Collaborative Study of the Oil Stability Index Analysis

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The Oil Stability Index Analysis method was subjected to a fifteen-laboratory collaborative study in which the participants used currently available commercial and home-built instruments to provide data to support the approval process as an Official Method of the American Oil Chemists' Society. The overall average coefficient of variation was 11.3% for samples from 7 to 80 h of stability testing at 110°C.

KEY WORDS: AOM, instrument methods, oil stability, OSI, oxidation rancidity.

There are many reasons to make fats and oils as resistant to oxidation as possible. Such resistance is affected by the degree of saturation, the presence of antioxidants (natural or synthetic) or prooxidants (trace metals, chlorophyll, etc.) by their history of abuse or age, and the presence of chelating agents. Measurement of this resistance is an important guide to product performance and shelf life. The primary method for accelerated analysis of this resistance or oil stability has been the Active Oxygen Method (AOM), AOCS Cd 12-57 (1). It was introduced by Wheeler (2) and standardized by King *et al.* (3). It has been used extensively over the years because it provided a fast indication of the oxidative stability of products. The rapid aspect of AOM was needed for quality control of fats and oils, where results are needed in hours rather than days. The method's deficiencies have been presented by Matlock (4) and are partly inherent in the procedure and partly attributable to improper shortcuts commonly employed. Although the method requires at least two titrations each on two samples (Fig. 1), few laboratories run the analysis as specified but substitute a pass/fail system, wherein a sample is run for a predetermined length of time and a single peroxide value (PV) is then titrated. If the result is below a value set by specification, it passes. When this system is used, no information on the actual stability of an oil is obtained. Some laboratories even run the AOM at higher temperatures to shorten the analysis time for hard fats, which complicates matters even more.

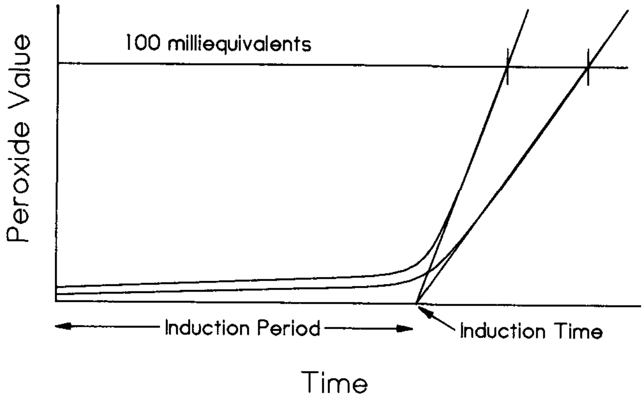

FIG. 1. A typical plot of peroxide values as function of time. Proper analysis requires at least two titrations on two different samples.

Even if the AOM is applied correctly, there are inherent deficiencies and difficulties. For one, the analysis is based on a dynamic system. The endpoint is determined by the amount of peroxides in the oxidized oil, but peroxides are unstable and decompose readily to more stable secondary reaction products, such as volatile organic acids. Some laboratories run the AOM at higher temperatures to shorten the analysis time for hard fats. This is a dangerous extrapolation, because of the simultaneous formation and degradation of the peroxides at different reaction rates, which are complex functions of temperature. This can cause dramatic endpoint shifts, which greatly influence reproducibility. Because the peroxide concentration often goes through a maximum, one may determine a false endpoint if the first, correct endpoint is missed, especially with the pass/fail system.

Another major deficiency is the determination of the endpoint during the oxidant-limiting, rapid oxidation phase of the test. During the rapid oxidation phase, the reaction is extremely susceptible to variation in the oxidant supply (see Fig. 1 at the 100-meq. point). This results in poor reproducibility between analyses of duplicate samples and contributes to the published 13.4% standard deviation (STD) for the method, which is understated. Examination of the 1987 Smalley Collaborative Laboratory Samples data produced an actual coefficient of variation (CV) of 35%, which means that, for an oil with a 100-h AOM specification, independent laboratories would estimate AOMs within plus or minus 35 h 68% of the time. The AOM procedure specifies that oxidant flow be controlled by delivering air through calibrated capillary tubes, but no caution is expressed about the head pressure required to enable these capillary tubes to function properly. Although Poiseuille's Law dictates that a minimum pressure of 29.4 psi is required to assure constant flow, most AOM tests are run improperly in the range from 1 to 5 psi, due to the chromic acid scrubber systems required by the analysis procedure to remove free fatty acids, etc. Because the procedure, AOCS Method Cd 12-57, does not inform the analyst of this limitation on the head pressure, the procedure may not be run properly in all laboratories.

