Oil Stability Index Correlated with Sensory Determination of Oxidative Stability in Light-Exposed Soybean Oil

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ABSTRACT: Validity of the oil stability index (OSI) as an accelerated test of oxidative stability has been questioned because of its high holding temperature, 110°C, which may cause reactions that would not occur at lower temperatures. The purpose of this study was to characterize the usefulness of OSI as an accelerated oxidative stability test for oil of varying metal catalyst content by correlating OSI with the sensory induction period of light-exposed soybean oil. Five 400-g aliquots of soybean oil were placed in Erlenmeyer flasks and treated with increasing levels of a metal pro-oxidant, Cu^{2+} 2-ethylhexanoate. Pro-oxidant concentration ranged from 0 to 3.13×10^{-5} M. Five-gram aliquots were taken from duplicate flasks and immediately tested using the Oxidative Stability Instrument. Heating block temperature was 110°C. Sample flasks were then exposed to 800 footcandles of light and held at ambient temperature for 3 wk. One-gram aliquots were regularly withdrawn and evaluated for rancidity by 10 trained panelists to determine the sensory induction period of each sample. Aliquots were also taken to determine OSI of light-exposed oil samples. Sensory induction periods were correlated with OSI, resulting in a squared partial correlation coefficient (r^2) of 0.920. The r^2 for OSI of light-exposed oil samples ranged from 0.897 to 0.979. OSI appears to be an acceptable accelerated method for measuring the oxidative stability of light-exposed soybean oil that varies in metal catalyst content.

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KEY WORDS: Accelerated methods, lipid oxidation, oil stability index, peroxide value, rancidity, Rancimat, sensory evaluation.

Unsaturated fatty acids, which are extremely susceptible to autoxidation, are prevalent in commercial food oils, affecting the quality and shelf life of such oils (1). Oxidation is initiated by homolytic breakage of a hydrogen bonded to carbon α to the double bond, resulting in lipid free radicals. The radicals react with atmospheric oxygen to form peroxides as the primary product of lipid oxidation. The organic peroxides then decompose to secondary products, including alcohols, carboxylic acids, aldehydes, and ketones. Both initiation and propagation reactions are catalyzed by singlet oxygen; exposure to light; the presence of pigments, such as chlorophyll and riboflavin; and heavy metals, such as copper, iron, and nickel (2).

Various tests, such as peroxide value (PV), thiobarbituric acid test and gas chromatographic analysis of volatile compounds, have been developed to determine the present status of oil oxidation (the actual amount of decomposition products at any given time). PV ranges for oxidized oil have been reported to be 3–5 for low oxidation, 10–12 for moderate oxidation, and 16–18 for high oxidation (3). Although these tests are accepted methods for determining the present status of an oil, they provide no information on its ability to resist oxidation, i.e., oxidative stability. Since lipid oxidation results in off-flavors and odors, indicating a poor-quality product, there is often a need to determine not only the present status of an oil but also its oxidative stability.

Resistance of oils and fats to oxidation depends on such factors as the degree of unsaturation, the presence of antioxidants or pro-oxidants, and prior abuse. The time before there is a dramatic increase in the rate of lipid oxidation is a measure of oxidative stability and is referred to as the induction period. Several tests have been designed to determine the induction period of oils under accelerated conditions. These tests attempt to determine the oil's response to oxidative catalysts, antioxidants, or what would happen under typical conditions, in less time than is required for room temperature shelf life studies. One method commonly used in the past is the Active Oxygen Method (AOM) (4); however, the AOM is labor intensive and time consuming. Another disadvantage of the method is that measurements have to be taken at intervals, resulting in an imprecise induction period determination (5–6).

An automated replacement for the AOM is the oil stability index (OSI), American Oil Chemists' Society (AOCS) Method Cd 12b-92 (4). In contrast to the AOM, which measures the PV of the oil, the OSI traps the volatiles from the oil sample, and a probe placed in the water trap continuously measures conductivity due to the increase in organic acids as autoxidation proceeds. The OSI measures the induction period by plotting conductivity against time and calculating the maximum of the second derivative.

