An Analysis Scheme for Estimation of Crude Oil Quality

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A seed analysis scheme was designed to rapidly estimate the quality of extracted oil. Factors of crude oil quality evaluated were: free fatty acids, oxidative status (Totox value), color, and phosphatides (soybean) or wax (sunflower). Soybean and sunflower seeds subjected to extended storage at varying moisture contents were sampled at incremental time periods to yield fifty storage-damaged samples of each oilseed. Oil was extracted from 50-g lots of each sample and analyzed for the crude oil quality factors according to standard methods. Alternative instrumental and chemical analyses of the quality factors were correlated with the standard methods. Hexanal content, measured by headspace-gas chromatographic analysis of the ground full-fat meal, was correlated to the oxidative status. Crude oils recovered by rapid extraction, using sonication, and desolventation were monitored by spectrophotometry for color correlation. Free fatty acid content was determined by titration methods and monitored by spectrophotometry. Modified turbidimetric methods estimated the phosphatides (soybean) or wax (sunflower seed) contents. The analysis scheme provides for the rapid estimation of oil quality as impacted by various pre- and post-harvest events that cause deterioration of oilseeds.

KEY WORDS: Color, damage, free fatty acid, oxidation, phospholipids, phosphatides, soybean oil, spectroscopy, sunflower, sunflower oil.

Soybeans and sunflower seeds are marketed on the basis of United States Department of Agriculture (USDA) Grading Standards (1) which assess the physical characteristics of the seeds, i.e., test weight, damaged seed, foreign material and split content. Grade factors can create incentives for improved quality, and given comparable world market prices, can be used as a competitive tool in increasing market share of world trade. These standards affect the long-term future of the industry and they play an important role in market efficiency, improved quality and competition among sellers. While the purpose of standards is to define uniform and accepted descriptive terms to facilitate trade, they should also provide tools for the market to create incentives to improve the overall quality of an oilseed. Standards should also provide information for the end user to help determine end product yield and quality. The quantity and quality of oil at the time of grading have economic significance in determining the value of the oilseed. The soybean grading system presently contains grade factors, such as seed damage from heat, insect, weather, etc., that may or may not be relevant to the quantity of oil in the seed and further, may or may not be relevant to oil quality. A review of the literature (2-24) indicates that the following factors are of critical importance to processors in ascertaining the quality of crude oils: free fatty acids, oxidative status, color, phosphatides (soybean) and wax content (sunflower). An oilseeds grading system to assess the quality of oil for end use purposes would require rapid and efficient procedures to measure oil quality factors.

Present near-infrared (NIR) technology is capable of rapidly measuring the quantity of oil in an oilseed (25), but no system is available to rapidly measure the factors affecting oil quality in addition to quantity. We report here an improved analysis scheme for the estimation of crude oil quality.

EXPERIMENTAL PROCEDURES

Soybeans and sunflower seeds were stored in a forced air oven at ambient temperature at specific moisture levels (13%, 16% and 20% for soybeans and 7%, 9%, 12% and 13% for sunflower seeds). Samples (200 g) were removed periodically over extended times; soybeans were dehulled and flaked and extracted with hexane (Soxhlet extractor); while sunflower seeds were ground without dehulling and extracted with hexane in a Soxhlet extractor. Fifty storage-damaged soybean samples and 50 storage-damaged sunflower seed samples were analyzed by traditional methods and by methods of a proposed analysis scheme to produce a learning set of samples. Oil quality factors were evaluated by traditional methods as follows: free fatty acid content (FFA) by AOCS Method Ca 5a-40; oxidative status measuring total oxidation (Totox) as peroxide value (PV) by AOCS Method Cd 8-53 and as anisidine value (AV) by the method of List *et al.* (26); wax content in sunflowers by Morrison and Robertson (11); phosphatide content in soybeans by AOCS Method Ca 12-55; color in soybeans by AOCS Method Cc 13c-50 (27) and in sunflower seeds by Ostric-Matijasevic *et al.* (17).

The proposed scheme of analysis uses measurement of volatiles for oxidative status, spectrometric absorbances for FFA and oil color, and turbidimetric measurements for phosphatides and wax content.

