Determination of Oil Content of Seeds by NIR: Influence of Fatty Acid Composition on Wavelength Selection[1,2]

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The oil content of nine different types of oilseeds has been determined by near-infrared reflectance (NIR) spectroscopy. A Northstar computer was used to select the wavelengths that best represent the oil content in these seeds. Selected wavelengths were often in the same area of the spectrum, but calibrations differed with respect to the number of wavelength points required and their order of selection. Wavelength assignments for typical functional groups in fatty acids are discussed. The fatty acid composition and the predominant fatty acid component appeared to influence the wavelengths used for the estimation of oil content in each seed type. The mathematical treatments used appeared to affect absorption maxima of all seed types. Spectra of seed oils and their fatty acids indicated variation and closeness of absorption maxima.

KEY WORDS: Derivative, monochromator, spectroscopy, wavelength.

One of the major concerns of oil chemists is the time-consuming methods available for routine analysis of seeds. For example, most official extraction methods take 8–10 hr to complete, yet it takes only about 5 min to unload a truck or railcar at an elevator. Introduction of nuclear magnetic resonance (NMR) technology in recent years has reduced the analytical time significantly, but not nearly enough to meet today's market requirements. This is because NMR analysis requires a minimum of 3 hr to dry the seeds prior to analysis. To by-pass this time lapse, the United States' Federal Grain Inspectors (FGIS) use NMR to determine oil content on sun-dried seeds and then correct for moisture from a chart. The moisture can also be determined (in 5 min) by use of microwave ovens; however, there is still room for improvement. The advent of near-infrared reflectance (NIR) technology in the grain industry in recent years appears promising as an analytical tool for the oilseed industry. NIR instruments are easy to operate, require no chemicals, are very rapid and, as a result, are cheaper to use than chemical procedures.

NIR technology is based on the absorbance of light energy at a given frequency by molecules (or radicals) having a permanent dipole which vibrates at the same frequency. The difference between incident light and light reflected from the surface of the sample is analogous to the familiar Beer-Lambert concept of absorbance/transmittance.

The technique was developed in 1964 for the measurement of moisture (1). It was then applied to the determination of moisture in grains and seeds in 1965 (2) and subsequently introduced to the grain industry in 1973 as a means of rapid analysis for oil, protein and moisture (3).

Since its original development, NIR technology has offered significant advantages for food analysis and has become an extremely important adjunct to the grain and food industries. At present, commercial NIR instruments available have capabilities to measure components such as protein, oil, carbohydrates, amino acids, fiber components and many other parameters in foods and food products. The technique is utilized as an analytical method for the estimation of the composition of feeds, pharmaceuticals and in medical research (4–8), as in the plastics, petrochemical and other fields. However, NIR has not been extensively applied to the analysis of oilseeds. The present study was carried out to determine the optimum wavelengths and mathematical treatments for the analysis of oilseed composition; and to determine the influence of fatty acid composition on the wavelengths thus selected.

MATERIALS AND METHODS

Oilseeds studied included the following commodities: cottonseed (*Gossypium hirsuta* L.) obtained from Syria and Venezuela; groundnut or peanut (*Arachis hypogaea* L.) obtained from the United States and South Africa; rapeseed (or canola, *Brassica napus* L.), safflower (*Carthamus tinctorius* L.) and flaxseed (*Linum usitatissimum* L.) obtained from Canada; soybean (*Glycine max* L.) and sunflower (*Helianthus annuus* L.) both obtained from Canada and the U.S.; sesame seed (*Sesamum indicum* L.) obtained from Mexico and Iran; and palm kernel (*Elaesis guineensis* L.) from Indonesia.

Reagent grade solvents were used in all oil extractions. Equipment and instruments used included Krups impeller-type mill, 75 mL capacity; Christie-Norris hammer mill fitted with a special screen with 8 mm round holes; vacuum oven; Goldfisch oil extraction apparatus; NIR scanning monochromator-Research Composition Analyzer (RCA) model 6250 from Pacific Scientific Instruments Inc. [currently called NIRSystems Inc. (Silver Spring, MD), a division of Perstorp]; a Northstar computer; and a bench-type quantitative NIR grain analyzer, DICKEY-john GAC III Model 781 from DICKEY-john Corporation, (Auburn, IL). An automated gas chromatograph was used to determine fatty acid profiles of all seeds.

Analytical methods. Prior to grinding, seeds were cleaned manually to remove dirt and other foreign materials. Approximately 25 g of the clean sample was ground in a Krups mill for 1 min (four 15-second bursts, each followed by thorough mixing to prevent clogging and expelling of oil). Palm kernel was initially ground,

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using the Christie-Norris mill, into a coarse meal and then further pulverized finely in the Krups mill.