Two commercial instruments that measure OSI are the Rancimat® (Metrohm, Herisau, Switzerland) and the Oxidative Stability Instrument® (Omnion, ADM, Rockville, MD).

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These instruments are similar except for the number of samples that can be simultaneously analyzed and the temperature range available.

Many experiments have been conducted using the Rancimat and the Oxidative Stability Instrument to determine the oxidative stability of oil (1,5,7–9) and foods containing oil (10,11). However, OSI usefulness has been questioned because of its high holding temperatures (110 or 130°C), which may cause reactions and create compounds that would not normally occur at lower temperatures (12). Gordon and Mursi (9) compared the stability of oil, as determined by Rancimat and storage at 20°C, with subsequent PV determinations of induction period. They found the correlation to be high (r = 0.966). Reviews on the topic (11,13) have stated the need for studies correlating sensory analysis with oxidative stability measurements to determine the usefulness of accelerated testing methods. Indeed, the onset of rancidity, as determined by human sensory analysis, is the ultimate test for calculating induction period. Thus, "sensory induction period" can be defined as the time required for a fat or oil to become slightly rancid as determined by a sensory panel.

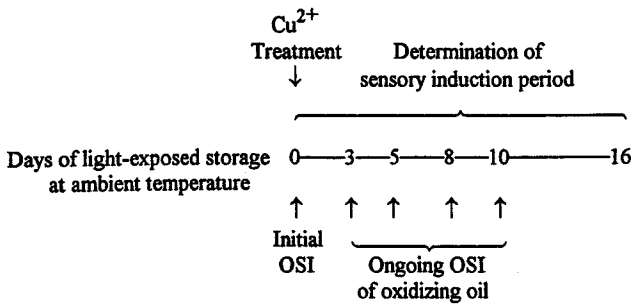
Commercial vegetable oil can contain trace amounts of contaminants, such as metals, which catalyze oxidation. Storage conditions might include light exposure, which also hastens oxidation. Light-catalyzed oil oxidation is a common problem for foodstuffs, particularly after oil-containing products are sold and stored by the consumer. Thus, there is a need to study the effects of these catalysts on the oxidative stability of oils. The purpose of this study was to characterize the usefulness of OSI as an accelerated oxidative stability test for soybean oil of varying metal catalyst content by correlating OSI with the induction period as determined by sensory analysis of light-exposed soybean oil.

EXPERIMENTAL PROCEDURES

The experimental design is shown in Scheme 1. Soybean oil was purchased from a local grocery store. Samples of soybean oil (PV ~0.5) were treated with metal pro-oxidant to obtain varying degrees of oxidation. Aliquots were immediately removed from treated samples for evaluation of oxidative stability using OSI. All samples were then exposed to light during ambient temperature storage. During storage, aliquots were periodically withdrawn for descriptive analyses, PV determinations, and additional OSI analyses. These additional OSI analyses were performed to determine the usefulness of OSI in evaluating oil that was at various stages of oxidation.

Metal pro-oxidant and sample preparation. A 2.6×10^{-4} M stock solution of metal pro-oxidant was prepared by first dissolving 0.0100 g Cu^{2+} 2-ethylhexanoate (Aldrich Chemical Co., Milwaukee, WI) in 0.50 g ethanol; 100 g of soybean oil was then added to the dissolved pro-oxidant and thoroughly mixed.

The following amounts of stock solution were placed in 500-mL Erlenmeyer flasks: 8.74, 17.49, 26.23, and 52.46 mL. Oil was added to bring the samples to 400 g. A control was provided by measuring 400 g of untreated oil into a flask. By



SCHEME 1

calculation, final concentrations of Cu^{2+} 2-ethylhexanoate were: 0, 5.22×10^{-6}, 1.04×10^{-5}, 1.57×10^{-5}, and 3.13×10^{-5} M. All five samples were thoroughly stirred. The experiment was replicated, i.e., 10 flasks were prepared, two at each concentration of pro-oxidant. Separate stock solutions and dilutions were prepared for each replicate.

