The Evaluation of Frying Oils with the *p*-Anisidine Value

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ABSTRACT: This study was conducted to examine the relationship of *p*-anisidine value with headspace volatiles, sensory evaluation, and polymers. Partially hydrogenated soybean frying oil was used to fry shoestring potatoes. The oil was evaluated by *p*-anisidine value, headspace volatile analysis, sensory evaluation, and polymer analysis. *p*-Anisidine value was found to be correlated with hexanal ($r = 0.81$), heptanal ($r = 0.66$), *t*-2-hexenal ($r = 0.81$), *t*-2-heptenal ($r = 0.71$), *t*-2-octenal ($r = 0.92$), and *t,t*-2,4-decadienal ($r = 0.86$) contents. *p*-Anisidine value was correlated with overall odor intensity ($r = 0.82$) and correlated with fried food odor ($r = 0.53$) and burnt odor ($r = 0.43$). *p*-Anisidine value and polymers were also correlated ($r = 0.84$).

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p-Anisidine value (1) is a measurement of aldehyde content in an oil, principally 2,4-dienals and 2-alkenals. Aldehydes are secondary oxidation products produced during the oxidation of lipids. Aldehydes account for almost 50% of volatiles produced during lipid oxidation, and many flavor-significant aldehydes are produced from the oxidation of soybean oil (2). Peroxide value and *p*-anisidine value may be combined to form an oxidation or "Totox" value. The *p*-anisidine method was developed to replace a similar method, the benzidine test, because benzidine is a known carcinogen (3).

List *et al.* (4) found highly significant correlations (−0.68 for oil from sound soybeans and −0.65 for oil from damaged soybeans) between the *p*-anisidine value of soybean salad oils and their flavor scores. A study of non-heated palm oil (5) found a correlation of −0.54 ($P < 0.10$) between sensory quality scores and the *p*-anisidine value in refined, bleached, and deodorized (RBD) palm oils, and −0.61 ($P < 0.10$) in red palm oil. Correlation coefficients between flavor intensity scores and *p*-anisidine value were 0.60 ($P < 0.05$) for RBD palm oil and 0.47 ($P < 0.10$) for red palm oil. Hawrysh *et. al.* (6) reported that the *p*-anisidine value of oil extracted from Schaal-stored tortilla chips tended to support sensory scores, but the *p*-anisidine value of oil extracted from practically stored tortilla chips did not. Also, the *p*-anisidine value of stored used frying oil generally did not correspond to sensory data for stored tortilla chips. Holm and Ekbom-Olsson (3) stated that the *p*-anisidine value method may not be useful for observing off flavors during storage at normal temperatures, but mentioned that the *p*-anisidine method lends itself to the observation of oxidative changes in heated oils.

Dubois *et al.* (7) used Fourier transform infrared spectroscopy (FTIRS) as an alternative method of measuring *p*-anisidine value. FTIRS-predicted aldehyde concentrations could be converted to "apparent" *p*-anisidine value by partial least squares technique in standards spiked with selected aldehydes ($r^2 = 0.994$). *p*-Anisidine value in thermally stressed canola oil was also predicted by FTIRS by partial least squares technique ($r^2 = 0.994$).

However, little is known about the relationship of *p*-anisidine value with other methods of frying oil evaluation. The objective of this study was to correlate *p*-anisidine value with sensory scores, volatile headspace analysis, and polymer content in soybean frying oil.

EXPERIMENTAL PROCEDURES

Frying protocol. Three Intedge F175A electric fryers (Intedge Industries, Inc., Whippany, New Jersey) were each filled with 5.22 kg of partially hydrogenated soybean oil (Creamy Liquid Frying Shortening, 102-050, ADM, Decatur, IL) and used to fry shoestring potatoes (Kraft Prestige Extra Fancy, 6804 A-3, Glenview, IL) in 454-g batches five times each day for six days. Potatoes were fried at 7:00 A.M.,8:00 A.M.,12:00 P.M.,4:00 P.M., and at 5:00 P.M. The oil was maintained at 180°C 12 h a day. Samples were collected from each fryer after 1 h of heating and at the end of each day, for a total of 21 samples. The fatty acid methyl ester (FAME) composition of the soybean oil is given in Table 1.

p-*Anisidine value.* *p*-Anisidine value was determined in triplicate for each of the samples based on AOCS Official Method Cd 18-90 (1).