The third major deficiency of the AOM is its reliance on manual titration for the peroxide value, AOCS Cd 8-53 (5) and the use of chloroform in the titration. The requirement for standardization of the reagents also makes the AOM labor-intensive. Finally, if a value of 175 meq is exceeded upon titration, the sample must be reanalyzed.

A new, superior method has had a long history of development: The Oil Stability Index (OSI) determines oil stability by measurement of the conductance produced when evolving volatile organic acids are collected in deionized water. These organic acids are the stable secondary reaction products when oil is oxidized by a stream of air bubbling through the oil. Figure 2 shows the typical apparatus needed for conducting the test. As in the AOM, the OSI test proceeds slowly at first because during the induction period, little acid is released. The endpoint is

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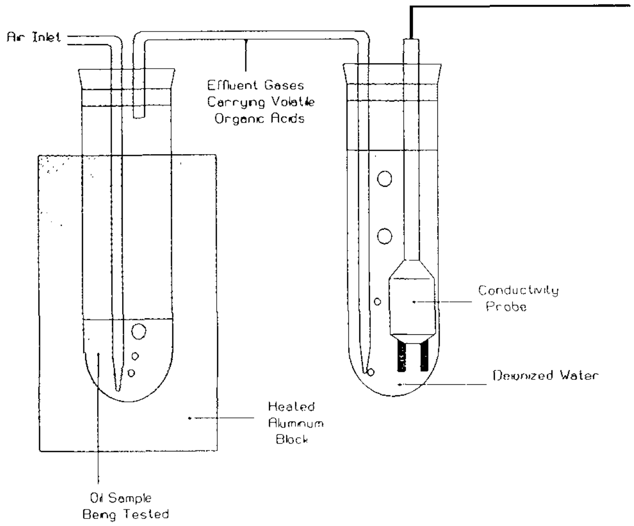

FIG. 2. Block diagram of a sample testing channel of the Oil Stability Instrument. Each instrument contains 24 such channels.

selected where the rapid rise in conductance begins. Figure 3 illustrates a typical curve. The primary fatty acid has been shown to be formic acid (6,7), when the oil is heated between 97.8 and 130°C. The first description was an automated version, the so-called "Swift-Test" (8). The Zn/Cu electrodes were later replaced by a conductometric cell (9), and a comparison of the two methods was published later (10). The latter method produced more ideal curves, but otherwise there were no significant differences. The commercial Brinkmann 617 Rancimat (Brinkmann Instruments, Inc., Westbury, NY) became available in the early 1980s and was capable of running six samples at the same time. The endpoints were determined manually by drawing tangents to pick the inflection point. The instrument has been superseded by the Rancimat 679, which still does six samples, but the endpoints are now determined automatically. In 1983, the Archer Daniels Midland (ADM) Company (Decatur, IL) developed a computer-assisted instrument that was capable of determining the endpoint automatically (11,12). Omnion, Inc. (Rockland, MA) now produces the instrument commercially under a license agreement with ADM. All commercial instruments provide a hard-copy trace of the conductance as a function of time.

A small preliminary collaborative study was carried out in 1985 to test the initial OSI analysis parameters, to determine the correlation between then available instruments and to develop an analysis method. That study showed the OSI method to be superior over the AOM method in many respects: (i) In the AOM, the end point does not determine the induction period, but is merely related to it, whereas the OSI end point determines the induction period precisely; (ii) the AOM provides a single data point, whereas the OSI provides continual data points; (iii) in the AOM, the end point can be exceeded which requires re-analysis, whereas in OSI, the end point cannot be exceeded; (iv) the AOM relies on analysis of unstable primary reaction products, while the OSI is based on analysis of secondary stable products; (v) in the AOM, the end point is determined during the oxidant-dependent, highly variable and difficult-to-reproduce rapid oxidation phase, whereas the OSI end point is determined at the end of the induction period, which is relatively insensitive to oxidant flow, (vi) the AOM depends on a manually obtained end point, whereas OSI has an instrumental automatic endpoint; (vii) the AOM is manual, labor-intensive and time-consuming, and OSI is automated; (viii) CV for the Smalley collaborative data is 35%, but only 5.7% on OSI instrumentation; (ix) air flow must be controlled accurately for the AOM, but is not as important for the OSI; (x) the AOM analysis at elevated temperatures introduced large errors, whereas OSI analysis can be run at higher temperature; (xi) the OSI requires no reagents, whereas the AOM PV titration currently requires chloroform and reagent standardization; recommended solvents to replace chloroform are not suitable for PVs above 50.

