Relationship of Electronic Nose Analyses and Sensory Evaluation of Vegetable Oils During Storage

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ABSTRACT: Off-flavors associated with oxidized oils make it difficult to recruit sensory panelists to evaluate the oils. Using an instrument called the "electronic nose" to monitor the formation of volatile compounds associated with off-flavors could help to interpret oil oxidation studies in part to supplement human sensory panels. No published studies evaluate the correlation of oil oxidation sensory data and "electronic nose" analyses. Therefore, this project was designed to determine the correlation between sensory evaluation and "electronic nose" analyses. Canola, corn, and soybean oils were stored at 60°C in the dark until sufficiently oxidized. On days 0, 3, 6, 9, and 12, oils were evaluated for peroxide value, for volatile compounds by "electronic nose," and for off-flavor by sensory evaluation. The results suggest that the "electronic nose" is capable of measuring changes in volatile compounds associated with oil oxidation and could be used to supplement data obtained from sensory evaluations.

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KEY WORDS: AromaScan, correlation, electronic nose, fatty acid, oxidation, peroxide value, sensory evaluation, vegetable oils.

A thorough study of lipid oxidation should include sensory evaluation of the oil-containing products. Because oxidized samples have off-flavors, it can be difficult to recruit sensory panelists to evaluate these samples. Furthermore, sensory panelists can give inconsistent measurements when tasting oxidized samples. Therefore, it is desirable to use objective test measures as a supplementary tool to discriminate flavor changes.

In recent years, advances in the technology of multisensor arrays and neural computing have made the development of the "electronic nose" of great interest to the food industry for discriminating between odors (1). This analysis is rapid, nondestructive, and objective. According to Bartlett *et al.* (1), the term "electronic nose" refers to an array of chemical sensors, where each sensor has partial specificity to a wide range of aroma molecules, and has a suitable pattern recognition system.

So far, most applications of the "electronic nose" in the food industry have been in quality control in food or beverage production for monitoring flavor changes. Such applications include the discrimination of coffee varieties (2), determination of meat or fish freshness (3,4), microbial classification of grains (5), discrimination between different vintage years of wine (6), and identification of different types of soft drinks or different brands of sausage (7).

Information about the value of an "electronic nose," such as the AromaScan, to monitor lipid oxidation is very limited. One current research approach used the "electronic nose" to predict shelf life of edible oils (8). Previous research demonstrated the ability of the AromaScan to monitor aroma changes during lipid oxidation (9). The application of the AromaScan to monitor lipid oxidation would be a useful way to facilitate the understanding of lipid oxidation, to provide an objective analysis of lipid oxidation, and to supplement in part human sensory panelists. The correlation between the analysis of the "electronic nose" and sensory evaluation, however, has not been established. This information is vital to verifying the capabilities of the "electronic nose" in measuring off-flavor development during lipid oxidation that parallel human perception. Therefore, the objective of this study was to determine the correlations between sensory evaluation and the "electronic nose" analyses during oxidation of vegetable oils.

EXPERIMENTAL PROCEDURES

Materials. Canola, corn, and soybean oils were used for this study. These oils were purchased from a local grocery store (Hy-Vee, Ames, IA). Canola oil (Crisco Puritan Canola Oil) and soybean oil (Crisco Pure Vegetable Oil) were manufactured by Procter & Gamble (Cincinnati, OH), and corn oil (Mazola Corn Oil) was manufactured by Best Foods Division, CPC International, Inc. (Englewood Cliffs, NJ).

Methods. (i) Oven storage test. Three oils (550 mL per replicate) were stored in 3-L beakers covered loosely with aluminum foil at 60°C in the dark for 12 d. Every third day, an aliquot (115 mL) of each oil was removed for analyses with no new oil added. Analyses on each oil were duplicated and the results averaged. The entire study also was replicated.