p-*Anisidine value and static headspace gas chromatograph analysis.* Samples for static headspace gas chromatograph (GC) analysis were spiked with internal standards and analyzed in triplicate on a Hewlett-Packard 5890 series II GC (Avondale, PA) (DB-5 column: 50 m × 0.32 mm (i.d.) × 0.52 µm film, starting at −50°C (6 min), followed by a temperature increase of 4°C/min to 85°C, and 25°C/min to 260°C (8

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TABLE 1
FAME Profile of Partially Hydrogenated Soybean Oil Used in *p*-Anisidine Value Study

Major peaks	Mean FAME profile (relative %)[a]
C16:0	11.87 ± 0.11
C18:0	7.41 ± 0.03
C18:1	40.49 ± 0.10
C18:2	37.9 ± 0.03
C18:3	2.33 ± 0.01

[a] $n = 3$; FAME, fatty acid methyl ester.

min); injector temperature = 200°C, flame-ionization detector (FID) temperature = 300°C, column pressure = 15 psi) equipped with a Perkin-Elmer (Norwalk, CT) headspace sampler HS 40 (vial temperature = 90°C, needle temperature = 110°C, transfer temperature = 115°C; GC cycle time = 10 min, heating time = 10 min, pressurization time = 7 min, injection time = 5 min, withdrawal time = 1 min, headspace pressure = 30 psi) and a Hewlett-Packard FID (Avondale, PA). Helium was the carrier gas.

p-*Anisidine value and sensory evaluation.* A ten-member descriptive panel was used to evaluate the odor intensity of soybean oil used for frying. The panelists were screened by the intensity ranking of oil samples. Panel training was done in one 1.5-h training session. Panelists were given odor attribute standards for (8): fried potatoes (fried), fish oil (fishy), hydrogenated soybean oil with iodine value <100 (hydrogenated), crude corn oil (burnt), commercial refrigerated bread dough (doughy), dilute acrolein, 0.2 ppm (acrid), and paraffin oil (waxy). Panelists then participated in the consensus scoring of three oil samples. The scorecard consisted of 15-cm unstructured line scales with word anchors of "none" to "intense" for overall intensity and each of the seven attributes listed previously. Panelists were asked to "zero" their noses between samples by smelling the back of their hand and waiting a minute between samples. The odor attribute standards and reference samples with their consensus scorecards were present for review during each of the testing periods.

Samples (10 mL) were labeled with random, three-digit codes and presented in amber glass vials with Teflon-lined lids that had been warmed in a water bath to 50°C. The samples were placed in foam blocks to minimize heat loss during evaluation. Presentation order was randomized among panelists.

p-*Anisidine value and polymer-content analysis.* Oil samples were diluted to 10 mg/mL with tetrohydrofuran (THF) for polymer-content analysis. This solution was separated on four connected gel-permeation chromatography (GPC) columns (Phenomenex P/no 00H-0442-KO Phenogel 5 100 A 300 mm × 7.8 micron s/no 47192, Phenomenex 00H-0442-KO Phenogel 5 100 A 300 mm × 7.8 micron s/no 171757, Phenomenex P/no 00H-0441-KO Phenogel 5 50 A 300 mm × 7.8 micron s/no 171756, and Phenomenex P/no 00H-0441-KO Phenogel 5 50 A 300 mm × 7.8 micron s/no 47191). The mobile phase was THF at 1.0 mL/min. A Waters 410 refractometer (Milford, CT) was the detector, and Millennium version 2.15.01 software (Waters Inc., Milford, CT) was used to integrate the data.

Statistics. The relationships of mean odor intensity scores, mean volatiles, and mean polymers to mean *p*-anisidine value were determined by statistical regression analysis and correlation coefficient analysis using a SAS (University of Illinois, Urbana–Champaign, 1993) statistical package.

RESULTS AND DISCUSSION

p-*Anisidine value and static headspace-GC analysis.* The regression models and correlations between *p*-anisidine value and headspace volatiles are shown in Table 2. The selected 2-alkenals and 2,4-dienal had highly significant correlations with *p*-anisidine value. *t*-2-Octenal had the highest correlation ($r = 0.92$, $P = 0.0001$)) with *p*-anisidine value, followed by *t,t*-2,4-decadienal ($r = 0.86$, $P = 0.0001$), *t*-2-hexenal ($r = 0.81$, $P = 0.0001$), and *t*-2-heptenal ($r = 0.71$, $P = 0.0002$). It was expected that the 2,4-dienal and the 2-alkenals would be significantly correlated with *p*-anisidine value. *A* study by Holm and Ekbolm-Olsson (3) showed that 2,4-dienals had the highest approximate molar absorbancy when reacted with *p*-anisidine, followed by 2-alkenals, and alkanals had the lowest approximate molar absorbancy.