The moisture content of the seed was determined on the ground sample, although most of the officially approved methods for moisture analysis require use of whole seeds. Preliminary tests showed that a significant amount of moisture still remained in the whole seed after drying, whereas virtually all the moisture was removed when the seed was ground prior to dehydration. Our aim was to remove all the free moisture present in order to ensure a good calibration. Ground samples were therefore dried at 100°C (± 2°C) for 16 hr in a vacuum oven and the water content subsequently calculated from the difference in weight.

For the purpose of this study, it was desirable to utilize one uniform method for oil extraction for all seed types. To ensure the maximum removal of neutral lipid material, anhydrous ether was used as solvent for extractions. Seeds were ground finely with a Krups coffee mill, vacuum-dried at 100°C for 16 hr in order to ensure complete removal of water and, subsequently, oil. Four grams of dried material were weighed, in duplicate, and extracted for 16 hr using Goldfisch reflux apparatus. Oil content was calculated on a dry basis and also converted back to "as is" basis (i.e., oil content of seed when moisture is present) using the moisture content value previously determined. Fatty acid composition of oils was determined by use of gas chromatography method as described by Hougen and Bodo (9).

In this method, 20 mg of oil is pipetted into a culture tube, then 5 mL isooctane is added and mixed vigorously. To this mixture is added 0.5 mL methanolic base ($NaOCH_3$), two drops of bromophenol blue indicator, 0.4 mL of 1N HCl and 0.6 mL aqueous sodium carbonate (0.15 M) is added to this mixture, and each addition is followed by thorough mixing. Then, 7.5 mL water is added to bring the isooctane layer to the top. One microliter of the solvent layer is then injected into the GC for separation into fatty acid components. The GC operating conditions used in this study were: a flame ionization detector at 250°C, a 15 m × 0.32 mm i.d. open tubular fused silica column with 0.5 μm Supelcowax 10 coating. Column temperature was 1 min at 220°C, then raised to 250°C at 10°C/min and held at 1 min. Helium gas (99.999% purity) was the carrier at a velocity of 52 cm/second and 230°C. Injection port temperature was 250°C, with a make-up gas flow rate of 18 mL/min He and a column head pressure of 32 KPa (4.75 psi).

Calibration of the NIR instruments involved the establishment of a mathematical relationship between NIR response and the standard or reference method results. This was followed by sample analysis which involved the use of the calibration constants for the establishment of relationship from which the concentrations of constituents were determined. Two sets of samples were used. One set of 35–65 samples (depending on availability) served as the calibration set, while the second set of 15–40 samples were used as the analytical (prediction) file. Calibration sets were selected on the basis of maximum variation in constituent concentration, with uniform distribution across the range. Both instruments were calibrated to measure oil, moisture, protein and crude fiber simultaneously.

Freshly-ground seed meals were scanned through both instruments, i.e., the scanning monochromator and the DICKEY-john discrete filter quantitative analyzer. NIR optical data for moisture, oil and protein were regressed against reference method data using linear multiple regression statistics. Composition of the "unknown" (prediction set) samples was then determined using regression equations obtained from the calibrations. The results were compared to those from the reference analyses and any bias was corrected in the instrument before further analyses were conducted. Oils extracted from the seeds were also scanned, and the spectra compared to those of the unextracted meal and those of individual fatty acids.

RESULTS AND DISCUSSION

The concentration of constituents (i.e., oil, protein, water, fiber) in all seeds, obtained from chemical analyses, were found to be comparable to reported data in the literature. Fatty acid composition obtained from GC analysis were also comparable to levels obtained by other workers in the field (Table 1, refs. 10–20). Interlaboratory variations in component concentration might be attributed to factors such as varietal, seasonal and locational differences. For example, compare the high oleic acid (C18:1 Ç 72.9%) variety of safflower seed used in this study to the generally low oleic acid (C18:1 Ç 10.8%), high linoleic acid (C18:2 Ç 79%) varieties reported in the literature (Table 1).

A set of regression constants were generated for each constituent separately from the calibrations. Equations A and B below illustrate the mathematical procedure used to calculate the concentration of components in both NIR instruments. Simultaneous determination of (percent) constituents were then made following any bias adjustment.

Equation A. For DICKEY-john GAC III.

$$\% \text{ Constituent} = KA + k_0 \times \text{Log}\,(1/R_0) + k_1 \times \text{Log}\,(1/R_1) + \ldots\ldots + k_5 \times \text{Log}\,(1/R_5)$$

where KA, intercept (or bias adjustment) for the calibration, k_0, regression coefficient (slope) for the first filter position; log $(1/R_0)$, first filter's instrument log of the measured reflectance (absorption); k_1, regression coefficient (slope) for the second filter position; and log $(1/R_1)$, second filter's instrument logarithm of the reciprocal reflectance (absorption).