(ii) Chemical analyses. Fatty acid compositions of oils before and after storage were analyzed after triacylglycerides had been converted into fatty acid methyl esters (FAME) according to a method described by Hammond (10). The FAME were injected onto a Hewlett-Packard 5890 Series II gas chromatograph (Kennett Square, PA) equipped with a flame-ionization detector, a split/splitless injector, and an automatic sampler. A DB-23 fused-silica capillary column with dimensions of 0.25 mm × 15 m × 0.25 μm film thickness was used (J&W

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Scientific Inc., Folsom, CA). Chromatographic parameters were set as follows: injector temperature, 250°C; detector temperature, 250°C; column temperature, 200°C; and head pressure of the column, 15 kPa. Calculated oxidizability was computed according to a formula presented at the bottom of Table 1, which was proposed by Fatemi and Hammond (11). Total saturated fatty acid (TSFA) is a sum of percentages of palmitic and stearic acids. Peroxide values (PV) were measured according to the modified Stamm test (12).

(iii) Aroma analyses. A 1-mL aliquot of oil from each replication was transferred with an Oxford BenchMate pipetter into a 500-mL air bag fitted with a one-way check valve. Prior to sampling, the bags were equilibrated in the sample chamber (35°C) for 5 min. This method was adapted from previous research (9) with the following modifications. Aroma profiles of oils were measured with an AromaScan A32S (AromaScan Inc., Hollis, NH), equipped with 32 polymer sensors. The working conditions were as follows: The sampling chamber temperature was set at 35°C, the air used to fill the sample bags contained 8% relative humidity, and the air used for the reference was set to contain 2.5% relative humidity. All air used by the instrument was first directed through an activated carbon filter (AromaScan Inc.) to remove aroma particles, then through Drierite (AromaScan Inc.) to reduce humidity, and finally through two sets of 0.45-μm gas filters (AromaScan Inc.) to provide air free from particles and dust.

The total running time per sample was 350 s, with the program set to include 20 s of referencing, 180 s of sampling, 30 s of washing, followed by 120 s of referencing. Triple-filtered deionized high-performance liquid chromatography-grade water vapor was used for the referencing. Referencing is a procedure that is used to zero the background noise of the sensors. The program was set to reference at the beginning and the end to correct the baseline and to zero the sensors. The wash portion of the program consisted of a 2% isopropyl alcohol in water solution to remove residual aroma particles from the sensors and the sensor housing. The sensors react to the aroma compounds present in the sample to varying degrees. Only the last 50-s segment of the 180-s sampling time was used to determine the AromaScan profile to ensure that the sensor housing was saturated with the sample vapor from the sample bag. Some sensors of the AromaScan are strongly sensitive to certain volatile compounds according to the AromaScan operation manual. Based on their strong sensitivity to ketones and short-chain esters, sensors #22, 23, and 28 were selected to determine the AromaScan profile changes during oven storage test. The data were processed by the AromaScan graphic program, provided by the instrument manufacturer, and were analyzed using principal component analyses.

(iv) Sensory analyses. Sensory evaluation was conducted according to AOCS Official Method Cg 2-83 (13) with the following modifications. The sample size provided to sensory panelists was 10 mL, and fresh vegetable oils were provided each time as references for panelists at each setting. The AOCS scoresheet for flavor quality evaluation was used to determine both overall quality scores and flavor description intensities. As such, the panelists were asked to give an overall quality score for each oil and to note whether 12 predefined attributes, including nutty, buttery, corny, beany, hydrogenated, burned, weedy, grassy, rubbery, melon, painty, fishy, and other, were present as weak, moderate, or strong for each oil.

(v) Statistical analyses. A completely randomized design was used for this experiment. Differences in mean values among treatments were determined by least significant difference (LSD) at a significance level of $P \leq 0.05$ (14) on the Statistical Analysis System (SAS) release 4.0 for Microsoft Windows. The standard deviation and correlation of measurements were computed using SAS for Windows (14). Each type of oil was considered to be a treatment, and there were two replicates per treatment.

