Temperature Effects on the Determination of Oxidative Stability with the Metrohm Rancimat

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Reproducibility of Oil Stability Index (OSI) values determined on the Metrohm Rancimat was measured with a single run and between experimental runs. Within a single experiment, a range of 0.13 h and a standard deviation of 0.066 h were determined. For multiple experiments, standard deviations of 0.24 and 0.26 were obtained for soybean and low-erucic rapeseed oil, respectively. The effect of temperature was determined for safflower, soybean, low-erucic rapeseed, corn, peanut and olive oils. A linear relationship was established between log (OSI) and temperature. The linear equation obtained for soybean oil was utilized to calculate variability of the OSI due to temperature differences in the heating block.

KEY WORDS: Oil stability, oil stability index, Rancimat, temperature, vegetable oils.

Oxidative rancidity is one of the most critical factors affecting the shelf life of processed foods. Polyunsaturated fatty acids are attacked by oxygen to yield peroxides, which then decompose further. Literature on the mechanisms involved in lipid oxidation has been reviewed by Frankel (1). A rapid test to predict resistance of oils to oxidation has long been sought. The Schaal oven test (2,3) and the active oxygen method (AOM) (4) are the oldest and the most widely used. These tests are of great utility when comparing oils for their general stability toward oxidation. Their major disadvantage is that they fail to predict stability, particularly the onset or nature of off-flavors, in lipid-containing products. Three reasons may be advanced for these limitations: i) Food products are often formulated as emulsions and the course of oxidation may be reasonably expected to be different than in a bulk oil; ii) many food emulsions, such as salad dressings, are acidic and acids are known to catalyze the decomposition of peroxides; and iii) food products are stored at ambient or at cold temperatures for long periods of time. If the mechanism of oxidation changes with temperature, lack of predictive ability by accelerated methods at high temperatures can be expected.

Recently, the Metrohm Rancimat (Metrohm Instruments, Herisau, Switzerland) has been advanced as a method to determine resistance of an oil toward oxidation (5). Several studies in the literature (6–10) have claimed a correlation between AOM and the Oil Stability Index (OSI) determined by the Rancimat. Advantages of the Rancimat technique are that it is a continuous measurement, which requires no periodic analytical determinations and, therefore, requires no organic solvents for titrations.

The present investigation was initiated to determine the reproducibility of the instrument and to determine the effect of temperature on the Oil Stability Index.

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MATERIALS AND METHODS

The Model 617 Rancimat, equipped with an electric heating block, was used without modification. Air flow rates were set at 20 L/h for all determinations. The temperature was measured by immersing a thermometer in a reaction cell containing 5 g of a high-stability triglyceride oil (Durkex 500, Van den Bergh Foods, Lisle, IL). The heating block and air were turned on and the temperature reading was taken after the system had equilibrated for 1 h. The temperature was set to the exact value by adjustment of the potentiometer.

Samples for all determinations were randomized to determine their position in the heating block. Initial baselines of the six channels were set to give adequate separations on the chart. Oil stability was determined by drawing a tangent to the curve and extrapolating the tangent line to the baseline. The measurement was converted into hours by calculation from the chart speed (20 mm/h).

Glassware was scrupulously cleaned according to the following procedures. Reaction tubes were treated with hot, saturated KOH in isopropanol for several hours and then rinsed with tap water. Treatment with the caustic solution was repeated if any visible evidence of polymerized oil remained. Tubes were then soaked overnight in an aqueous solution of Micro detergent and then rinsed thoroughly with tap water and distilled water. The anti-foam rings were cleaned using the same sequence. Conductivity cells and electrodes were first rinsed with acetone and then soaked overnight with Micro detergent solution. The procedure was completed with tap water and distilled water rinse. All glassware was allowed to dry completely before use.

Reproducibility of measurement. The heating block of the Rancimat was set to 120°C. Temperature was measured in each of the six block positions, and the range was found to be 0.6°C. Identical samples (5 g) of refined, bleached and deodorized (RBD) soybean oil were measured at a chart speed of 20 mm/h. To determine run-to-run variability of measurements, two samples of RBD soybean and RBD canola oil were periodically spotted in with other experimental runs at 120°C. Samples were sparged with nitrogen and stored at ambient temperature between experiments.

