Comparison of Dispersive and Fourier-Transform NIR Instruments for Measuring Grain and Flour Attributes

P. R. Armstrong, E. B. Maghirang, F. Xie, F. E. Dowell

Abstract. *Dispersive and Fourier-transform (FT) near-infrared (NIR) instruments were compared for their predictive performance of several wheat flour and grain constituents. Protein, moisture, and hardness index of whole grain wheat and protein, ash, and amylose of wheat flour were used to develop prediction equations between reference data of these constituents and their spectra. Partial Least Squares (PLS) regression was used to develop the prediction equations. Models were selected using F-test criteria (α = 0.05). NIR and FT-NIR spectrometers collected spectra over the wavelength ranges of 1100 to 2498 nm and 1142 to 2502 nm, respectively. Results show that FT-NIR and NIR instruments were comparable in prediction performance and there is no apparent advantage of one over the other. Wheat flour protein and ash, whole grain wheat protein, and moisture models had good quantitative prediction based on ratios of the standard error of prediction to the standard deviation of the reference data (RPD), i.e. RPD values were greater than 5. Wheat flour amylose and whole grain wheat hardness index predictions were qualitative with RPD values near 3.*

Keywords. *Grain, Flour, Near infrared, FT-NIR, Quality.*

Near-infrared reflectance (NIR) spectroscopy is widely used for the quantitative determination of quality attributes such as moisture, protein, fat, and kernel hardness in agriculture and food products (Williams and Norris, 2001). It is an approved method (AACC, 2002) for quantitative measurement of wheat protein and moisture content. NIR instruments for grain and grain product measurement have predominantly used grating monochromators to obtain spectral information, which is measured with a single or diode array detector. NIR instruments use various hardware configurations to obtain spectral information, and Fourier-transform near-infrared reflectance (FT-NIR) instruments are only one method to do this. FT-NIR hardware is generally more complex but advances in electronics, methods, and manufacturing have significantly improved the detector sensitivities, resolution, and immunity from vibrational effects (Williams and Norris, 2001).

Submitted for review in August 2005 as manuscript number IET 5995; approved for publication by the Information & Electrical Technologies Division of ASABE in March 2006.

Mention of trademark or proprietary product does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture and does not imply its approval to the exclusion of other products that may also be suitable.

The authors are **Paul R. Armstrong, ASABE Member,** Agricultural Engineer, **Elizabeth B. Maghirang, ASABE Member,** Agricultural Engineer, Grain Marketing and Production Research Center, USDA ARS, Manhattan, Kansas; **Feng Xie,** Research Associate, Department of Grain Science and Industry, Kansas State University, Manhattan, Kansas; and **Floyd E. Dowell, ASABE Member Engineer,** Research Leader/ Agricultural Engineer, Grain Marketing and Production Research Center, USDA ARS, Manhattan, Kansas. **Corresponding author:** Paul R. Armstrong, Grain Marketing and Production Research Center, USDA ARS, 1515 College Ave., Manhattan, KS 66502; phone: 785-776-2728; fax: 785-537-5550; e-mail: paul.armstrong@gmprc.ksu.edu.

FT-NIR records the intensity of the entire spectrum as a function of the optical path differences (OPD) between two NIR beams in an interferometer. The two beams are created by splitting the measurement beam, i.e., the beam that is transmitted through or reflected from the specimen. One split beam travels over a different optical path length, via a moving mirror, and is recombined with the second beam to create an interference signal. The total interference signal results from the mirror traveling through a range of wavelengths and is transformed to spectral components via a fast Fourier transform. (Skoog, 1998) gave a detailed explanation of FT-NIR and cited its advantages over conventional grating NIR spectroscopy as 1) higher signal-to-noise ratios, 2) extremely high resolutions, and 3) fast and accurate frequency determinations. The first advantage is realized because there are fewer optical components to attenuate radiation which leads to greater power reaching the detector and a better signal-to-noise ratio. The second advantage is that resolution at discrete wavelengths is much better, and thus elements which interact within very narrow bands can be detected. The third advantage states that spectral collection is much faster than with a dispersive instrument, since all wavelengths are measured simultaneously. While this last advantage is somewhat true, it can also be misleading since simultaneous measurement occurs only at discrete mirror positions. The total interference signal must be measured at discrete points during the mirror's travel, which requires a finite time period. After the entire time-domain interference signal is measured, it is then transformed to the frequency (spectral) domain via a fast Fourier transform (FFT) to obtain discrete wavelength information.