RESULTS AND DISCUSSION

Fatty acid compositions and TSFA compositions of oils at initiation (day 0) and after storage (day 12) are listed in Table 1. Compositions of all fatty acids changed slightly during storage, as observed by other researchers (15–17). The calculated oxidizability of oils is also listed in Table 1 and is computed according to the formula presented at the bottom of the table (11). According to the calculated oxidizability, canola oil should have oxidized the least quickly among the oils studied. The PV is routinely used to determine lipid oxidation, especially during

TABLE 1
Fatty Acid Methyl Ester (FAME) Percentage of Vegetable Oils Before and After Storage at 60°C in the Dark (for 12 d)

		FAME by GLC (relative area %)[a]						
Oil	Days	16:0[b]	18:0	18:1	18:2	18:3	TSFA[c]	CO[d]
Canola	0	3.7 ± 0.15[e]	2.2 ± 0.10	65.7 ± 1.30	20.1 ± 0.56	8.4 ± 0.53	5.9	4.5
	12	3.7 ± 0.05	2.1 ± 0.13	67.4 ± 0.76	19.2 ± 0.48	7.6 ± 0.36		
Corn	0	9.2 ± 0.06	2.1 ± 0.06	31.2 ± 0.37	56.6 ± 0.31	1.0 ± 0.06	11.2	6.3
	12	9.4 ± 0.29	2.0 ± 0.21	31.4 ± 1.26	56.4 ± 1.39	0.9 ± 0.10		
Soybean	0	9.1 ± 0.22	4.5 ± 0.05	26.6 ± 0.40	52.8 ± 0.39	7.0 ± 0.17	13.6	7.2
	12	9.2 ± 0.17	4.3 ± 0.19	26.8 ± 0.68	52.9 ± 0.49	6.9 ± 0.38		

[a]Values are the average of duplicate analyses of two replications.
[b]16:0 = palmitic acid, 18:0 = stearic acid, 18:1 = oleic acid, 18:2 = linoleic acid, and 18:3 = linolenic acid.
[c]TSFA = total saturated fatty acids = 16:0 + 18:0.
[d]CO means calculated oxidizability = [18:1% + 10.3(18:2%) + 21.6(18:3%)]/100.
[e]Data presented are the mean of two replicates with two injections each ± standard deviation. GLC, gas–liquid chromatography.

TABLE 2
Peroxide Values[a] (meq/kg) of Vegetable Oils During Storage at 60°C in the Dark

Day	Canola oil	Corn oil	Soybean oil
0	0.15 ± 0.02^{b}	0.48 ± 0.01^{c}	0.15 ± 0.01^{b}
3	1.4 ± 0.94^{b,c}	2.0 ± 0.15^{b}	0.8 ± 0.10^{c}
6	14.3 ± 5.36^{b}	9.2 ± 1.72^{b}	10.3 ± 3.50^{b}
9	39.4 ± 9.19^{b,c}	46.9 ± 3.87^{b}	34.4 ± 5.49^{c}
12	64.9 ± 7.76^{b}	126.0 ± 3.28^{c}	67.5 ± 4.87^{b}

[a]Data presented are the mean of two replicates with two duplications each ± standard deviation.
[b,c]Values in the same row with different superscripts were significantly different ($P \leq 0.05$).

the beginning oxidation stages. The PV increases as lipid oxidation progresses, plateaus after reaching a certain point, then finally decreases. At the beginning of storage (Table 2), both canola and soybean oils had the same PV, but the PV of corn oil was significantly greater than that of canola and soybean oils, although only 0.33 meq/kg greater. This significant difference may explain its significantly greater PV than that of canola and soybean oils at the end of storage.

At the beginning of storage, there were no differences among the oils in sensory scores (Table 3). As oxidation occurred, the sensory evaluation scores decreased, which represents a decrease in oil quality. The sensory evaluation scores for corn oil, which tended to be the highest (best) among the oils, contradicted its relatively high ending PV. When panelists were asked to describe the flavor according to the given attributes, they gave relatively high marks on nutty and corny attributes. Perhaps the "corny" flavor and/or "nutty" flavor masked the off-flavor of oxidized corn oil.