Light-exposed, ambient storage. Sample flasks were left uncovered to allow oxygen absorption and placed on a clear plastic platform within an enclosed shaker (Blue M, Blue Island, IL). A separate shaker was used for each replicate. Two 13 in., 8-W fluorescent lights were placed along the bottom of each shaker 3 cm below the clear platform, and the sample flasks were placed directly over the light source. The bottoms of the 500-mL Erlenmeyer flasks were consequently exposed to 800 footcandles of light and were shaken continuously at 90 rpm.

Sensory and PV measurements of light-exposed samples. Ten panelists were selected from a larger panelist pool based on their ability to distinguish fresh oil from oil samples varying in degree of rancidity. After training, the panelists evaluated each sample and replicate every weekday. One-gram aliquots were removed from each flask and placed in a test tube (13×100 mm). Aliquots were labeled with three digit code numbers, covered with foil, and placed in an aluminum heating block (VWR Scientific, Boston, MA) held at 50°C. Panelists were asked to smell each aliquot and rate the degree of rancidity by marking a 150-mm line (Fig 1). Three reference samples were provided as anchors on the line and were labeled as being not rancid (PV = 0.5, 0 mm), slightly rancid (PV = 3.0, 60 mm), and extremely rancid (PV = 50.0, 134 mm). These reference samples were prepared at the beginning of the study and stored under refrigeration. One-gram aliquots were removed from the refrigerated reference solutions and placed in test tubes for evaluation during each testing session. Each day panelists were asked to smell the reference aliquots before evaluating the 10 oil sample aliquots to remain familiar with the differences between fresh and rancid oil.

Panelist scores for each sample were averaged each day and plotted against time. Regression analysis was performed and provided a best fit line for each sample over time. The point (time in days) where the line crossed the "slightly rancid" anchor of 60 mm was defined as the sensory induction period. Regression analysis of sensory induction periods and OSI was performed to determine the relationship between the two tests.

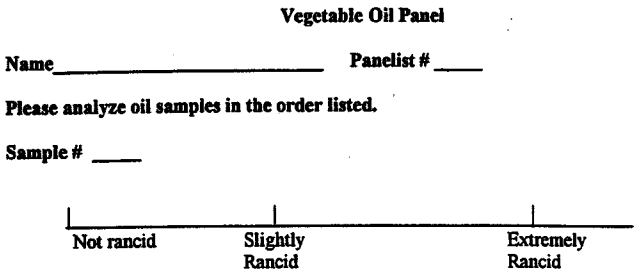


FIG. 1. Abbreviated panelist sample score sheet.

Duplicate aliquots of each replicate were removed from storage every other day for PV determination (meq peroxide/kg oil) using AOCS method Cd 8b-90 (4). PV were recorded as an objective measure of oxidation during light-exposed storage to verify that samples were oxidizing in a manner consistent with the copper treatment, not for the purpose of subsequent correlation with OSI.

OSI. The OSI was determined as outlined in AOCS method Cd 12b-92 (4). Duplicate 5-g aliquots were removed from each flask (initially before light-exposed storage and then periodically throughout light-exposed storage) and analyzed using the Oxidative Stability Instrument. Instrument parameters were 110°C and an air flow of 6 psi.

RESULTS AND DISCUSSION

Sensory scores for each sample are plotted against time in Figure 2. Induction periods for all samples could be deter-

