sensory analysis. Sensory analysis involved rancid odor intensity.
INSTRUMENTATION

The stability of the lipid in intact food. The length of time needed to determine the induction time at 85°C may limit its usefulness where analysis time is critical. The OSI curves generated at 115°C generally do not permit the data acquisition software to determine the induction time, which must be calculated manually (Figure 4). Additionally, a “purging” step may be necessary for other lipid foods analyzed by the OSI to allow for initial data acquisition.

Limitations
Recently, Frankel (19) provided an excellent review of methods to evaluate natural antioxidants and oxidative stability in food lipids. Frankel, among others (29), indicates high-temperature tests (AOM, conduc-tometric method, oxygen bomb and oxygen uptake) are unreliable due to a significant change in the mechanism of lipid oxidation at the elevated temperatures necessary in the mentioned tests. Frankel also discusses the relationship that these elevated temperature tests have with sensory analysis. Oxidation stability indexes based on oils oxidized at 100°C and above may be questionable because the PVs of such oils typically are in

Figure 4. Tangential method for determining the OSI induction time of pulverized potato chips analyzed at 115°C

chips. Apparently, these samples contained volatile compounds that caused a rapid increase in conductivity. By allowing these samples to purge for a certain measured time (1 h for 115°C and 3 h for 100°C), the volatile compounds could be removed, and an OSI curve could be attained by normal operation. Purging of the potato chip sample was accomplished by disconnecting the tubing that carries the oxidation volatile effluent to the DI conductivity tube.

The OSI software normally extrapolates the time that is considered the induction time for lipid oxidation. However, if at the start of a run the conductivity increases rapidly enough, a time will be chosen. Figure 4 contains the curve generated from potato chips at 115°C, and purged for 1 hr prior to data collection. To obtain the OSI, tangents were drawn on the curves surrounding the inflection point.

The results obtained for potato chips and the corresponding extracted lipid indicate that the OSI and Rancimat may be used to accurately predict the stability of the lipid in intact food.
excess of 50. It has been reported that soybean oil flavor may be unacceptable at a PV lower than 10 (30).

More experimentation is needed to determine the relationship between sensory evaluation and the oxidation stability indexes determined by the conductimetric method. Studies that correlate sensory analysis with various elevated oxidative stability measurements are essential to determine the true utility of accelerated stability methods.

References