Analysis of volatiles was performed in a Perkin-Elmer Sigma 2000 gas chromatograph (GC) (Perkin-Elmer Corp., Norwalk, CT) equipped with a HS-100 automatic headspace sampling accessory (28). Ground meal from the whole soybean or sunflower seed (0.5 g) was weighed into a 20-mL vial and sealed with a Teflon-coated septum; the vial was then placed in the automatic sampler. Each sample was heated at 90°C for 30 min; sampling of the headspace volatiles was made by pneumatic helium injection, and the volatiles were eluted onto a DB-1701 capillary column (14% cyanopropylphenyl), which was 30 m × 0.32 mm with 1-micron film thickness (J&W Scientific Co., Anaheim, CA). The injection was made in the splitless mode with a helium velocity of 28 cm/sec at 100°C. The GC oven was held at 50°C for 5 min, then temperature programmed to 250°C at 5°C/min. Duplicates were run for each sample. Quantitation of volatiles was accomplished by adding hexanal in hexadecane

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[1]The mention of firm names or trade products does not imply that they are endorsed or recommended over other firms or similar products not mentioned.

(approx. 30 mg/mL) to 0.5 g silicic acid in increments of 5 μL up to 50 μL. Peak area of hexanal from headspace-gas chromatographic (HS-GC) data was correlated to the ppm of hexanal.

An abosorbance method has been developed for prediction of the FFA content in crude oil. Crude oil (0.5 g) was weighed into a 10-mL volumetric flask; 1.0 mL of indicator solution (0.1 g bromocresol green in 200 mL of 95% ethanol with the pH adjusted to 7.5 by means of 0.01 N sodium hydroxide) was added; 1.0 mL 1-octanol was measured into the volumetric flask, which was filled to the volume line with spectrograde hexane and mixed for 10 sec in a vortex mixer (Genie Scientific Industries, Inc., Bohemia, NY). Absorbance measurements were obtained at 622 nm with a Bausch and Lomb Spectronic 2000 Spectrophotometer (Bausch and Lomb Company, Rochester, NY).

Phosphorus in crude soybean oil was determined rapidly in a Hach Ratio Turbiditric Meter (Hach Model 18900 Ratio Turbidimeter, Hach Chemical Co., Loveland, CO), which measures the light scattered by the fine phospholipid precipitate (29). Crude soybean oil (0.33 g) was weighed into a 50-mL volumetric flask and acetone was added; the flask was stoppered and shaken. The mixture was poured into the sample cell, capped, shaken and placed in the instrument. After stabilization of 30 sec, the reading was taken.

Wax content in sunflower oil was determined in the Hach Turbidity instrument (30); 1.5 g of crude sunflower oil was weighed into a 25-mL volumetric flask and filled with test solvent (12.5% dewaxed sunflower oil by vol in acetone). The mixture was poured in the cell vial and well shaken; the vial was placed in the instrument and the reading was made when it stabilized. Samples were run in triplicate. Standard mixtures of wax in sunflower oil were correlated (r^2=0.98) to turbidity readings.

The spectrometric method for the determination of oil color is an AOCS official method (Cc 13c-50). Spectral absorption measurements made at four wavelengths are combined in a mathematical expression to yield an index that correlates with Wesson color values. The procedure was modified for crude soybean oil by adding 33% crude oil (wt/vol) to hexane and adjusting the measurements by 0.33. The small sample size used in this study was an insufficient amount for color measurement with a commercial Lovibond instrument. For sunflower oil, evaluations were made at a single wavelength, 455 nm for carotenoid pigment (16).

An analysis scheme was devised to quickly estimate the quality of the oilseeds. Fifty grams of oilseeds were ground with a small Varco electric dry food grinder (Varco, Inc., Belleville, IL); 100 mL hexane was added to 44 g of the meal and the mixture was sonicated for 5 min (Cole Parmer Instrument Co., Chicago, IL). After extraction, the miscella was filtered through a Buchner funnel and desolventized by roto-vap. The crude oil was evaluated by the described titration method for FFA content and by turbidity for phosphorus in soybean oil and waxes in sunflower; color was determined on the crude oil by the spectrometric methods. One gram of the meal was used for volatile analysis by headspace-GC to measure oxidation and 5 g was reserved for NIR analyses to determine oil and protein content (25). The proposed analysis scheme was then applied to the evaluation of soybean and sunflower seed samples collected from various sources during the 1985 and 1986 crop years. One hundred samples each of soybeans and sunflower seed were randomly divided so that every tenth sample was divided into five portions for replicate analysis. Estimations of oil quality factors were obtained from derived correlation equations.