Pre-collaborative experiments. Prior to running the collaborative study, a number of OSI parameters were investigated. The first was the effect of oxidant flow on the induction period. Various oils were analyzed by the OSI at two temperatures, 110 and 130°C, and the air flow rate was varied from 25 to 425 mL/min. Figure 4 is typical and illustrates the effect of air flow on the OSI end point for

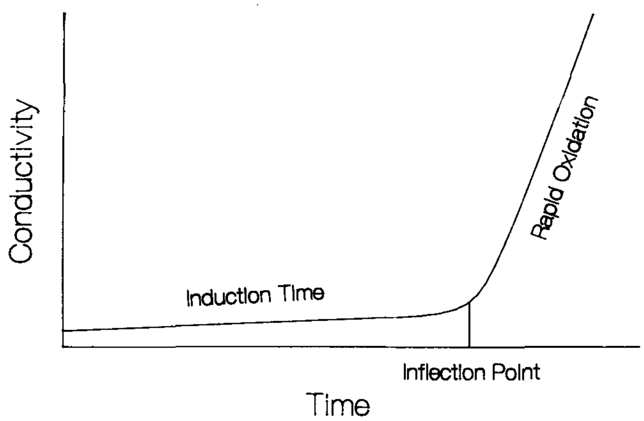

FIG. 3. The Oil Stability Index test is based on the rise in conductivity due to the volatile acids formed in the heated oil during oxidation.

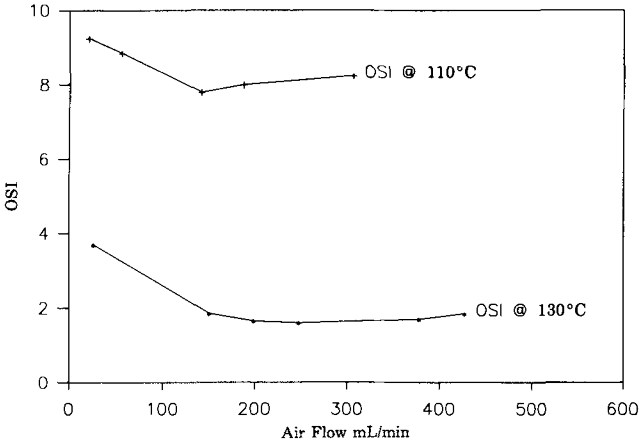

FIG. 4. Above 150 mL/min, air flow does not affect the Oil Stability Index (OSI) end point for soybean oil.

soybean oil. There was no change in end point between flow rates of 150 and 425 mL/min. So, 150 mL/min is likely sufficient to continually saturate the oil sample with oxygen during the induction phase. Although the slope may change significantly by variations in air flow during the rapid oxidation phase, the OSI end point has been determined well before its effect.

Quick analysis is a desirable feature in any analytical method. Because the OSI determines the end point by using conductance based on stable secondary reaction products, it can be run at various temperatures, and the results are all related mathematically. To illustrate this point, a refined, bleached and deodorized soybean oil was tested at temperatures between 85 and 140°C. The range between 97.8 and 115°C was most critical, and experiments were carried out in duplicate. The OSI values ranged from 1.25 to 46.9 h (Table 1), and least-squares analysis provided the exponential curve

$$\text{Log OSI} = 9.71 - 0.06921\text{T} \qquad [1]$$

where OSI is expressed in hours, T is the temperature in °C, and $R^2 = 0.9930$.