Temperature effects on OSI. Three commercial oils [RBD soybean (Kraft Food Ingredients, Memphis, TN), RBD corn (Kraft) and RBD canola (Agro Ingredients, Des Plaines, IL)], to which no antioxidants had been added, were selected for investigation. Three consumer oils [olive (Bertolli Extra Light brand), safflower (Hollywood brand) and peanut (Planters brand)] also were selected for the temperature-effect experiment. Duplicate measurements were carried out at 100, 110, 120, 130 and 140°C. The chart speed for all runs was 20 mm/h. Mean OSI values were plotted against temperature as shown in Figure 1. Log OSI values were also plotted *vs.* temperature (Fig. 2). An RS/1 program (BBN Software Products Corp., Cam-

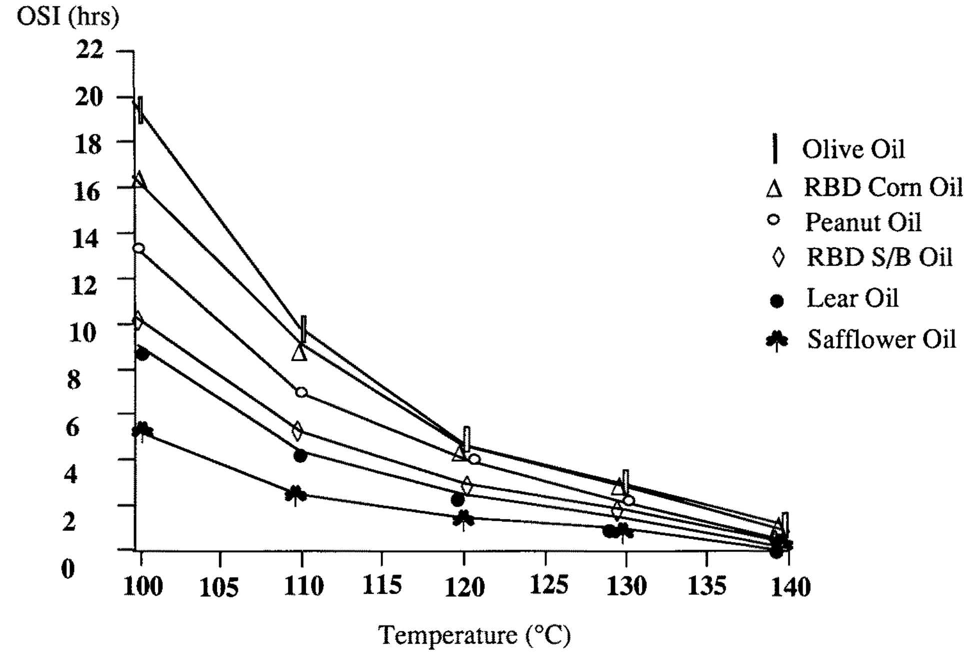

FIG. 1. Oil Stability Index (OSI) as a function of temperature.

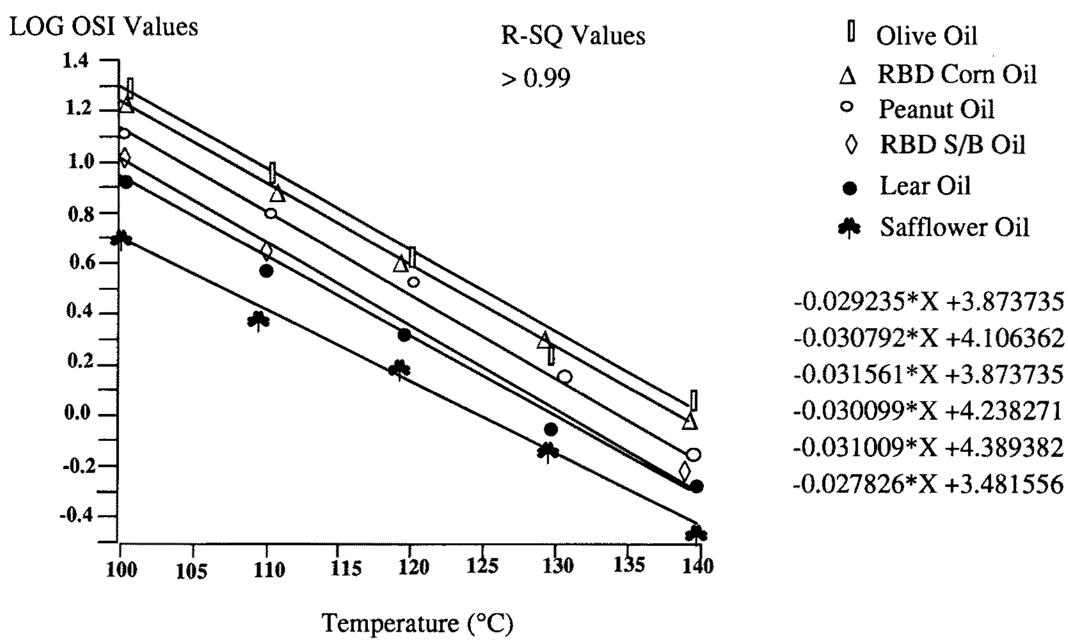

FIG. 2. Log OSI as a function of temperature.

bridge, MA) was used to fit lines to the data. Equations for each line were also determined.