RESULTS AND DISCUSSION

Samples from the learning set of soybeans and sunflower seeds were analyzed; results from the traditional methods were correlated with those obtained from the proposed quick methods and regression equations were derived.

Several individual volatile compounds generated by oxidation and total volatile concentration of the ground oilseeds were evaluated and correlated with PV, AV, and Totox. In previous work, hexanal was shown to be one of the primary volatiles formed in oxidized soybean and sunflower oils (28). The best equations in the current work were obtained when hexanal concentration (ppm) determined by volatile headspace analysis of the meal was correlated with Totox. Regression equations are: Totox = 1.1 + 0.21 × hexanal(ppm) for soybeans [standard deviation (SD) = 1.2; r^2 = 0.94] (Fig. 1) and Totox = 1.6 + 0.85 × hexanal (ppm) for sunflower seeds [SD = 1.3; r^2 = 0.72] (Fig. 2). High-quality crude soybean oils will generally have a Totox value of less than 3; for crude sunflower oil, the value is generally less than 5. Use of the headspace volatile-GC analysis to measure hexanal content on ground meal gives a good prediction of the oxidative status of the extracted crude oil.

Absorbance (abs) was correlated with titratable FFA as shown in Figure 3 (soybean, r^2 = 0.86) and Figure 4 (sunflower, r^2 = 0.89). Free fatty acid content was determined with correlation equations: FFA = 2.27-1.51 × abs for soybeans (SD = 0.19) and FFA = 2.39-1.75 × abs for sunflower seeds (SD = 0.16). This technique is applicable with oils having FFA contents up to 2.0%, well above the acceptable limit for quality crude oils. Oilseeds yielding oils with higher FFA would most likely fail other quality evaluations as well.

Phosphorus content is measured by turbidity, determined as nephelometric turbidity units (NTU) and is calculated directly from the equation, P = 316.4 + 5.89

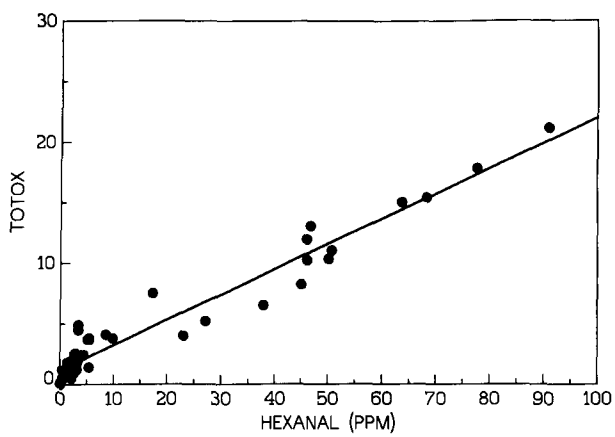

FIG. 1. Estimation of soybean Totox by headspace-gas chromatography derived from the learning samples. Y = 1.1 + 0.21 X; r^2 = 0.94.

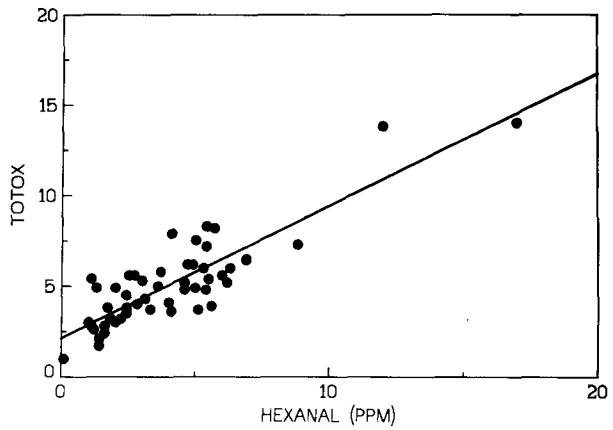

FIG. 2. Estimation of sunflower Totox by headspace-gas chromatography derived from the learning samples. Y = 1.6 + 0.85 X; r^2 = 0.72.