If the slope of linear plots of log OSI *vs.* T is constant for oils of varying stabilities, the OSI values can be converted from one temperature to another. This means that samples can be analyzed at a higher temperature, say 130°C, to shorten analysis time, and the OSI value can then be factored back to the standard 110°C. To test this hypothesis, a series of experiments was conducted with a set of oils in which the stability was changed by adding various levels of a prooxidant to a base oil. An organic soluble iron, *tris*(1-phenyl-1,3-butanediono)iron III (NBS reference material 1079b), was used in soybean oil. Figure 5 shows that the slope was indeed nearly constant and that only the intercept, which represents the relative stability of the oils, changed. We found that, for soybean oil, the following equation may be used to convert the measured OSI value at a higher temperature T to a value at the standard 110°C:

$$\text{OSI}_{110} = \text{OSI}_{\text{T}} \cdot \text{Exp}[0.6921(\text{T-}110)] \qquad [2]$$

TABLE 1

Oxidation Stability Index (OSI) Values of Soybean Oil Heated at Various Temperatures

Temperature (°C)	OSI value
85.0	46.90
97.8	19.45 ± 0.10[a]
105.0	11.48 ± 0.07[a]
110.0	8.18 ± 0.07[a]
115.0	5.83 ± 0.02[a]
120.0	4.15
125.0	2.50
130.0	1.75
140.0	1.25

[a] Average of duplicate runs.

The correlation between OSI and AOM was also examined (data not presented). In general, if the AOM is run correctly, an equation correlating OSI to AOM can be obtained with a coefficient of $R^2 = 0.999935$ over a range of 20 h to more than 450 h for a series of soybean oils hydrogenated to different iodine values.

Finally, to determine the effect of air moisture on the OSI, two extremes in relative humidity were studied with the same lightly hydrogenated soybean oil. Double triplicate runs were carried out with air passed through a tube of Drierite and compared with a similar set where air was bubbled through water. Essentially, no differences were observed. For 100% humidity, the averages of the triplicate runs were 13.67 ± 0.15 and 14.10 ± 0.25, and for 0% humidity, they were 13.70 ± 0.15 and 13.87 ± 0.18.

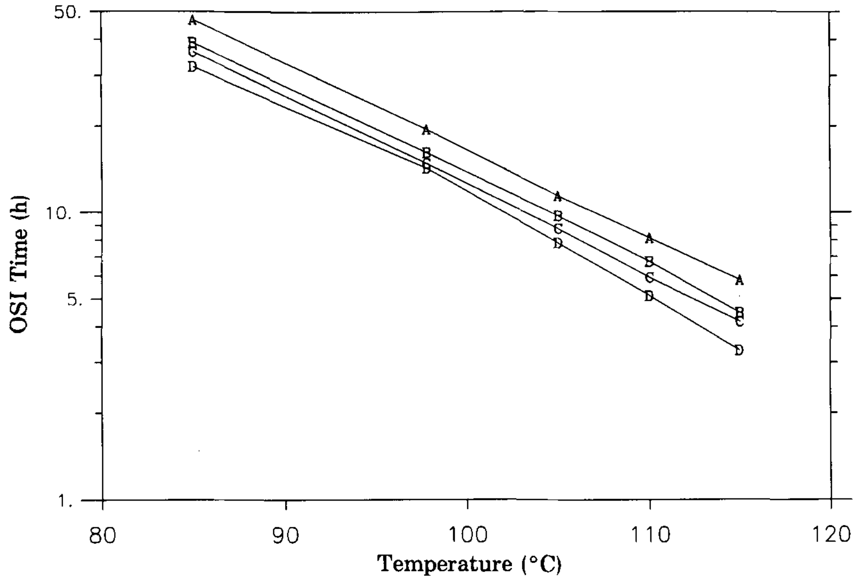

FIG. 5. Temperature effect on Oil Stability Index (OSI) values of refined, bleached soybean oil, which was spiked with various levels of Fe^{3+} as prooxidant: A = 0 Fe; B = 200 ppm Fe; C = 400 ppm Fe; D = 800 ppm Fe.

Collaborative study. This collaborative study was developed and performed to establish relative error statistics, confidence limits and effective sample stability ranges for the OSI analytical method [AOCS Method Cd 12b 92 (13)] for all instruments available. In designing the study, it was decided that oils of a wide range of stabilities should be used, but that the study would be restricted to vegetable oils only.

EXPERIMENTAL PROCEDURES

Fifteen analysts from fifteen laboratories participated in this study and were assigned blind identification numbers. Table 2 shows the instrument types and the type of glassware used with the instrument in each laboratory.

