SHORT COMMUNICATION

FTIR Estimation of Free Fatty Acid Content in Crude Oils Extracted from Damaged Soybeans

A.C. Lanser*, G.R. List, R.K. Holloway and T.L. Mounts

National Center for Agricultural Utilization Research, Agricultural Research Service, U.S. Department of Agriculture,[1] Peoria, Illinois 61604

A user-interactive computer-assisted Fourier transform infrared (FTIR) method has been developed for estimation of free fatty acids (FFA) in vegetable oil samples by deconvolution of the infrared (IR) absorbances corresponding to the triglyceride ester and FFA carbonyl bonds. Peak areas were used to determine FFA as a percentage of the total carbonyl areas in weighed standards of refined, bleached, deodorized soybean oil containing from 0 to 5% added oleic acid. These data for percent FFA by FTIR were compared to corresponding FFA data obtained by two titration methods—the AOCS Official Method Ca 5a-40 and the Official Method with a slight modification. Correlation coefficients were 0.999 for the Ca 5a-40, 0.999 for the modified and 0.989 for the FTIR methods. FFA in samples of crude soybean oils extracted from damaged beans (0.5 to 2.1% FFA) were measured by FTIR and compared to data obtained by titration of the same samples (correlation coefficient, 0.869).

KEY WORDS: Deconvolution, free fatty acid, FTIR, soybean oil, triglyceride.

Crude oils extracted from field- or storage-damaged soybeans have higher free fatty acid (FFA) content (1,2), which results in increased losses during refining and lower flavor quality in finished edible oils (3). We have had some success in measuring the free fatty acid content in extracted crude oils by Fourier transform infrared (FTIR) through deconvolution of the carbonyl bands at 1710 cm^{-1} (for FFA) and 1746 cm^{-1} (for triglyceride ester) (4) and, thus, in assessing the extent of oil deterioration.

EXPERIMENTAL PROCEDURES

Materials. Fatty acids and soybean oils used in these experiments were obtained as follows: oleic acid was purchased from Nu-Chek Prep, Elysian, MN—>99%, verified by gas chromatography (GC) and thin-layer chromatography (TLC); refined-bleached-deodorized soybean oil (RBD-SBO) was prepared at National Center for Agricultural Utilization Research (NCAUR), Peoria, IL, (titrated at 0.11% FFA); crude oil samples were extracted from soybeans stored at 13 to 20% moisture for from 5 to 50 days (5).

A set of 11 mixtures used as standards was prepared by adding weighed amounts of oleic acid to RBD-SBO to give FFA levels from 0.11 to 5.13%.

Methods. Titrations were performed according to the Official AOCS Method for free fatty acids (Ca 5a-40) (6) or a modified version of this method, which used 6–7 g of oil for all samples.

A Perkin-Elmer Infrared Fourier Transform Model 1750 Spectrometer (Perkin-Elmer, Inc., Oak Brook, IL) with a fast recovery, deuterated triglycine sulfate (FR-DTGS) detector was used for the analyses. This instrument was connected to a Perkin-Elmer Model 7300 professional computer equipped with its related Infrared Data System software (7). Spectra were taken of a thin layer of oil created from one drop pressed between two KBr plates. Each spectrum resulted from averaging 50 scans taken under the preselected conditions of a wavenumber interval of 1 and a medium Beer-Norton apodization function.

Software resident in the 7300 computer provides a user-interactive procedure to distinguish overlapping spectral bands through deconvolution. The "enhance" function of this software allows the user to combine data points to smooth the spectral band (width parameter) and to decrease the observed width of the spectral bands to sharpen and clarify peaks (factor parameter). The criteria used for selecting the "enhance" parameters for each individual sample were those suggested in the user manual (7): The width parameter was increased until it matched the half-width of the absorption band as determined by no further increase in band height; and the factor parameter was increased until the overlapping peak was most prominent or baseline noise became excessive. The effect of each selected change was followed on the computer monitor. This deconvolution procedure was applied to absorbance spectra between 2000 and 1600 cm^{-1}. Once optimum deconvolution of the free fatty acid and the triglyceride carbonyl bands was achieved, exact wavenumbers were manually specified, thus defining the end-points for the computer to calculate band areas. FFA was expressed as a percentage of the total carbonyl areas.

RESULTS AND DISCUSSION

When this FTIR method was tested against two titration methods on a set of weighed standards (Table 1), the average difference and standard error, as well as the 95% confidence limits for these data were: Ca 5a-40 titration, 0.09 ± 0.02 percentage points (0.07 to 0.24); modified titration, 0.27 ± 0.06 (−0.12 to 0.66); FTIR areas, 0.09 ± 0.08 (−0.63 to 0.45). The FTIR method had the largest variation from the standards when low (<0.7%) FFA content was being determined. Unfortunately, this is especially inherent in this method because identifying a small shoulder on the ester absorbance and trying to obtain an accurate area calculation is extremely difficult.