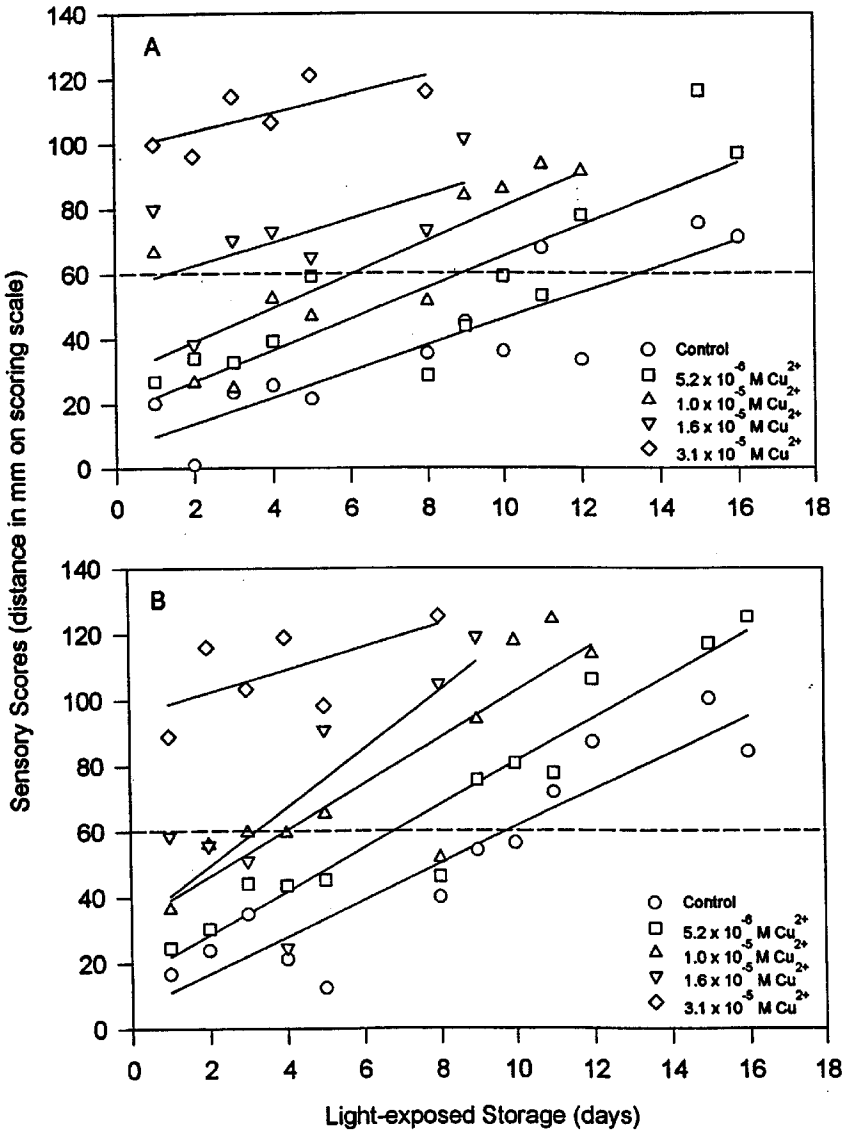


FIG. 2. Sensory scores for soybean oil samples during light-exposed storage for replicates A and B. Sensory induction period was the time at which the linear regression line crossed 60 mm. (Each data point is the average of all panelists' scores for that replicate.)

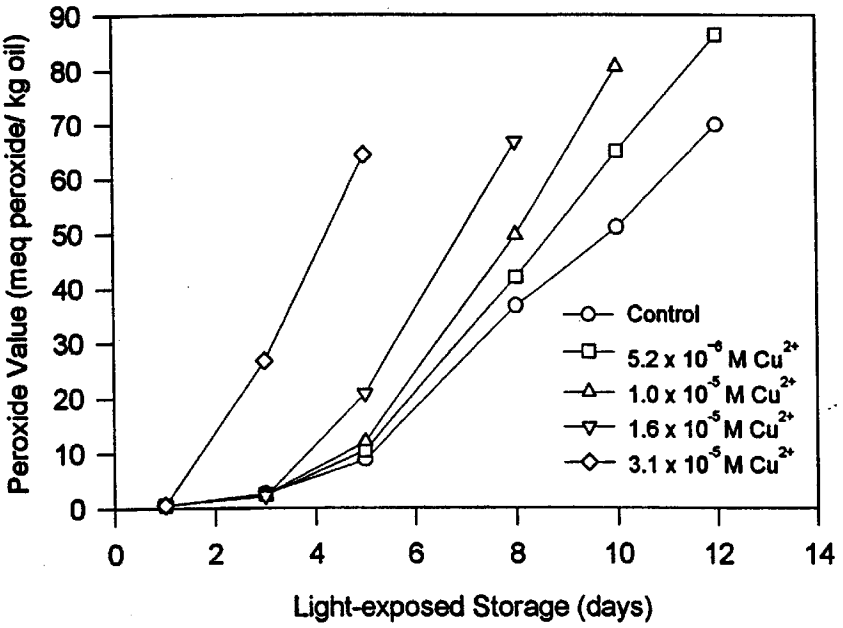


FIG. 3. Peroxide values of soybean oil samples during light-exposed storage. (Data shown is from one replicate of sample flasks. Each data point is the average of duplicate determinations.)

mined except for the sample containing the highest level of pro-oxidant. This sample immediately received high sensory scores, thus exceeding the "slightly rancid" anchor. Therefore, this sample was not used in subsequent correlations.