Equation B. For the monochromator-RCA 6250.

$$\% \text{ Constituent} = KO + k_1\,[f(\lambda_1/\lambda_2)] + k_2\,[f(\lambda_3/\lambda_4)] + k_3\,[f(\lambda_5/\lambda_6)] + k_4\,[f(\lambda_7/\lambda_8)]$$

where KO, intercept (or bias adjustment) for the calibration; $f(\lambda)$, log (1/R) data or the derivative (i.e., mathematical transformation) of log (1/R) data at an optimum wavelength (λ) term; λ_1-λ_8, subset of the 700 recorded wavelengths (λs) for each sample; k_1-k_4, regression coefficients (slopes).

TABLE 1

Fatty Acid Composition of Common Edible Vegetable Oils (a Comparison)

Commodity	Ref.	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0	20:1	22:0	22:1	24:0
Cottonseed	10	1.0 (0.7)[a]	23.4 (23.2)	0.8 (0.6)	2.5 (2.5)	17.9 (13.7)	54.2 (56.5)	0.0 (0.2)	0.0 (0.1)	0.0 (0.1)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
Flaxseed	11	0.0 (0.0)	5.9 (4.8)	0.2 (0.0)	3.8 (4.7)	19.2 (19.9)	16.8 (15.9)	53.4 (52.7)	0.0 (0.0)	0.4 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
Groundnut (a)	12	9.2 (0.0)	0.0 (11.0)	0.0 (0.0)	3.1 (3.8)	57.2 (40.7)	23.4 (33.9)	0.0 (0.1)	1.4 (1.8)	1.4 (0.9)	2.6 (3.4)	0.0 (0.0)	1.8 (1.3)
(b)	13	0.0	10.7	0.3	3.4	49.0	28.0	0.0	2.0	2.0	3.0	0.1	1.4
Rapeseed (canola)	[b]	0.0 (0.0)	3.9 (3.8)	0.3 (0.3)	1.1 (1.5)	59.7 (60.3)	23.3 (20.1)	8.6 (9.5)	0.8 (0.5)	0.8 (0.5)	0.2 (0.3)	0.3 (0.7)	0.0 (0.2)
Safflower	14	0.0 (0.1)	7.6 (5.0)	0.0 (0.0)	2.0 (1.4)	10.8 (72.8)	79.6 (19.9)	0.0 (0.1)	0.0 (0.3)	0.0 (0.3)	0.0 (0.2)	0.0 (0.0)	0.0 (0.0)
Sesame		(0.0)	(9.0)	(0.2)	(5.2)	(41.6)	(42.3)	(0.4)	(0.6)	(0.2)	(0.1)	(0.0)	(0.0)
Soybeans (a)	15	0.0 (0.1)	15.3 (10.6)	0.0 (0.0)	4.2 (3.8)	23.6 (24.8)	48.2 (52.4)	8.7 (7.7)	0.0 (0.3)	0.0 (0.3)	0.0 (0.3)	0.0 (0.0)	0.0 (0.0)
(b)	16	0.0	12.4	0.0	3.7	25.4	50.2	7.9	0.0	0.0	0.0	0.0	0.0
(c)	17	0.1	10.5	0.2	3.2	24.9	51.5	8.4	1.0	1.0	0.0	0.0	0.0
Sunflower (a)	18	0.1 (0.1)	5.8 (6.0)	0.1 (0.0)	5.2 (4.3)	16.0 (23.1)	71.5 (65.1)	0.2 (0.1)	0.2 (0.3)	0.1 (0.0)	0.7 (0.8)	0.0 (0.0)	0.1 (0.0)
(b)	19	0.0	6.4	0.1	3.8	23.8	64.6	0.3	0.3	0.2	0.6	0.0	0.0
(c)	11	0.1	6.6	0.1	4.3	18.3	68.7	0.4	0.4	0.3	0.7	0.0	0.0
		6:0	8:0	10:0	12:0	14:0	16:0	18:0	18:1	18:2	18:3		
Palm kernel		(0.3)	(3.0)	(3.0)	(44.7)	(15.4)	(8.2)	(1.9)	(17.1)	(2.9)	(0.1)		

[a]Our data in brackets.
[b]Downey, R.K., unpublished data.