RESULTS AND DISCUSSION

Previous experience with the Rancimat had demonstrated that temperature control and scrupulous cleaning of glassware between runs were critical to obtaining good data. Even slight contamination of reaction tubes could result in a difference in OSI values of several hours. Therefore, we developed a stringent protocol for cleaning of all glassware between experiments.

Reproducibility within a single experimental run appeared to be excellent, as shown by the data in Table 1. A range of only 0.13 was observed among the six runs. The major experimental difficulty encountered was that the tangent lines on the chart paper were close together, and extrapolation required great care. The newer Rancimat models with linear regression software have alleviated this difficulty. Larger variability was seen in data

TABLE 1

Reproducibility of Rancimat Values Within an Experimental Run

Tube no.	OSI Value
1	2.28
2	2.38
3	2.41
4	2.31
5	2.36
6	2.28
Mean	2.34
Range	0.13
SD	0.055

TABLE 2

Reproducibility of Rancimat Values Between Experimental Runs

Date	OSI SB[a] oil	OSI Lear[b] oil
12/2/87	2.79	2.98
12/11/87	2.98	2.40
1/6/88	2.98	2.60
1/6/88	2.70	2.70
1/18/88	2.50	2.50
1/21/88	2.40	2.21
1/30/88	2.50	2.41
2/12/88	2.40	2.21
Mean	2.66	2.50
SD	0.24	0.26

[a]SB, soybean.

[b]LEAR, low-erucic acid rapeseed.

between experimental runs. However, the method of this determination may have contributed to experimental error. Samples of the same lots of RBD soybean and RBD canola oil were slotted into other experiments where two heating block positions were available. Between runs the oils were nitrogen-sparged and stored in the dark at ambient temperature. The skew of the data toward lower OSI values with the passage of time suggests that some oxidation may have occurred during the study. Storage protocol was changed for subsequent experiments for the determination of temperature effects. Samples were thoroughly nitrogen-sparged and frozen at −40°C between experiments. This can be seen in Table 2.

To determine the effect of temperature on oxidative stability and OSI values, six vegetable oils were selected which were expected to show a fairly wide range of oxidative stability. Each set of oils was measured in duplicate at five temperature settings on the Rancimat. An attempt was made to measure stability at 150°C. However, the curves appeared to be inverted concave downward, which made placement of tangent lines difficult. Therefore, data at this temperature are not reported.

As expected, the data in Figure 1 show that, at higher temperatures, stability of the oil towards oxidation is much lower. Olive oil was the most stable at all temperatures, and the safflower oil sample was the least stable. Data were consistent because none of the curves crossed. The curves appeared to be nonlinear and, possibly, exponential functions. Linear plots were obtained, as shown in Figure 2, when the log OSI values were plotted *vs.* temperature. Fitting of lines to the data showed a high degree of correlation; all coefficients exceeded 0.99. A set of linear equations also was generated which, in principle, could permit extrapolation of the lines.

The linear equation for soybean oil was selected to predict the variability that should have occurred due to temperature variation in the heating block. Predicted variation was calculated as follows: Range OSI = OSI (119.8°) − OSI(120.4°) = 2.615 − 2.506 = 0.109. The experimental value from the earlier experiment (Table 1) was 0.13 h. Therefore, the largest part of experimental error involved in samples within a single experiment can be accounted for by temperature variation in the heating block.

While it may be tempting to extrapolate the temperature-dependent lines and assign some significance to storage of oils at ambient temperatures, the validity is still questionable. Mechanistic changes may occur at lower temperatures, resulting in unexpected shift values. The question in need of an answer is whether the lines remain linear between 100°C and ambient temperature. The newer Rancimat models are now capable of measurement down to 50°C. Therefore, the data required to answer part of this pressing question should be readily available. Extrapolation of data from 50°C to ambient would be much more convincing.

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