Coates (1994) mentioned that when using FT-NIR at the shorter NIR wavelengths, compared to mid-infrared, the interference pattern is more influenced by misalignment and may cancel any added advantage FT-NIR may have over

  ISSN 0883−8542

grating NIR instruments. Thus small perturbations in mirror positioning or misalignment are sources of error and as a result, lasers are commonly incorporated to provide a position reference. To achieve a position reference, monochromatic laser output is directed through the interferometer onto its own detector. The precision of this alignment is not generally specified by the manufacturer. Other literature (Williams and Norris, 2001) indicated that advantages of FT-NIR/IR are in the mid-infrared region, not the NIR region, because of the higher signal/noise (S/N) ratio using detector-noise-limited instrumentation. NIR instruments do not use detector-noise limited instrumentation. Biological materials absorb over broad regions in the NIR, not at discreet wavelengths. Thus, the advantage of FT-NIR being able to detect absorbance in very narrow bands may not be a significant benefit.

FT-NIR has been applied to study various attributes such as fat, protein, cholesterol, lactose, and internal quality in products of agriculture and food industries (Peirs et al., 2002; Paradkar and Irudayaraj, 2002). Sorvaniemi et al. (1993) first used FT-NIR to study moisture, protein, wet gluten, water absorption, and falling number of wheat flours. Promising correlations of FT-NIR spectra to these parameters were obtained, except for falling number. Manley (2002) used FT-NIR to determine the hardness, protein, and moisture content of whole wheat flour. This study yielded a standard error of prediction (SEP) = 2.13%, 0.51%, and 0.15%, and r = 0.42, 0.81, and 0.85, for hardness, protein, and moisture content, respectively. In their study, hardness was determined by the modified particle size index test.

At present, FT-NIR has not been commonly applied to study grain quality except for wheat flour, and its relative performance compared to NIR has not been quantitatively addressed. The objective of this study was to compare an FT-NIR-based instrument with that of a conventional grating NIR method by parallel measurement of grain and flour attributes. Specific attributes measured were wheat flour protein, amylose and ash content; moisture, and protein and hardness index (HI) of whole wheat grain. Several of these are commonly measured attributes using NIR, with the exception of amylose and ash.

Materials and Methods

Instrumentation

This study used two commercially available instruments, Brukers Optic's Matrix™-I FT-NIR (Bruker Optics, Billerica, Mass.) spectrometer (835 to 2502 nm) and a model 6500 Foss-NIR (FOSS-NIR Systems, Inc., Silver Spring, Md.) reflectance spectrophotometer (450 to 2498 nm). Both instruments are commercially available for grain analysis. The FT-NIR spectrometer was provided by Cognis Corporation, QTA Group (Cincinnati, Ohio) and the NIR spectrometer was provided by FOSS, North America (Eden Prairie, Minn.). The NIR system had a 2-nm resolution and averaged 32 scans/spectrum. The FT-NIR system resolution is variable and was set at 8 cm^{-1} (~0.5 nm resolution at 835 nm and 4.5 nm at 2500 nm) and averaged 200 scans/spectrum.

The FT-NIR spectrometer was equipped with an integrating sphere in the sample viewing area (25-mm diameter), which permits analysis using the diffuse reflectance technique. A sample was placed in a cylindrical bowl (85-mm diameter) with a glass bottom which rotated over the spectrometer viewing area. A fixed stirring paddle was used to mix the sample as multiple scans were made. The NIR spectrometer utilized either a moving sample attachment and a rectangular sample cell or a rotating attachment with a standard ring cell. The rectangular cell was either a ¼ rectangular (55 × 40 mm) or full rectangular (45 × 200 nm). The instrument spectral resolution and ring or rectangular sample attachments were selected based on the available sample size and manufacturer recommendations.