Oil samples. Table 3 presents the list of samples used in the study, together with their code letters. Special handling instructions were as follows: (i) all samples are to be refrigerated immediately; (ii) samples A through F are regular samples with no special handling instructions; (iii) samples G and H are margarines, which need to be heated and phase-separated prior to analysis; (iv) samples I and J will have very long induction times (90 to 100 h at 110°C), and deionized water should be added periodically during the run to keep water level constant; (v) sample K will be very fast at 100°C and need not be run at 130°C; (vi) sample L is a crude corn oil and will require one drop of the provided Dow Corning antifoam (Dow Chemical, Midland, MI).

TABLE 2

Instruments and Glassware Used by Collaborators

Laboratory	Instrument	Glassware
1	Auto Rancimat	Nondisposable
2	Auto Rancimat	Nondisposable
3	Manual Rancimat	Disposable
4	Auto Rancimat	Nondisposable
5	Home-Built	Disposable
6	Oxidative Stability Instrument	Disposable
7	Oxidative Stability Instrument	Disposable
8	Oxidative Stability Instrument	Disposable
9	Oxidative Stability Instrument	Disposable
10	Auto Rancimat	Nondisposable
11	Auto Rancimat	Disposable
12	Auto Rancimat	Nondisposable
13	Auto Rancimat	Nondisposable
14	Auto Rancimat	Nondisposable
15	Auto Rancimat	Nondisposable

TABLE 3

Sample Identification Codes[a]

Sample	ID letter	Analyzed at °C
Sunflower/SBO[b] blend	A	110, 130
Nonhydrogenated SBO	B	110
Liquid hydrogenated SBO blend	C	110, 130
Hydrogenated SBO/CSO[b] blend	D	110, 130
Liquid/hydrogenated corn blend	E	110, 130
Hydrogenated corn/CSO blend	F	110, 130
Table margarine	G	110
Bakers' margarine	H	110
Jojoba oil	I	110, 130
High-stability oil	J	110, 130
Free fatty acids	K	110
Crude corn oil	L	110

[a] Samples included in analysis #1: A–L at 110°C and A, C, D, E, F, I, J at 130°C. Samples included in analysis #2: A, B, C, D, E, F, I, J, L at 110°C and A, C, D, E, F, I, J at 130°C.

[b] SBO = soybean oil; CSO = cottonseed oil. ID, identification.

All samples were obtained from commercial production sources. The "high stability oil" was provided by Karlshamns USA Inc. (Columbus, OH) and is an Akorex 'B'-type product with the following fatty acid composition: C14:0, 0.2%; C16:0, 7.6%; C16:1, 0.3%; C17:0, 0.1%; C17:1, 0.1%; C18:0, 3.0%; C18:1, 73.5%; C18:2, 13.4%; C20:0, 0.3%; C20:1, 0.5%; and C22:0, 0.3%. A copy of the analytical procedures was included with the samples.

Instruments and methods. Four different instruments were included: Nine Automatic Rancimats Model 679 (Brinkmann Instruments, Inc.); four Oxidative Stability Instruments (Omnion, Inc.); one Manual Rancimat Model 617 (Brinkmann Instruments, Inc.) and one home-built apparatus. The OSI used in this study were all preproduction models built in-house at ADM Company. Information on the home-built instrument was unavailable. Each instrument was operated in accordance with its standard procedures, except for the changes made to create more uniform methods for this study: (i) standard thermometers were supplied with the samples and (ii) a temperature standardization procedure was developed for all collaborators to follow. They were instructed to adjust and record all temperature readings as follows: (i) fill a sample tube with silicone oil (or any other thermally stable oil) to 1″ above the thermometer's (ASTM #95C; American Society for Testing and Materials, Philadelphia, PA) immersion line. The bottom line of the thermometer should be approximately 1/8″ off the bottom of the sample tube; (ii) allow oil temperature to equilibrate for 30 min before reading the thermometer without moving it up or down in the oil; (iii) adjust the block temperature controller to compensate for any difference if the block temperature is not within 0.2°C of the target temperatures of 110 and 130°C; (iv) after adjustments have been made, wait until the new temperature shows and then allow the oil to equilibrate for 15 min. Read again and repeat Steps 3 and 4 until the target temperature is reached; and (v) record the exact oil temperature daily on the OSI Collaborative Results sheet.