TABLE 2

Analytical Data for Oil Content of Oilseeds Using a Scanning Monochromator and a Discrete Filter (DICKEY-john GAC III) Analyzer

				DICKEY-john GAC III		Monochromator-RCA 6250	
Commodity	N[a]	Mean[b]	SD[c]	r[d]	SEP[e]	r[d]	SEP[e]
Flax	65	40.0	1.887	0.965	0.524	0.999	0.132
Safflower	40	24.4	6.663	0.951	2.082	0.942	0.724
Canola (rapeseed)	40	40.7	1.810	0.947	0.532	0.988	0.119
Soybean	35	21.9	1.330	0.966	0.179	0.990	0.082
Sunflower	58	47.6	1.890	0.960	0.555	0.999	0.160

[a]Number of samples.
[b]Percent oil on "as is" basis.
[c]Standard deviation of reference analyses results.
[d]Correlation coefficient between NIR and reference analyses.
[e]Standard error of performance (prediction) of NIR analysis.

TABLE 3

Analytical Data for Oil Content (Percent, "as is" Basis) for all Seed Types Using a Scanning NIR Monochromator and Log 1/R Algorithm

		Regression statistics				Wavelength (λ) in nanometers				
Commodity	N[a]	Mean	SD[b]	r[c]	SEP[d]	λ_1	λ_2	λ_3	λ_4	λ_5
Cottonseed	35	23.0	1.183	0.955	0.151	2140[e]	1640	2240	1440[e]	—
Flax	65	40.0	1.887	0.999	0.132	2140[e]	2220	1700[e]	2440	2160
Groundnut	60	51.2	2.849	0.993	0.309	2300[e]	—	—	—	—
Palm kernel	50	47.1	1.100	0.663	0.916	1920[e]	1960	1700[e]	1740[e]	1880
Rapeseed (canola)	40	40.7	1.810	0.988	0.119	1700[e]	2200	1240	1200[e]	1520
Safflower	40	24.4	6.663	0.942	0.724	1660	2300[e]	—	—	—
Sesame	38	48.7	2.139	0.996	0.264	1740	2420	2440	1260	2100[e]
Soybean	35	21.9	1.330	0.990	0.082	1600	1720[e]	2440	1260	2100[e]
Sunflower	58	47.6	1.890	0.999	0.160	2280	2320[e]	2240	—	—

[a]Number of samples.
[b]Standard deviation of results of reference analyses.
[c]Correlation coefficient between NIR and reference analyses.
[d]Standard error of performance (prediction) of NIR analysis.
[e]Oil bands.

The DICKEY-john GAC III is a bench-type instrument in which constituents are measured at discrete wavelength points (i.e., fixed wavelength filters) and log 1/R mathematics. For oil content determination, the optimum wavelength employed in the DICKEY-john GAC III model 781 is at 2310 nm. Results in Table 2 indicate good correlations between DICKEY-john GAC III model 781 and chemical (reference) data. These results are also comparable to those obtained from the monochromator (Table 2), but the SEP (standard error of prediction) data indicate that the monochromator results would, in subsequent analyses, produce higher accuracy. For example, the SEP for canola is 0.532 and 0.119 for the DICKEY-john and the monochromator, respectively. Ideally, the standard deviation (SD) of the calibration set should be ten times (or more) larger than the SEP to ensure a good calibration. The above results showed that for canola oil the ratio of the SD and SEP was only 3.4, while that of the monochromator is 15.2 (standard deviation divided by the standard error of prediction). Thus, the monochromator calibrations would produce more accurate results than those from the DICKEY-john in subsequent analyses. Up to five wavelength points were required to give low SEP values when the monochromator was used, whereas the DICKEY-john utilizes only one wavelength point for the same purpose. This indicated that when the log 1/R algorithm is used, more than one wavelength point is required for improved analytical results (compare Tables 2 and 3). In general, ensuring a wide range in constituents in the calibration results in both lower SEP and improved accuracy of subsequent analyses.

Although the 2310 nm wavelength is used in the discrete filter instrument for oil estimation, other wavelength points were selected when the monochromator was used (Tables 3, 4 and 5). Different wavelengths were selected for the same constituent for different seed types. These wavelengths were close or similar (but not exactly the same) and differed in the order in which they were selected as well (Tables 3, 4 and 5). These variations in the selected wavelengths might be attributed to several factors. These include:

i) Variations among commodities both in chemical composition and physical morphology. For example, sunflower seed is physically different from groundnut

TABLE 4

Analytical Data for Oil Content (Percent, "as is" Basis) for all Seed Types Using a Scanning NIR Monochromator and First Derivative of Log 1/R Algorithm