Wheat Flour Protein and Amylose Content

A total of 193 ground wheat samples (28 low amylose and 165 medium to high amylose) were obtained from Dr. Steve Delwiche (ARS-USDA, Beltsville, Md.). These samples, which were previously used for their work on identification of waxy wheat by NIR reflectance spectroscopy, were ground in a laboratory scale cyclone grinder (Udy Corp., Ft. Collins, Colo.), and spectra obtained on the NIR instrument using a standard ring cell. Delwiche and Graybosch (2002) describe details of the sample preparation and spectra collection. Flour protein ranged from 11.24% to 17.15%; amylose ranged from 0.35% to 26.85%. Due to the relatively small flour sample size (10 grams), the sample holder of the FT-NIR spectrometer was modified. The modification allowed for wheat flour to be poured into a funnel, which then flowed into and fully covered the 25-mm diameter spectra collection window. A spectrum for each flour sample was obtained and saved. FT-NIR settings were 835- to 2502-nm scan range, 8 cm^{-1} wavenumber resolution, and 200 scans/spectrum. Instrument settings for the NIR spectra, obtained from Dr. Steve Delwiche, used a standard ring cell, 835- to 2502-nm scan range, 2 nanometer resolution, and 32 scans per spectrum. Particle size of flour can have a significant effect on NIR spectra and thus in the prediction of constituents. For this study though, predictions developed for instruments were used to compare instrument performance and not for the purpose of developing calibrations and sample preparation procedures. Each instrument collected spectra on the same material with the advantages or limitations of the viewing method each had, and was exposed to the same particle size within the sample.

Wheat Flour Ash Content

Hard red winter wheat flour samples from different mill streams were obtained from the Kansas State University Pilot Mill (Manhattan, Kan.). Ash reference analysis was completed using AACC-approved method 08-01 (AACC, 2002). Combinations of the mill streams were then combined to create samples (n = 41) in which ash content was evenly distributed across a range of 0.26% to 0.86%. NIR spectra were collected using a 1/4-rectangular sample cell over 450- to 2498-nm at 2-nm resolution and 32 scans/spectrum. FT-NIR settings were 835- to 2502-nm scan range, 8-cm^{-1} wavenumber resolution, and 200 scans/spectrum.

Whole Grain Wheat Moisture Content

Eight, 250-g samples of high-moisture hard white wheat samples were obtained. Wheat cultivars used were Betty 9RP, Betty ORL, Heyne, and Trego. Two, 10-g samples were taken from each sample and used to determine the initial moisture content following the ASAE Standard Procedure

S352.2 (*ASAE Standards*, 2003). Initial moisture content of these samples ranged from 15% to 17%. Each 250-g sample was divided into two, 100-g sub-samples and dried at approximately 1% moisture content increments using a convection oven set at 38°C. Based on a pre-drying sample weight, the moisture content of each sub-sample was monitored to check when the desired moisture content was achieved. Samples reaching their test moisture content were allowed to cool for about 10 min in a desiccator. FT-NIR and NIR measurements were taken immediately after cooling. NIR and FT-NIR spectra collection was the same as that used for flour ash. A total of 166 samples were scanned with moisture contents ranging from 7.73% to 17.22%.

Whole Grain Wheat Protein Content

Ninety hard red winter wheat samples were obtained from USDA-ARS Grain Quality and Structure Research Unit with protein content ranging from 9.72% to 15.08%. Crude protein content was determined by combustion, using a Leco model FP-528 nitrogen analyzer (St. Joseph, Mich.) using AACC-approved method 46-30 (AACC, 2002). NIR and FT-NIR spectra collection was the same as that used for flour ash content.

Whole Grain Wheat Hardness

The bulk wheat hardness index (HI) of soft and hard wheat samples was obtained from the average of 100 single-kernel hardness measurements using a Perten SKCS 4100 (Perten Ind, Springfield, Mo.). One hundred samples were selected from these, which represented a broad HI range (-15 to 81). HI is an empirical value based on crushing forces and other information obtained from the SKCS 4100 instrument. NIR and FT-NIR spectra collection was the same as that used for flour ash.