Figure 1 shows, in three-dimensional (3-D) graphics using all 32 sensors, the development of AromaScan intensity of soybean oil stored in an oven at 60°C for 12 d. Each symbol in Figure 1 represents an individual measurement of AromaScan intensity. There were five individual measurements for each duplicate treatment and two replications for each of the duplicates. Therefore, 10 symbols are shown in Figure 1 for each day of analysis. This graph was computed using the AromaScan intensity of soybean oil at day 0 (fresh oil) as a reference. AromaScan intensities of soybean oil at other days were subtracted by the AromaScan intensity of soybean oil at day 0. The numbers of both x- and y-axes shown in Figure 1 were generated by the

TABLE 3
Sensory Evaluation Scores[a] of Vegetable Oils Stored at 60°C in the Dark

Day	Canola oil	Corn oil	Soybean oil
0	8.5 ± 1.1^{b}	8.6 ± 1.4^{b}	8.7 ± 1.3^{b}
3	7.1 ± 1.6^{b}	6.7 ± 1.5^{b}	7.3 ± 1.8^{b}
6	4.8 ± 2.1^{b}	6.4 ± 1.8^{c}	5.5 ± 2.0^{b,c}
9	3.7 ± 1.9^{b}	5.5 ± 1.9^{c}	4.3 ± 1.7^{b,c}
12	2.9 ± 1.7^{b}	4.5 ± 2.2^{c}	3.5 ± 1.6^{b,c}

[a]A score of 10 = weakest and 1 = strongest off-flavor, and the data presented are the mean of two replicates with two duplications each ± standard deviation.
[b,c]Values in the same row with different superscripts were significantly different ($P \leq 0.05$).

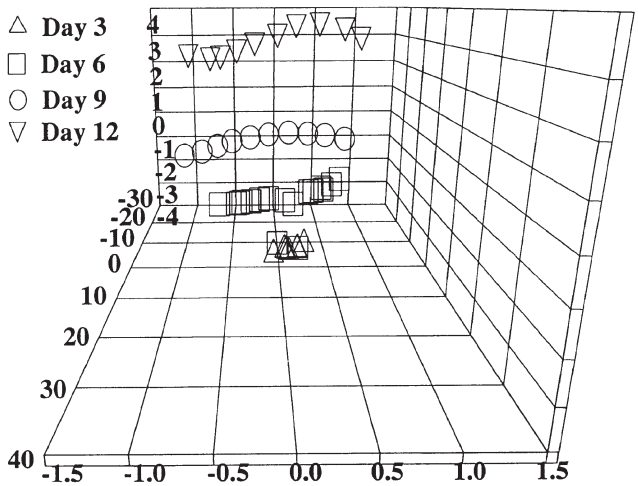

FIG. 1. Changes in AromaScan intensities of soybean oil stored at 60°C in the dark for 12 d using the AromaScan (AromaScan Inc., Hollis, NH).

AromaScan graphic program. The numbers only reflect relative positions in 3-D space. As oxidation progressed, the AromaScan intensity increased, moving to a relatively higher position.

The AromaScan data were processed by using the AromaScan graphic program, which was able to eliminate the variations of aroma in sample air and sample bags. Figure 2 was computed by using the normalized data of AromaScan intensity of soybean oil stored in an oven at 60°C for 12 d after subtracting the data from values recorded on day 0. The increase of AromaScan intensity in Figure 2 is reflected with the increase of the distance from the x-axis, which progresses with lipid oxidation. The AromaScan intensity does not have units, and both positive and negative deviations show similar changes in the intensity with the same distance from the x-axis.

The correlations between PV of vegetable oils and sensory evaluations, between PV and AromaScan intensities, and between AromaScan intensities and sensory evaluations are listed in Table 4. The linear correlation coefficients between PV and sensory evaluations were –0.93 for canola oil, –0.92 for corn oil, and –0.96 for soybean oil. All of these values are significant at a probability level of less than 0.05, which clearly showed that the panelists were able to detect the flavor changes corresponding to PV during oxidation.