		Regression statistics				Wavelength (λ) in nanometers				
Commodity	N[a]	Mean	SD[b]	r[c]	SEP[d]	λ_1	λ_2	λ_3	λ_4	λ_5/λ_n[e]
Cottonseed	35	23.0	1.183	0.998	0.077	2292[f]	1718[f]	2188[f]	1428[f]	—
Flax	65	40.0	1.887	0.998	0.136	2296[f]	1634	2046	1854	—
Groundnut	60	51.2	2.849	0.981	0.482	—	—	—	—	1640/2122[f]
Palm kernel	50	47.1	1.100	0.937	0.286	—	—	—	—	1850/1434[f]
Rapeseed (canola)	40	40.7	1.810	0.998	0.087	2218	1642	2086	1936[f]	—
Safflower	40	24.4	6.663	0.999	0.230	1774[f]	1282	2074	—	—
Sesame	38	48.7	2.139	0.998	0.167	2426	2306[f]	—	1464	—
Soybean	35	21.9	1.330	0.969	0.151	—	—	—	—	2302[f]/2424
Sunflower	58	47.6	1.890	0.999	0.088	2090	—		—	—

[a]Number of samples.
[b]Standard deviation of results of reference analyses.
[c]Correlation coefficient between NIR and reference analyses.
[d]Standard error of performance (prediction) of NIR analysis.
[e]Quotient mathematics.
[f]Oil bands.

TABLE 5

Analytical Data for Oil Content (Percent, "as is" Basis) for all Seed Types Using a Scanning NIR Monochromator and Second Derivative of Log 1/R Algorithm

		Regression statistics				Wavelength (λ) in nanometers				
Commodity	N[a]	Mean	SD[b]	r[c]	SEP[d]	λ_1	λ_2	λ_3	λ_4	λ_5/λ_n[e]
Cottonseed	35	23.0	1.183	0.952	0.137	1766[f]	—	—	—	—
Flax	65	40.0	1.887	0.999	0.108	2312[f]	2390[f]	1400[f]	2000[f]	—
Groundnut	60	51.2	2.849	0.992	0.299	2396[f]	—	—	—	—
Palm kernel	50	47.1	1.100	0.784	0.846	—	—	—	—	1828[f]/1156[f]
Rapeseed (canola)	40	40.7	1.810	1.000	0.051	—	—	—	—	2402/2344[f]
Safflower	40	24.4	6.663	0.969	0.979	1806[f]	2170[f]	2362	1230[f]	—
Sesame	38	48.7	2.139	0.997	0.108	1804[f]	—	—	—	—
Soybean	35	21.9	1.330	0.999	0.066	—	—	—	—	2304[f]/2390[f]
Sunflower	58	47.6	1.890	1.000	0.078	2398[f]	2130[f]	2372[f]	1812[f]	—

[a]Number of samples.
[b]Standard deviation of results of reference analyses.
[c]Correlation coefficient between NIR and reference analyses.
[d]Standard error of performance (prediction) of NIR analysis.
[e]Quotient mathematics.
[f]Oil bands.

with respect to seed coat and shape. Thus, the particle size distribution of their ground meals are quite different and, since NIR instruments are known to be sensitive to particle size distribution (21), it is likely that this difference would influence the wavelengths selected for constituents in these two seeds.

ii) Interaction between constituents of the same seed, e.g., oil and fiber. The major absorption area for oil (around 2300 nm) is very close to that of fiber (around 2335 nm). Thus, there might be a tendency for one constituent to "mask" the other in this area, depending on the proportions of each component present.

iii) The mathematical treatment used influences wavelength selection as well. Wavelengths selected for log 1/R math are different from those selected for both the first and second derivative mathematical treatments (Tables 3, 4 and 5). Taking the derivative serves a dual purpose: i) "removal" of overlapping peaks; and ii) removal of slope in linear baselines, both of which result in sharpened peaks and facilitate band assignment. Quotient mathematics, or normalization, in which all data points are divided by data at a reference wavelength point, also serves to correct for scatter and hence improve linearity.

TABLE 6

Physical and Chemical Characteristics of Oilseeds

Commodity	Iodine value	Saponification value	% Dodecanoic (12:0 Laureate)	% Octadecenoic (18:1 Oleate)	% Octadecadienoic (18:2 Linoleate)	% Octadecatrienoic (18:3 Linolenate)	% Docosenoic (22:1 Erucic)	% Saturated fatty acids	% Unsaturated fatty acids	
									Mono-	Poly-
Cottonseed	110	199		13.7	56.5			26.8	14.4	56.6
Flaxseed	182	196		19.9	15.9	52.7		9.5	19.9	68.6
Palm kernel	20	244	44.7	17.1	2.9			21.3	41.7	34.0
Groundnut	94	196		40.7	33.9			76.5	17.1	3.0
Rapeseed (canola)	113	193		60.3	20.1	9.5	0.7	6.3	62.8	29.6
Safflower[a]	97	191		72.8	19.9			7.0	73.1	20.0
Sesame	110	193		41.6	42.3			15.1	42.0	42.6
Soybean	132	193		24.8	52.4	7.7		15.2	24.8	60.0
Sunflower	133	192		23.1	65.1			11.6	23.1	65.3

[a]High oleic sample.
Normal IV is 145.5.
Normal Linoleic is about 77%.