Data Analysis

NIR and FT-NIR spectral data were analyzed using partial least squares (PLS) regression, GRAMS AI software, (Galactic Industries, Salem, N.H.). Spectra were mean centered but no other pretreatments were applied. Little benefit is often realized by pretreatments such as first or second derivatives (Delwiche and Reeves, 2004) and would not affect the relative comparison made in this study. Cross-validation was performed with a single sample removed, i.e. remaining samples were used to generate a prediction equation, the sample left out was predicted, and the squared residual error was determined at each factor level. The prediction residual error sum of squares (PRESS) value at each factor level is the sum of all of the squared residual errors as each sample is sequentially left out and predicted. Initial PLS analysis used the full spectrum for each instrument but was then limited to 1100 to 2502 for the FT-NIR and 1100 to 2498 for the NIR instruments, as regression coefficient distribution in the 450- to 1100-nm region was considered too random and noisy to provide any meaningful contribution to the model.

Measured constituents of flour and wheat are summarized in table 1 for each of the previously mentioned specific methods.

Table 1. Flour and wheat samples used in study.

Sample	Constituent Range	Units	n
Wheat flour protein	11.24% to 17.15%	% protein	193
Wheat flour amylose	0.35% to 26.85%	% amylose	193
Wheat flour ash	0.26% to 0.86%	% ash	41
Whole grain wheat MC	7.73% to 17.22%	%MC wet basis	166
Whole grain wheat protein	9.72% to 15.08%	% protein	90
Whole grain wheat HI	−15 to 81	Hardness index	100

Results and Discussion

Models at factor levels determined from using the F-test criteria are shown in table 2. F-ratio equals the PRESS value at a given factor level divided by the minimum PRESS value. This ratio indicates the relative significance of each model to the model at the minimum PRESS value and can be assigned a statistical significance based on the number of samples used for calibration. F-test criteria used to select the number of factors was at a significance level of $\alpha = 0.05$. The F-ratio has been suggested by Haaland and Thomas (1988) as a better method for model development when the model will be used to predict future unknown samples.

An overall comparison of NIR and FT-NIR (table 2) revealed that both instruments perform similarly for the F-test models developed in this study. Wheat flour protein, amylose, and ash, and whole grain wheat protein and moisture models had good quantitative prediction based on RPD values, whereas only qualitative predictions of whole grain wheat HI could be achieved. The RPD value is the ratio of the standard deviation of the reference measurements divided by the standard error of cross validation (SECV) from PLS regression. Williams (1997) suggested that RPD values of 2.5 to 3 were suitable for rough screening; a value of 5 to 8 could be used for quality control, while an RPD of 8 or higher was excellent. The lower predictability of HI relative to other constituents in this study is similar to results from previous research for whole grain measurement; Manley et al. (1996) found similar correlation ($r^2 = 0.77$) of spectra with whole grain hardness measured by particle size index.

Regression coefficients for the calibration models are shown in figures 1 and 2. Regression coefficients indicated

Table 2. Comparison of FT-NIR and NIR performance for prediction models developed from F-test criteria.

	Wheat Flour					
	Protein (%)		Amylose (%)		Ash (%)	
	NIR	FT-NIR	NIR	FT-NIR	NIR	FT-NIR
No. factors	8	10	8	9	6	6
R^2	0.99	0.99	0.92	0.91	0.96	0.97
SECV	0.10	0.11	1.92	2.13	0.03	0.03
RPD	13.25	12.81	3.62	3.26	5.27	5.53

	Whole Grain Wheat					
	Protein (%)		Moisture (%)		HI	
	NIR	FT-NIR	NIR	FT-NIR	NIR	FT-NIR
No. factors	11	9	7	7	4	5
R^2	0.96	0.92	0.99	0.99	0.80	0.83
SECV	0.24	0.33	0.30	0.20	12.45	11.46
RPD	4.83	3.52	8.85	13.20	2.25	2.45