Hexanal and heptanal were also highly significantly correlated to *p*-anisidine value ($r = 0.81$, $P = 0.0001$ and $r = 0.66$, $P = 0.0009$, respectively). Nonanal was not significantly correlated to *p*-anisidine value (0.33, $P = 0.1299$). Nonanal was the only selected aldehyde that would be primarily formed by the breakdown of oleic acid, and it was the only selected aldehyde not significantly correlated to *p*-anisidine value. The other aldehydes would be primarily formed by the breakdown of linoleic and linolenic acids.

TABLE 2
Regression Models and Correlation Between Mean Volatile Compounds and *p*-Anisidine Value

Volatile compound	Model (y = volatile compound (ppm), x = p-anisidine value)	Pearson correlation coefficient	Significance
t-2-octenal	$y = -0.002033x^2 + 0.166418x + 0.426961$	0.92	0.0001
tt,2,4-decadienal	$y = -0.04292x^2 + 2.941761x + 1.229471$	0.86	0.0001
t-2-hexenal	$y = 0.008613x + .193857$	0.81	0.0001
Hexanal	$y = 0.071206x + 1.811850$	0.81	0.0001
t-2-heptenal	$y = -0.003461x^2 + 0.233796x + 1.186553$	0.71	0.0002
Heptanal	$y = 0.007565x + 0.297576$	0.66	0.0009
Nonanal	$y = 0.036381x + 4.426942$	0.33	0.1299
Total selected volatiles	$y = -0.039358x^2 + 3.154369x + 11.283858$	0.89	0.0001

TABLE 3
Regression Models and Correlation Between Mean Sensory Scores and *p*-Anisidine Value

Odor	Model (y = odor intensity score, x = *p*-anisidine value)	Pearson correlation coefficient	Significance
Overall	$y = 0.030086x + 4.693492$	0.82	0.0001
Fried food	$y = 0.011479x + 1.791809$	0.53	0.0142
Burnt	$y = 0.006629x + 0.266730$	0.43	0.0527
Acrid	$y = -0.00795x + 1.692808$	−0.34	0.1290
Fishy	$y = 0.005803x + 1.666863$	0.16	0.4824
Doughy	$y = -0.002809x + 1.221347$	−0.16	0.5069
Hydrogenated	$y = 0.001682x + 0.746262$	0.10	0.6615
Waxy	$y = -0.000181x + 0.980309$	−0.01	0.9745

p-*Anisidine value and sensory evaluation.* Sensory evaluation is often the best method of evaluating food samples. However the expense, availability, and inconvenience of conducting a sensory panel often make it impractical, and alternative instrumental methods must be used instead. Therefore, it is important to know the relationship between an instrumental method, such as between *p*-anisidine value, and sensory evaluation.

Both the *p*-anisidine value and the overall odor intensity of the oil samples tended to increase with frying/heating time. The regression models and correlations between odor intensity scores and *p*-anisidine value are shown in Table 3. There was a positive correlation of 0.82 between *p*-anisidine value and average odor intensity score ($P = 0.0001$). Fried-food odor intensity showed a slight tendency to increase with frying/heating time, and the correlation between fried–food odor intensity and anisidine value was 0.53 ($P = 0.0142$). Fried-food flavor is associated with *t,t*-2,4-decadienal (9), and volatile analysis showed *t,t*-2,4-decadienal's correlation with *p*-anisidine value to be highly significant. The correlation between burnt odor intensity and anisidine value was 0.43 ($P = 0.0527$). None of the other aroma attributes were significantly correlated with anisidine value at $P < 0.10$.

p-*Anisidine value and polymer content analysis.* Both polymer content and *p*-anisidine values generally increased with greater heating/frying time. The following regression model shows that polymer content and *p*-anisidine value had a highly significant correlation coefficient of 0.84 and a significance of 0.001:

$$y = 0.003119x^2 - 0.076348x + 0.244847$$

where y = polymer content and x = *p*-anisidine value.

Conclusion. p-Anisidine value generally had strong relationships to the techniques of headspace volatile analysis (for all selected aldehydes but nonanal), polymer analysis, and sensory evaluation of overall odor intensity.

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