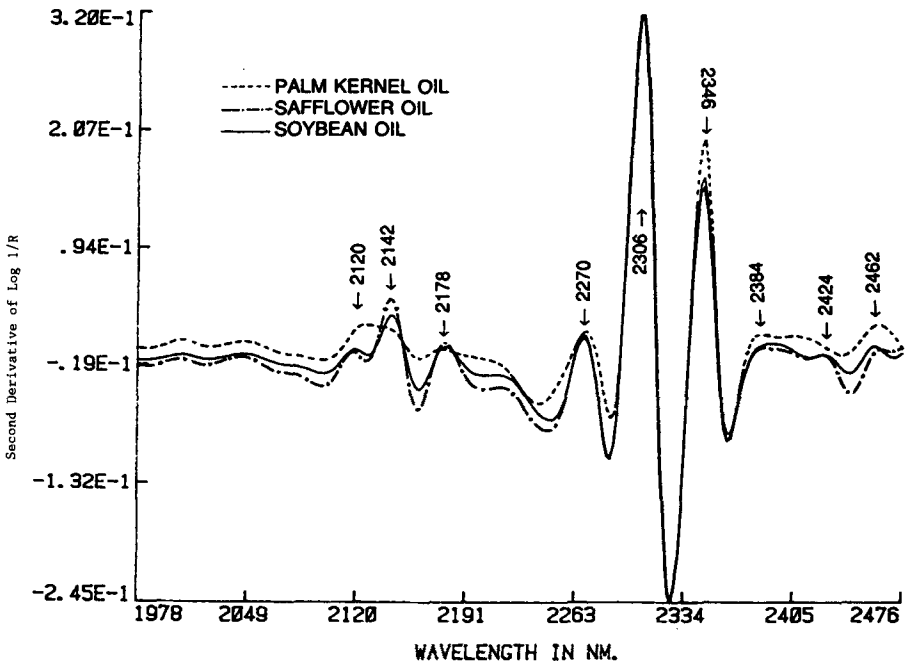

FIG. 1. Second derivative spectra of palm kernel, safflower and soybean oils.

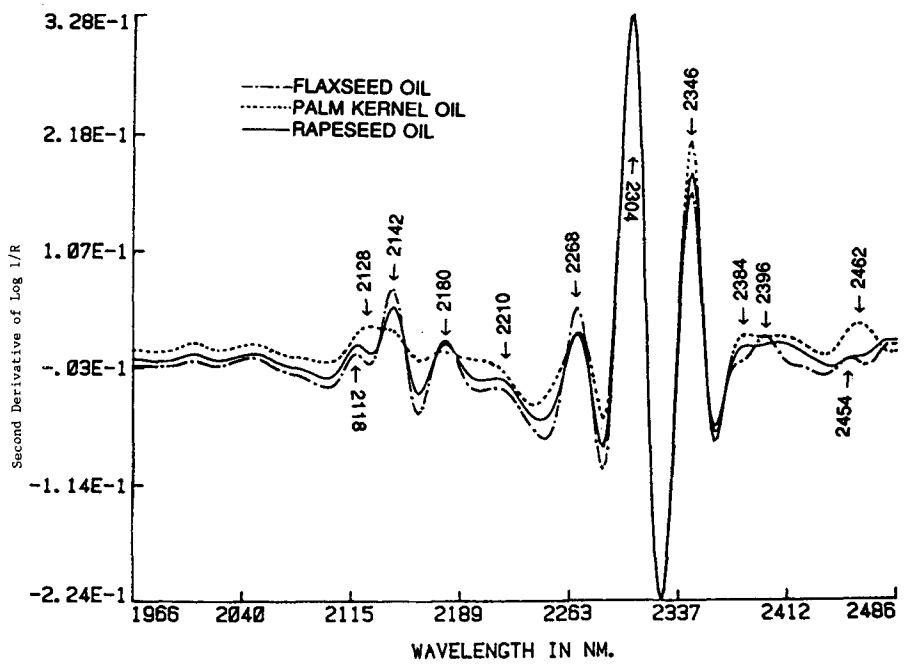

FIG. 2. Second derivative spectra of flaxseed, palm kernel and rapeseed oils.