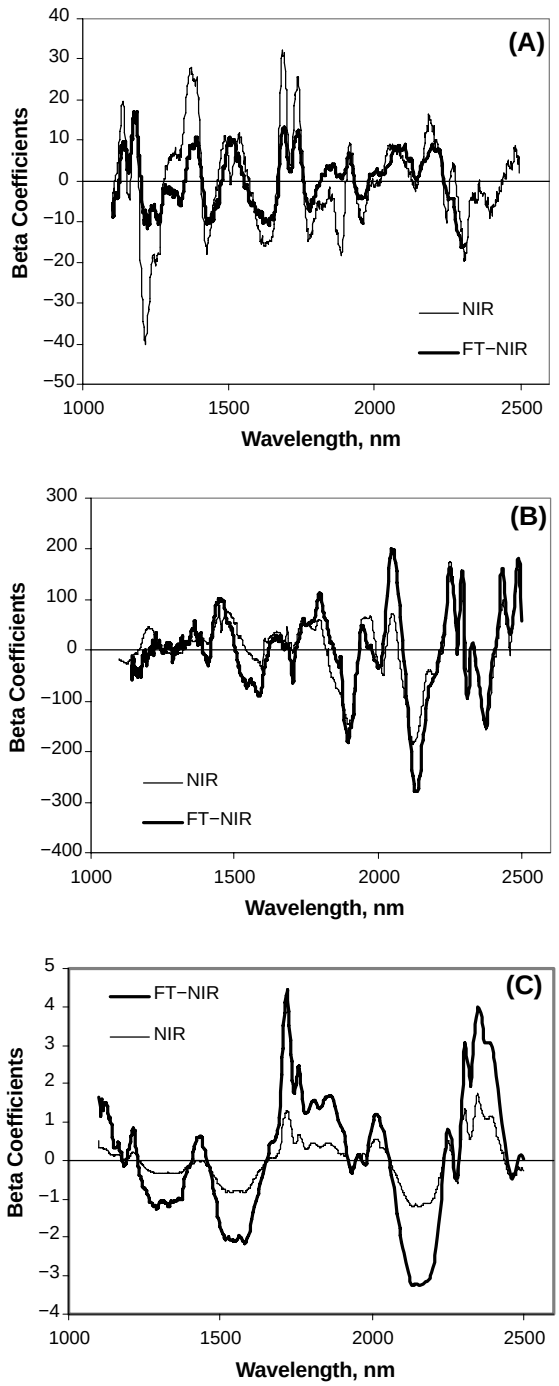

Figure 1. Regression coefficients for FT-NIR and NIR prediction models for wheat flour protein (A), amylose (B), and ash (C) using the number of factors indicated in table 2.