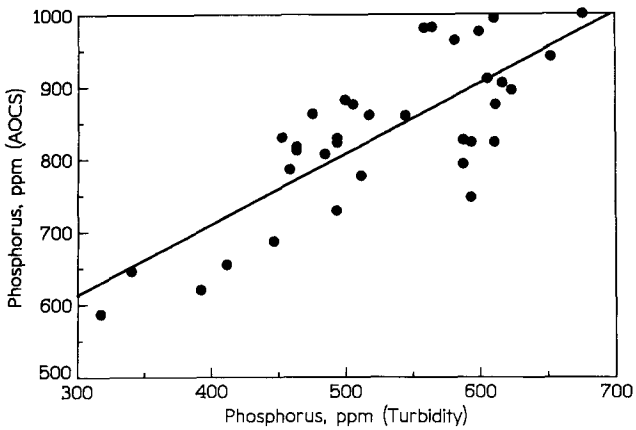

FIG. 5. Relationship of phosphorus determinations on oil extracted from flaked beans (AOCS method) vs oil extracted ultrasonically from ground beans (turbidimetric method).

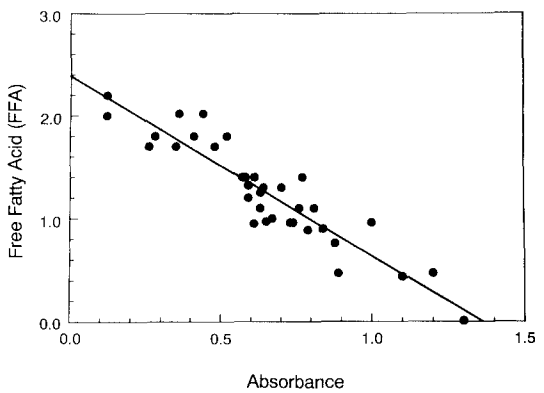

FIG. 3. Correlation titratable FFA vs absorbance at 622 nm derived from the learning samples — soybean. Y = 2.27 - 1.51 X; r^2 = 0.86.

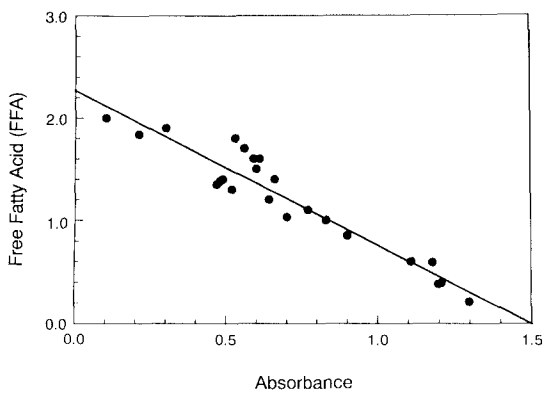

FIG. 4. Correlation titratable FFA vs absorbance at 622 nm derived from the learning samples — sunflower. Y = 2.39 + 1.75 X; r^2 = 0.89.

× NTU, which was reported by Sinram (29). A phosphorus content of less than 400 ppm is indicative of poor oil quality (31). Crude oil extracted from ground soybeans was lower in phosphorus content, as determined by turbidity, than oil extracted from flakes. As reported, particle size of soybeans may affect the amount of phospholipids in the extracted oil (32). Therefore, turbidimetric phosphorus content in the oil extracted from the ground beans by the ultrasonic method was related with AOCS phosphorus content in oil obtained by Soxhlet extraction of flakes from the same beans (Fig. 5).

Wax content of sunflower oil was closely related to turbidity readings. Wax content in a sunflower oil sample was predicted by linear regression; wax = 40.1 + 39.2 × NTU; standard deviation = 1.9; r^2 = 0.999 as reported by Moulton (30).

The correlation of photometric color to Wesson red color has been reported (33). Good quality crude soybean oils will have a red color of 10 or less. Deterioration of sunflower seed is marked by an increase in the percentage transmittance due to destruction of the carotenoids in the oil.