PV for light-exposed samples are plotted in Figure 3. Initially all samples had PV of approximately 0.5 meq peroxide/kg oil. As expected, the PV of the sample with highest level of pro-oxidant quickly increased to 26 meq peroxide/kg oil by the third day of the study, and the PV of all other samples increased consistent with the amount of copper treatment.

Correlation of initial OSI with sensory induction period. Sensory-determined induction periods are correlated with initial OSI values of unoxidized oil in Figure 4. This correlation had a squared partial correlation coefficient (r^2) of 0.920. Sensory score variability negatively influenced the correlation, although there is also variability among OSI values of replicate samples.

As a result of variations in oil due to processing, handling, and storage, the line equation for the correlation of OSI and sensory induction period will vary from one oil sample to the next. Therefore, the line equation cannot be used to predict the shelf-life of a particular soybean oil. It should also be remembered that the present study only investigated soybean oil and that the correlation of OSI with sensory induction period of other oil types remains to be determined.

It is interesting to note that panelists scored many samples as having lower levels of rancidity than their PV would suggest, i.e., that a PV of 3 to 5 corresponds to low levels of oxidation as indicated by previous work (3). This discrepancy may be due in part to differences between studies in how panelists are trained to score samples with increasing rancidity.

Correlation of ongoing OSI determinations in light-exposed samples with sensory induction period. OSI values for each of the treatment samples were taken on an ongoing basis during the storage period to determine how OSI of oil that was partially oxidized correlates with the sensory induction period (See Scheme 1). The squared partial correlation coefficients of OSI of light-exposed oil with sensory induction period ranged from 0.897–0.979, as shown in Figures 5–8. The partial correlation coefficients for the OSI values of light-exposed samples (samples stored over the 10-d period) were

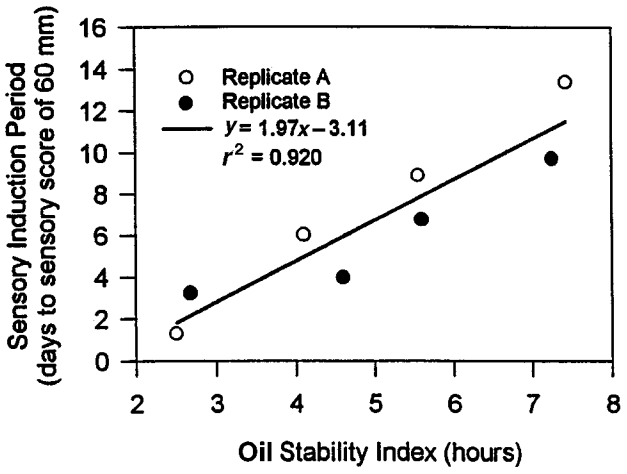


FIG. 4. Sensory induction period correlated with oil stability index measured before light-exposed storage.

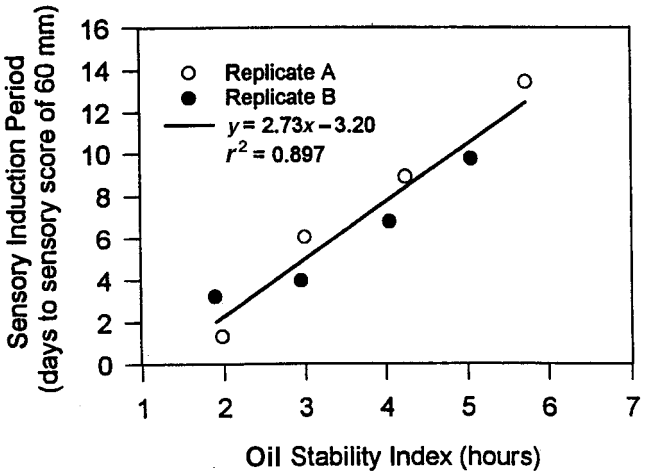


FIG. 5. Sensory induction period correlated with oil stability index measured after 3 d of light-exposed storage.