Step 1 of this procedure proved to be inadequate for the Rancimat instruments. Apparently, when set at 110°C, the oil reads only 93°C if the tube is filled to the recommended level of 1″ above the thermometer immersion line. Rancimat temperature readings are also sensitive to air flow. Therefore, Step 1 was revised to read: Silicone oil is added to the reaction tube to a level equivalent to 5 g of vegetable oil. The air flow is adjusted as directed in Item 6 under the Apparatus Section (2.5 mL/s).

Even with this revision, constant temperatures were difficult to establish with the Rancimats. Several collaborators reported temperature fluctuations as much as 0.5°C and suggested that room temperature fluctuations might be a possible cause for this problem. Rancimat instruments also required temperature modification on an instrument-to-instrument basis. The range of settings for the Rancimats varied from 113.0 to 118.5°C to achieve 110°C, and from 134.0 to 138.8°C to reach 130°C. On the other hand, all OSI instruments required settings of 110.0

to 110.1 and of 130.0 to 130.1°C to achieve the required analysis temperatures, respectively.

In the collaborative study, samples were run in two sets of duplicates. Instrument temperature readings were recorded once for each sample duplicate set. All samples were run at 110°C, and all samples except B, G and H were run at 130°C. The induction times for those three samples were too short at 130°C.

Statistical analysis. The data were evaluated by Chauvenet's Criterion, which is a statistical screening for anomalies (14). This criterion was applied as a cut-off point of two STDs from the mean against the standard residuals of each data set. Under this criterion, no outliers were found, and all induction time data were used to determine STDs by the N-1 method. All weighted means of means were calculated as follows:

$$\mu_w = \Sigma(n_i \cdot x_i)/\Sigma n_i \qquad [3]$$

where μ_w = weighted mean of population, x_i = mean of data set i, and n_i = number of items in data set i. CVs were calculated as follows:

$$CV = 100\ (\sigma/\mu_w) \qquad [4]$$

where CV = coefficient of variation and σ = standard deviation of sample population. Significant differences in CVs were determined with two-tailed *t*-tests at $P = 0.01$ (15). Results are reported as *t*-score and degrees of freedom (df) under two assumptions, unequal variances between the two groups and equal variances.

RESULTS AND DISCUSSION

For the purpose of objective discussion, any direct comparison of instrument types has been kept to a minimum. Table 4 shows a typical example of pertinent data obtained for oil sample A at 110°C. It gives the instrument type, the mean induction time in hours, STD, CV and the range of induction times measured in N experiments. Table 5 lists the variations by instrument type for the actual reported temperatures. Reported temperatures had an average range, for all instruments, of ±0.2°C, with extremes from the target temperature of approximately ±0.5°C.

TABLE 5

Temperature Variation as Function of Instrument Type

Instrument type	110°C N	Mean (h)	STD	130°C N	Mean (h)	STD
Auto Rancimat	374	110.45	1.00	231	130.30	1.05
Manual Rancimat[a]	—	—	—	—	—	—
Home-Built	48	110.23	0.17	27	130.11	0.08
OSI	136	110.00	0.00	82	129.99	0.03
OSI[b]	43	109.96	0.14	25	129.90	0.10

[a] Temperature data not available.

[b] Oil Stability Index (OSI) with temperature control altered by user.

The results for the margarine samples were extremely variable. The instructions for working up the margarine samples before analysis were probably not explicit enough to avoid laboratory-to-laboratory differences. Separation of the oil and aqueous milk solids phase appears to have been the problem. Drying the oil phase with anhydrous calcium chloride and filtering prior to analysis could have improved results by minimizing carry-over of milk solids, salts and water, which appear to have varied greatly among laboratories. Also, the free fatty acid sample was impossible to analyze under the conditions of the test. Most Rancimat instruments could not register the short induction time for that sample (less than 1 h at 110°C). Because of these problems, samples G, H and K were eliminated from the statistical analysis.

Table 6 shows the average CV for each laboratory before and after elimination of samples G, H and K, because the skewing effect of these three samples is evident. The average CV value for each laboratory represents how well each instrument agreed with itself within a laboratory–intralaboratory variation. To be more concise, the remaining data were analyzed after elimination of the three problem samples.