Nineteen samples of crude soybean oil extracted from beans damaged during storage were analyzed for FFA by the FTIR method and the modified AOCS method (Table 2). Agreement, in general, is quite good on these samples (correlation coefficient, 0.869). The average difference between the titration and FTIR estimates was 0.02 ± 0.06

*To whom correspondence should be addressed at National Center for Agricultural Utilization Research, Agriculture Research Service, U.S. Department of Agriculture, 1815 North University Street, Peoria, IL 61604.

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

TABLE 1

Comparison of Titration and FTIR Methods for Estimation of Percent Free Fatty Acid (Oleic Acid) in Refined-Bleached-Deodorized Soybean Oil

		By AOCS titration methods		By areas
Sample number	Weighed	Ca 5a-40[a] (r = 0.999)[b]	Modified (r = 0.999)	FTIR (r = 0.989)
1	0.11	0.03	0.10	0.50
2	0.41	0.35	0.38	0.90
3	0.81	0.77	0.72	0.80
4	1.14	1.07	0.89	1.40
5	1.64	1.61	1.44	1.80
6	2.13	1.92	1.88	2.00
7	2.76	2.55	2.43	2.70
8	3.01	3.00	2.75	2.60
9	3.79	3.80	3.30	3.80
10	4.51	4.40	4.05	4.80
11	5.13	4.98	4.55	5.10

[a]Average of three titrations.

[b]Correlation coefficients with weighed values.

TABLE 2

Estimation of Free Fatty Acids in Crude Soybean Oils from Stored Beans

		Free fatty acid (%) by:	
Bean type	Days stored	FTIR	Titration
Century '83	5	0.8	0.88
Century '83	7	1.2	1.01
Century '83	11	0.8	0.60
Century '83	14	0.8	0.85
Century '83	19	1.8	1.81
Century '83	22	1.1	1.28
Century '83	26	1.7	2.04
Century '83	27	1.2	0.75
Century '83	35	1.4	1.40
Century '83	41	1.2	0.80
Century '83	47	0.8	0.80
Century '83	50	1.2	1.35
Century '84	8	0.7	0.50
Century '84	36	1.2	1.23
Century '84	49	1.2	1.25
Decatur	8	1.1	0.70
Decatur	15	1.1	1.37
Decatur	27	1.4	1.30
Decatur	49	1.7	2.14

with a 95% confidence interval of −0.50 to 0.54. Thus 95% of the time, the rapid FTIR estimate of FFA should be within 0.5 percentage points of the titration estimate. Although the percent error of these values may be large, the actual estimated FFA content is good, and as a practical matter, is not a limiting factor for the use of FTIR to estimate hydrolytic deterioration of crude soybean oil.

New technologies and computer capabilities associated with modern instruments provide new analytical approaches which, with prudent use, allow quicker and less tedious analyses. As shown in this study, a computer-assisted semi-automatic FTIR analysis procedure that requires only one drop of crude soybean oil to obtain estimates of FFA can provide a measure of hydrolytic deterioration of oil and, thus, a quick indication of oils that may present processing difficulties. As FFA increases, the individual carbonyl bands should become more easily discernible and provide more accurate and expanded uses of this FTIR method.

REFERENCES

1. Krober, O.A., and F.I. Collins, *J. Am. Oil Chem. Soc. 25*:296 (1948).
2. Robertson, J.W., W.H. Morrison III and D. Burdick, *Ibid. 50*:443 (1973).
3. Sanders, J.H., *Ibid. 21*:357 (1944).
4. Dyer, J.R., *Applications of Absorption Spectroscopy of Organic Compounds*, Prentiss Hall Inc., Englewood Cliffs, NJ, 1965, pp. 34–35.
5. Snyder, J.M., T.L. Mounts, R. Holloway and K. Joyce, *J. Am. Oil Chem. Soc. 64*:682 (1987).
6. *Official and Tentative Methods of the American Oil Chemists' Society*, 3rd edition, edited by R.O. Walker, American Oil Chemists' Society, Champaign, IL, 1981.
7. In *Instructions: Infrared Data System (CDS-3 Application Program-Rev. D)*, Perkin-Elmer Corporation, Oak Brook, IL, January, 1985, Section 5, p. 199.

[Received September 20, 1990; accepted March 19, 1991]