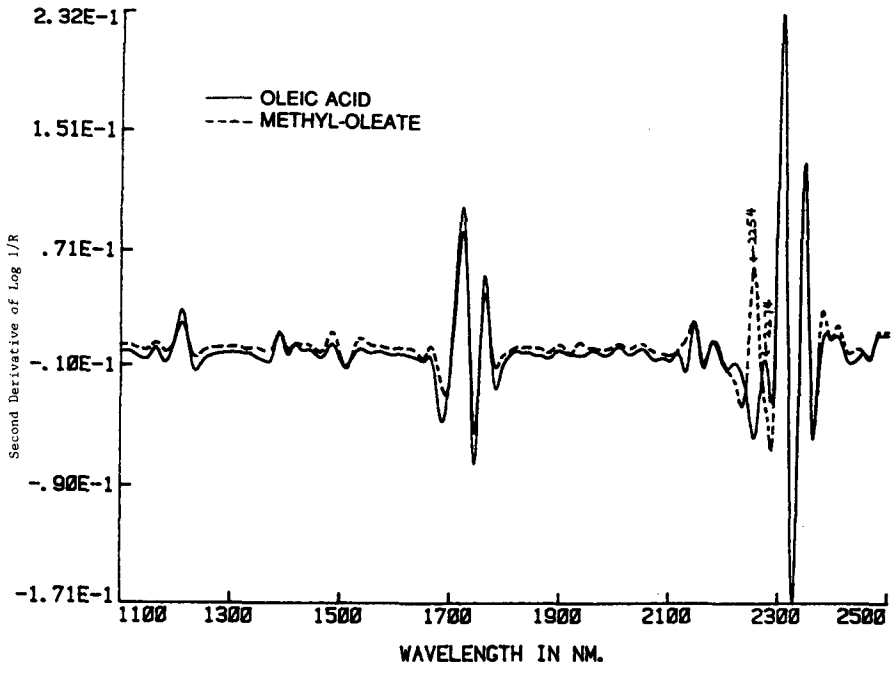

FIG. 3. Second derivative spectra of oleic acid and methyl-oleate.

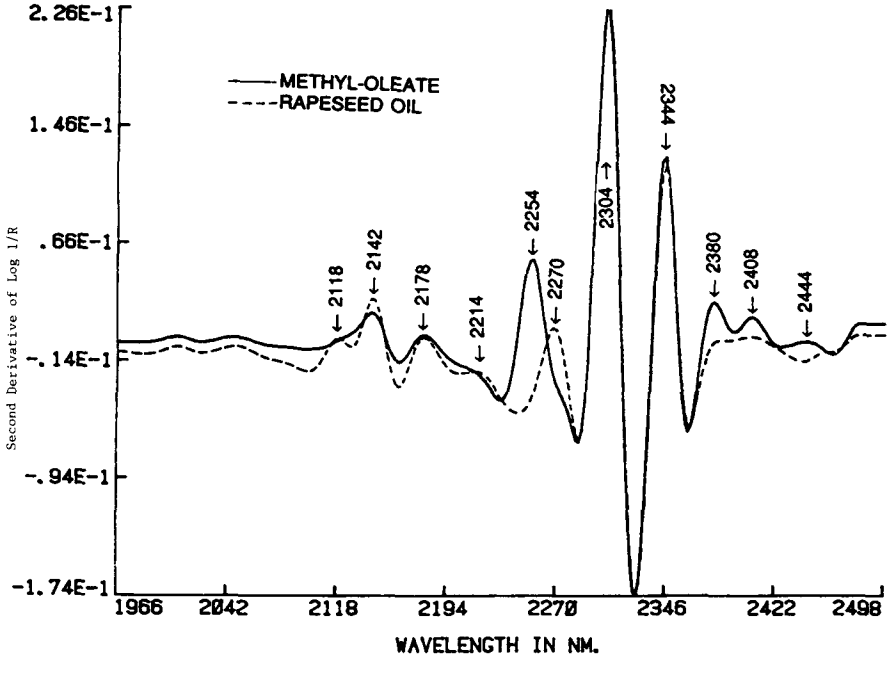

FIG. 4. Second derivative spectra of methyl-oleate and rapeseed oil.