TABLE 4

Typical Variation Found Among Laboratories for Sample A at 110°C[a]

Instrument	Mean (h)	STD	CV	Range (N)
Auto Rancimat	9.713	0.344	3.540	9.38–10.10 (4)
Auto Rancimat	9.505	0.979	10.303	8.57–10.40 (4)
Manual Rancimat	8.915	0.120	1.348	8.83–9.00 (2)
Auto Rancimat	9.197	0.165	1.796	9.05–9.43 (4)
Home-Built	10.275	0.126	1.225	10.10–10.40 (4)
OSI	10.963	0.499	4.552	10.50–11.55 (4)
OSI	11.187	0.206	1.838	10.95–11.45 (4)
OSI	10.438	0.132	1.260	10.25–10.55 (4)
OSI	10.513	0.307	2.916	10.30–10.95 (4)
Auto Rancimat	11.200	0.535	4.780	10.60–11.70 (4)
Auto Rancimat	12.825	1.253	9.767	11.70–14.10 (4)
Auto Rancimat	9.138	0.160	1.747	8.98–9.28 (4)
Auto Rancimat	10.675	0.359	3.367	10.20–11.00 (4)
Auto Rancimat	8.675	0.427	4.924	8.40–9.30 (4)
Auto Rancimat	8.862	1.238	13.967	7.10–9.75 (4)

[a] Mean = the induction time in hours; STD = the standard deviation; CV = coefficient of variation and Range (N) gives the extreme values measured in N experiments; OSI, Oil Stability Index.

TABLE 6

Intralaboratory Variation in Coefficients of Variation (CV) for All Samples and for Those Excluding Samples G, H and K

Laboratory	All samples Number of results	All samples Average CV	G, H & K excluded Number of results	G, H & K excluded Average CV
1	63	5.2	56	3.7
2	72	4.7	63	4.8
3	15	2.8	14	3.0
4	76	1.5	64	0.8
5	75	4.7	63	3.5
6	70	6.0	59	4.2
7	76	4.2	64	1.8
8	72	3.5	61	2.5
9	71	4.5	60	4.4
10	72	5.7	64	4.0
11	72	11.7	64	11.6
12	62	3.6	53	3.2
13	52	3.5	52	3.5
14	76	5.9	64	4.1
15	59	13.0	56	12.1

TABLE 7

Average Intralaboratory Coefficient of Variation (CV) by Instrument Type

Instrument	N	Average CV
Auto Rancimat[a]	7	3.4
Manual Rancimat	1	3.0
Home-built	1	3.5
OSI	4	3.2

[a]Laboratories 11 and 15 excluded as outliers; OSI, Oil Stability Index.

Table 7 reports the intralaboratory CV values for each instrument type. In this analysis, laboratories 11 and 15 were excluded as outliers in the Auto Rancimat class. However, in further analysis, where data based on the laboratories' individual sample sets were used, no outliers were found, and laboratories 11 and 15 were included. No significant difference was found between the intralaboratory CVs of the Auto Rancimat and the OSI ($P < 0.01$; assumed unequal variance, $t = 0.24$, df = 6.1; assumed equal variance, $t = 0.25$, df = 9). Thus, when examining only one laboratory, these two instruments are statistically equal in variation. No such comparison could be made with the Manual Rancimat and the home-built instrument, because no STD could be computed for the CV.

Table 8 lists the average CV by instrument, sample and temperature. The CV values are averaged for each sample type across all instruments of the same type, weighted by the total number of runs for that sample by each laboratory. These data provide information on how each laboratory fared with each sample type. For example, the Auto Rancimat tended to have higher CVs for samples analyzed at 130°C than for those done at 110°C, whereas OSI showed similar CVs for both temperatures. Also, the crude corn oil sample caused the highest CV values for both instruments (data not shown).

Table 9 reports the average CVs for both temperature classes and the overall values by instrument type. These averages are derived by weighting the number of results for each temperature class and instrument. They represent the variation of the instrument when viewed across many instruments of that type, showing how well each instrument agreed with other instruments of the same type. The Manual Rancimat and the home-built instruments show low variation, because the first samples were run in only one duplicate set, and for both units, the