Soybean and sunflower seed samples were collected from various sources during the 1985 and 1986 crop years and evaluated by the quick analyses techniques; estimations of oil quality were determined from the derived correlation equations that were obtained from the learning set of samples. Reproducibility of the soybean results is shown in Table 1. The average standard deviation is +/-0.4 for Totox, +/-27 for phosphorus and +/-1.5 for Wesson red color measurement. To determine the accuracy of the results, 70 of the 100 soybean samples previously analyzed by the quick estimated methods were also checked with the traditional analytical methods. Two-variable data analysis was made on the values obtained by "traditional" and "quick" methods.

The Totox values estimated from hexanal concentration (mean = 4.4, SD = 5.1) were not consistently (as determined by analysis of variance, $p<.05$) different from the Totox values from the analytical method (mean = 3.9, SD = 6.9); the values from the two methods were correlated (r = 0.83). The phosphorus values estimated from NTU units (mean = 817, SD = 122) were not significantly different from the analytical phosphorus values (mean = 839, SD = 148); correlation coefficient from the two methods was 0.61.

The quick analysis scheme for sunflower seeds was almost the same as for soybeans except nephelometry was used for determining waxes and color was measured by one wavelength at 455 nm. Reproducibility of the

TABLE 1

Reproducibility of Soybean Results[a]

Totox (mg/meq)	Phosphorus (ppm)	Color (Wesson red)
1.2 (0.1)[b]	797 (25)	8 (1.0)
1.7 (0.3)	756 (13)	8 (1.5)
1.7 (0.2)	806 (13)	8 (2.1)
2.6 (0.2)	910 (21)	8 (1.0)
2.2 (0.2)	896 (31)	6 (0.8)
7.1 (1.5)	731 (27)	7 (1.1)
1.7 (0.1)	885 (28)	8 (1.8)
2.6 (0.3)	922 (39)	9 (2.7)
1.4 (0.1)	683 (36)	7 (1.1)
11.6 (0.9)	803 (33)	9 (1.8)

[a]Average of five trials on every 10th sample/100 sample set.

[b]Numbers in parentheses represent standard deviation.

results is shown in Table 2. The average standard deviation was +/–0.66 for Totox, +/–113 for wax and +/–0.06 for color measurement at 455 nm. To check the accuracy of the estimated data, Totox was determined analytically for sunflower oil from 25 samples of the 100 sunflower samples analyzed by the quick methods and was related to the estimated Totox value; there was no significant difference at $p<0.05$. The statistical result from a two-variable data analysis showed that the Totox value estimated from the hexanal concentration in the sunflower seeds (mean = 5.5, SD = 2.9) was not different from the analytical Totox (mean = 6.7, SD = 3.8); the two methods were correlated ($r = 0.71$).

TABLE 2

Reproducibility of Sunflower Results[a]

Totox (mg/meq)	Wax (ppm)	Color (abs. at 455 nm)
7.1 (0.3)[b]	1804 (105)	1.7 (0.16)
5.1 (0.3)	1255 (96)	0.6 (0.07)
2.8 (0.0)	1475 (115)	1.5 (0.08)
12.0 (1.7)	1506 (154)	1.2 (0.05)
4,5 (1.3)	1553 (125)	1.3 (0.09)
8.2 (0.4)	879 (91)	0.6 (0.04)
10.2 (1.2)	1757 (181)	1.3 (0.02)
5.9 (0.8)	1248 (116)	0.7 (0.03)
6.6 (0.5)	1004 (77)	0.9 (0.03)
2.9 (0.1)	1091 (72)	0.8 (0.08)

[a]Average of five trials on every 10th sample/100 sample set.

[b]Numbers in parentheses represent standard deviation.

The procedures developed in this study permit the measurement of critical oil quality factors. Use of the headspace volatile-GC analysis to measure hexanal content on ground meal gives a good prediction of the oxidative status of the crude oil obtained from the oilseed. Photometric color measured on crude soybean oil is a rapid method to determine Lovibond (Wesson) red color. Darkening of oil color is related to immature soybeans and/or damage. The measurement of transmittance at 455 nm of crude sunflower oil is indicative of damage to sunflower seed. Phosphorus content of crude soybean oil can be measured by nephelometry. Phosphorus contents below 400 ppm indicate deterioration to phosphatides arising from damage to soybeans. Wax content of crude sunflower oil can be measured by a modified nephelometric method. High levels of wax are related to immature sunflowers and indicate lower quality seed. Free fatty acid content can be monitored by absorption methods.

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