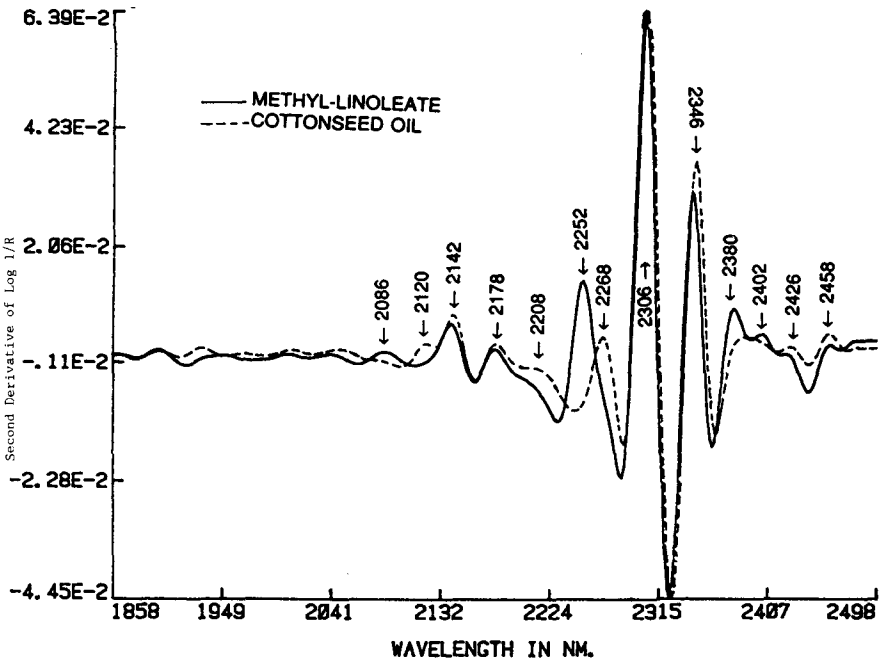

FIG. 5. Second derivative spectra of methyl-linoleate and cottonseed oil.

iv) Fatty acid composition was found to be a factor influencing wavelength selection. In 1956, Holman and Edmondson (22) reported that both chain length and degree of unsaturation cause band shifts in the NIR region. These workers studied the spectra of several fatty acids and other lipids and reported that, as the chain length of the fatty acids increased, methyl (CH_3) C-H absorption bands at 1690, 1720 and 1730 nm were overshadowed by stronger methylene (CH_2) C-H bands at 1740 and 1770 nm. In addition, fatty acids having *cis* double bonds exhibited strong absorption bands at 2150 and 2190 nm, and the intensity of these bands increased with increasing unsaturation.

The fatty acid composition and other physicochemical characteristics of all seed types are presented in Tables 1 and 6. Some seeds appeared to be similar with respect to the types of fatty acids present in them. For example, cottonseed oil appeared to have a fatty acid profile similar to that of sesame seed oil, and the soybean oil profile appeared similar to that of sunflower seed oil (Table 1). However, the quantity of each fatty acid differed markedly (e.g., C16:0 for cottonseed and sesame seed). Furthermore, a breakdown of the fatty acids into saturated and unsaturated fractions indicated little similarity among the seeds. It has been reported that unsaturated fatty acids generally give combination bands in the 2100–2200 nm range; weak first overtones around 1650–1780 nm and second overtones in the 1150–1200 nm area (of the spectrum) due mainly to the presence of double bonds and C-H vibrations (11). The mixture of wavelength points presented in Tables 3, 4 and 5 suggest that band shifts occur in complex matrices (such as oilseed meals) as a result of interactions between constituents. Double bonds (especially in *cis* configuration) of methyl and methylene groups might compete for absorption bands and the predominant group might show the prominent peak. Figures 1–5 illustrate the closeness of absorption bands and the complexity of band assignments.

Variations in the selected wavelength apparently do not occur because the C-H vibration in one seed oil is different from that of another oil, but are more likely to be due to the numbers (i.e., chain lengths) and types (CH_3-methyl or CH_2 methylene) of C-H groups present in the oil; the position or geometry of any double bonds (because trans double bonds have no absorption bands in the near-infrared region) (11), the ratio of saturated to unsaturated fatty acids present and the quantities of other absorbers in the product under study (Table 6 and Fig. 1–5). These differences should not, however, be regarded as a system failure; in fact, they were anticipated because they allow differentiation of one oil type from another and followed the general principle of infrared spectrometry. Minor differences in the structure of compounds cause shifts in bands that enable their differentiation in IR spectrometry. The same phenomenon has been found in NIR analysis. Filters with specific wavelengths might consequently be developed for the analysis of different seeds. The wavelengths found in this study are quite close, and narrow bandpass filters would be ideal for routine analysis of different seeds by one instrument. Results also showed that the second derivative mathematic was best-suited (i.e., gave more accurate results) for the estimation of

oil, as well as other constituents (protein, moisture, crude fiber) in oilseeds than log 1/R and the first derivative math.

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