TABLE 8

Coefficient of Variation (CV) by Instrument, Sample and Temperature

		110°C				130°C			
Instrument	Sample	N	Mean (h)	STD	CV	N	Mean (h)	STD	CV
Auto Rancimat	A	36	9.977	1.445	14.5	33	2.531	0.409	16.2
	B	36	7.575	1.102	14.6				
	C	36	17.365	2.367	13.6	33	4.465	0.525	11.8
	D	36	23.058	2.319	10.1	35	5.699	0.705	12.4
	E	36	13.317	1.168	8.8	36	3.448	0.603	17.5
	F	36	44.185	4.510	10.2	36	10.584	1.841	17.4
	I	27	58.863	9.964	16.9	25	10.787	2.027	18.8
	J	31	68.919	14.612	21.2	33	15.948	3.093	19.4
	L	31	16.485	3.308	20.1				
Home-built	A	4	10.275	0.126	1.2	4	2.975	0.126	4.2
	B	4	7.950	0.265	3.3				
	C	4	18.500	0.668	3.6	4	5.000	0.216	4.3
	D	4	23.950	1.201	5.0	4	6.350	0.129	2.0
	E	4	14.125	0.395	2.8	4	3.925	0.150	3.8
	F	4	47.875	1.417	3.0	3	12.067	0.603	5.0
	I	4	78.950	3.442	4.4	4	12.900	0.638	4.9
	J	4	78.875	2.361	3.0	4	18.000	0.365	2.0
	L	4	23.938	0.945	3.9				
Oxidative Stability Instrument	A	16	10.775	0.429	4.0	15	2.642	0.140	5.3
	B	16	7.841	0.497	6.3				
	C	15	17.910	0.964	5.4	14	4.232	0.239	5.6
	D	16	24.506	0.829	3.4	16	5.953	0.301	5.1
	E	14	14.296	0.312	2.2	16	3.500	0.203	5.8
	F	14	47.754	1.574	3.3	14	11.132	0.488	4.4
	I	16	75.075	2.931	3.9	16	13.131	0.401	3.1
	J	14	75.364	4.592	6.1	16	16.791	1.421	8.5
	L	16	21.550	3.803	17.6				
Manual Rancimat	A	2	8.915	0.120	1.3				
	B	2	12.000	0.467	3.9				
	C	2	21.500	0.354	1.6				
	D	2	27.670	0.354	1.3				
	E	2	16.500	0.240	1.5				
	F	2	54.500	0.000	0.0				
	I	2	99.125	11.137	11.2				

TABLE 9

Interlaboratory Coefficient of Variation (CV) by Instrument Type and Temperature

Instrument	Temperature (°C)	Number of samples	Number of instruments	Average CV by sample and temperature
Auto Rancimat	110	305	9	14.2
	130	231	9	16.1
	Overall	536		15.0
Manual Rancimat	110	14	1	3.0[a]
	130	—	—	—
Home-built	110	36	1	3.4[a]
	130	27	1	3.7[a]
	Overall	63		3.5[a]
Oxidative Stability Instrument	110	137	4	5.9
	130	107	4	5.4
	Overall	244		5.7

[a] Not true interlaboratory CV because only one laboratory had this instrument type.

data could not be compared with other units. The interlaboratory CVs at both 110 and 130°C for the Auto Rancimat (14.2 and 16.1, respectively) and for the OSI (5.9 and 5.4, respectively) were significantly different at $P < 0.01$. At 110°C, $t = 4.07$ and df $= 15.9$, where an unequal variance is assumed, and $t = 4.07$ and df $= 16.0$ for an equal variance. At 130°C, the values are $t = 8.37$ and df $= 9.3$ for unequal and $t = 8.37$ and df $= 12$ for equal variance assumption. Table 9 reveals an almost threefold difference in the CVs between the Auto Rancimat and the OSI. This difference was probably caused by the variation in temperatures reported for the Rancimat during the collaborative study. The difference is statistically significant at $P < 0.01$ (assumed unequal variance, $t = 7.36$ and df $= 29.8$; assumed equal variance, $t = 7.36$ and df $= 30$). The overall collaborative CV for all samples was 15.7%. Exclusion of samples G, H and K reduced that value to 11.3%.

This collaborative study reports relative error statistics for the OSI analysis for all available instruments, as well as factors that could possibly influence this error. Temperature fluctuation of an instrument is a major factor in induction time variation. Intralaboratory CVs ranged from 0.84 to 4.79%. For instruments used to run complete sample sets at both 110 and 130°C, the average intralaboratory variations by instrument type were: Auto Rancimat, 3.43%, and OSI, 3.21%; and the average interlaboratory variations were: Auto Rancimat, 14.99% and OSI, 5.68%.

A compilation of all the original data may be obtained from the Technical Director of the American Oil Chemists' Society, 1608 Broadmoor Drive, Champaign, IL 61821.

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