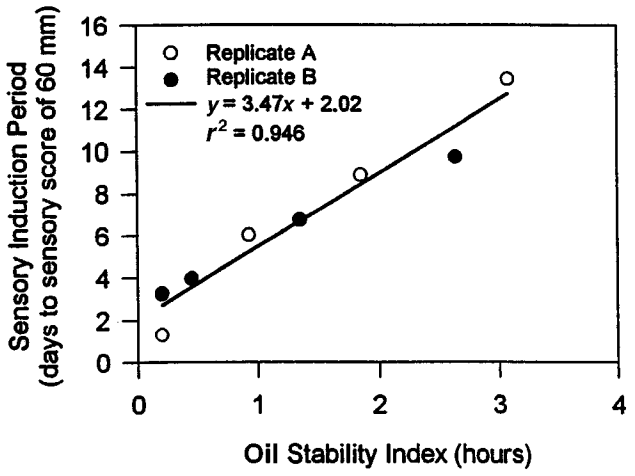


FIG. 7. Sensory induction period correlated with oil stability index measured after 8 d of light-exposed storage.

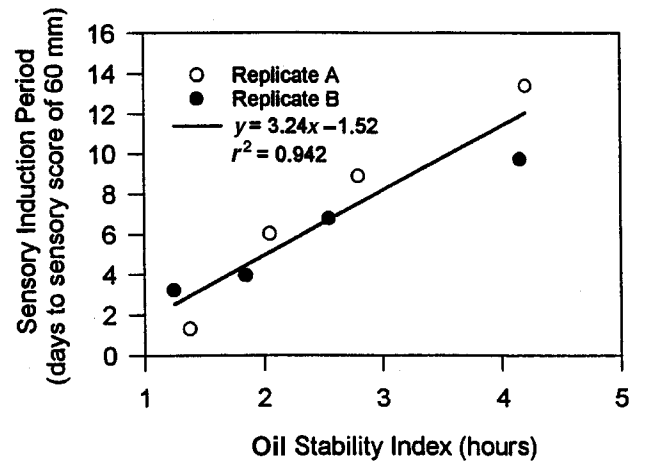


FIG. 6. Sensory induction period correlated with oil stability index measured after 5 d of light-exposed storage.

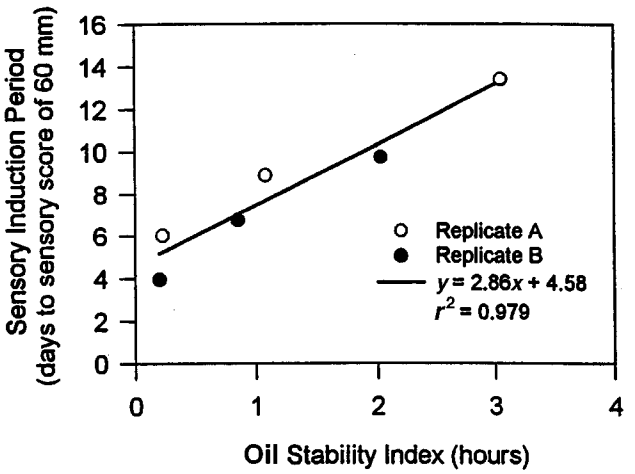


FIG. 8. Sensory induction period correlated with oil stability index measured after 10 d of light-exposed storage.

significantly different from zero with $P \leq 0.001$. Thus, the OSI gave a good indication of oxidative stability even in oil that was partially oxidized. This is helpful since the extent of oxidation in a given sample is often unknown. In general, the squared partial correlation coefficient of OSI with sensory determination of oxidative stability is approximately 0.90 or better, regardless of the extent of sample oxidation.

In conclusion, despite the different oxidation reaction pathway occurring at elevated temperatures, OSI appears to be a valid accelerated method for measuring oxidative stability of light-exposed soybean oil that varies in metal catalyst content

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