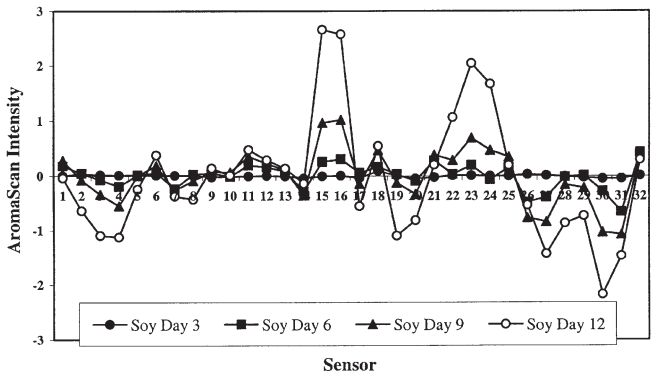

FIG. 2. Profiles of AromaScan intensity of soybean oil during storage at 60°C in the dark for 12 d. See Figure 1 for company address.

TABLE 4
Correlation Coefficients and Probabilities Between Different Measurements

Correlation	Sensor#	Canola oil	Corn oil	Soybean oil
PV-SEN[a]	—	–0.93 ($P = 0.0001$)	–0.92 ($P = 0.0002$)	–-0.96 ($P = 0.0001$)
AS-PV[b]	22	0.99 ($P = 0.0004$)	0.98 ($P = 0.0028$)	0.97 ($P = 0.0063$)
	23	0.99 ($P = 0.0021$)	0.99 ($P = 0.0011$)	0.99 ($P = 0.0021$)
	28	–0.91 ($P = 0.0314$)	–0.97 ($P = 0.0073$)	–0.95 ($P = 0.0153$)
AS-SEN[c]	22	–0.99 ($P = 0.0005$)	–0.89 ($P = 0.0410$)	–0.97 ($P = 0.0055$)
	23	–0.94 ($P = 0.0177$)	–0.90 ($P = 0.0369$)	–0.99 ($P = 0.0003$)
	28	0.81 ($P = 0.0976$)	0.76 ($P = 0.1345$)	0.94 ($P = 0.0179$)

[a]PV-SEN means correlations between peroxide values and sensory evaluations. The correlation coefficients were calculated according to the logarithmic values of both peroxide values and sensory evaluations.
[b]AS-PV means correlations between AromaScan intensities of different sensors measured by AromaScan and peroxide values.
[c]AS-SEN means correlations between AromaScan intensities of different sensors measured by AromaScan and sensory evaluations. For canola and soybean oils, the cube roots of values of AromaScan intensities and the logarithmic values of sensory evaluations were used to calculate the correlation coefficients. For corn oil, the values of the AromaScan intensities and the logarithmic values of sensory evaluations were used for calculating the correlation coefficients.

To determine correlations of the AromaScan intensities of vegetable oils with PV and sensory analyses, three sensors were selected (#22, #23, #28) from the AromaScan analyses because they are capable of detecting ketones and short-chain esters, which are common secondary decomposition products formed during lipid oxidation. PV correlated very well with AromaScan intensities (Table 4), ranging from 0.91 to 0.99 at $P \leq 0.05$, also indicating that both of these instruments were able to measure some aspects of lipid oxidation. Since PV is widely accepted as an index of lipid oxidation, these high correlations provide further confirmation that analysis of lipid oxidation using electronic noses has great potential.

The correlations between AromaScan intensities and sensory evaluations are also listed in Table 4. The correlation coefficients, ranging from 0.76 to 0.99, showed that the AromaScan was able to detect the progress of lipid oxidation in a fashion similar to that of the sensory panel.

In short, the "electronic nose" was capable of measuring changes in volatile compounds associated with oil oxidation and could be used to supplement data obtained from sensory evaluations. The data of AromaScan intensity obtained from the AromaScan correlated closely with PV and sensory evaluations.

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