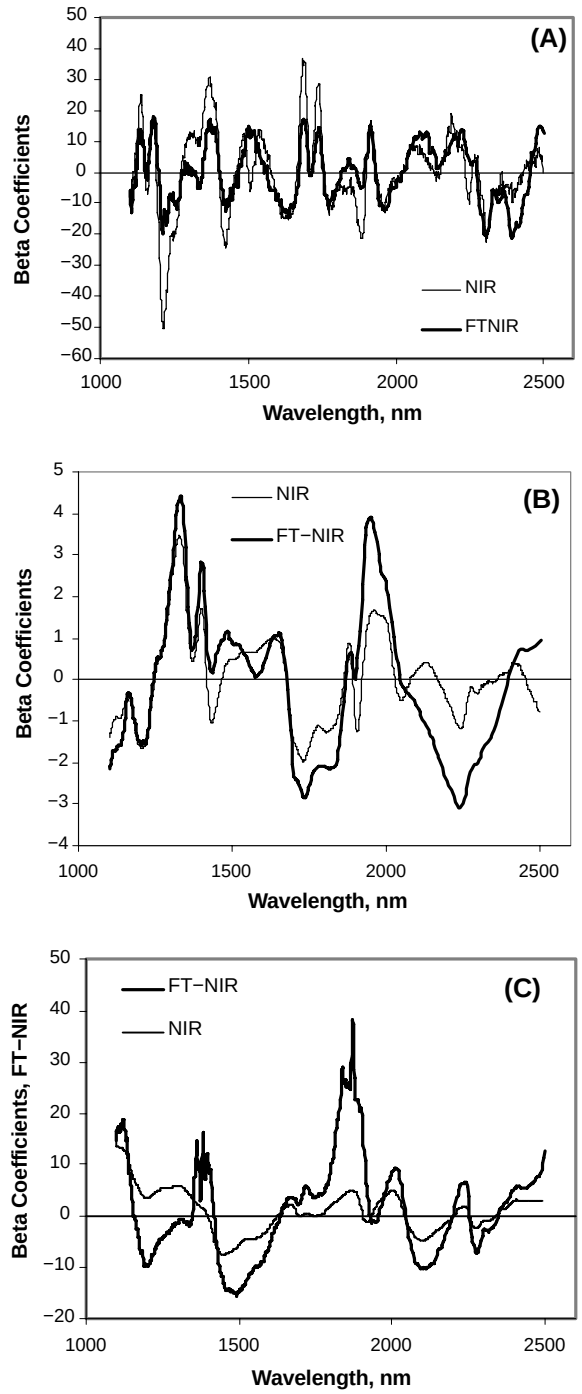

Figure 2. Regression coefficients for FT−NIR and NIR prediction models for whole grain wheat protein (A), moisture content (B), and HI (C) using the number of factors indicated in table 2.

that both NIR and FT-NIR models use similar spectral information to predict their respective constituents in all cases. For wheat moisture-content prediction (fig. 2), large positive and negative coefficients near 1400, 1780, and 1950 nm correspond to water absorption bands. The regression coefficients also illustrate the fact that NIR spectroscopy uses the combination bands and overtones of molecular-light absorbance which have overlapping absorbance species. Thus absorbance bands are broad and the ability of Fourier transform instruments to measure specific wavelengths becomes less significant in the near-infrared region as opposed to the mid− and infrared spectral region. Because of this, the dispersive NIR and FT-NIR may perform similarly in the near-infrared region.

CONCLUSIONS

FT-NIR and NIR instruments were comparable in predictive performance and there seemed to be no advantage of either method over the other for the constituents measured. As for other considerations, the general consensus by users

was that the FT-NIR had an easier method for sample preparation and presentation, as the sample was simply dumped into a cylindrical bowl. The glass bottom of the bowl provided the scanning area for the FT-NIR. One disadvantage of this was that it required about twice the sample size compared to the NIR 1/4-cup system. Scan times of the FT-NIR and NIR instruments were approximately equal at 1 min.

Acknowledgements

Thanks are given to GIPSA for samples; Kendall McFall, KSU Grain Science Dept. for samples and analysis; Dr. Steve Delwiche for samples, analysis, and spectra; and GQSRU for analysis. We gratefully acknowledge Cognis Corp. and FOSS North America for providing instruments.

References

AACC. 2002. Approved methods of the AACC, Methods 39-10, 39-11, 46-30 and 08-01. St. Paul, Minn.: American Association of Cereal Chemists.

ASAE Standards. 2003. S352.2. Moisture measurement — unground grain and seeds. St. Joseph, Mich.: ASAE.

Coates, J. 1994. Designing the ideal process analyzer −− or at least making an attempt. *NIR News* 5(2): 7-9.

Delwiche, S. R., and R. A. Graybosch. 2002. Identification of waxy wheat by near-infrared reflectance spectroscopy. *J. of Cereal Science* 35(1): 29-38.

Delwiche, S. R., and J. B Reeves. 2004. The effect of spectral pre-treatments on the partial least squares modeling of agricultural products. *J. of Near Infrared Spectroscopy* 12(3): 177-182.

Haaland, D. M., and E. V. Thomas. 1988. Partial least-squares methods for spectral analysis. 1. Relations to other quantitative calibration methods and the extraction of qualitative information. *Analytical Chemistry* 60(11): 1193-1202.

Manley, M., A. McGill, and B. G. Osbourne. 1996. Whole wheat grain hardness measurement by near-infrared spectroscopy. In *Near Infrared Spectroscopy: The Future Waves*, eds. A. M. C. Davies and P. Williams. Chichester, UK: NIR Publications.

Manley, M., L. Van Zyl, and B. G. Osborne. 2002. Using Fourier transform near-infrared spectroscopy in determining kernel hardness, protein, and moisture content of whole wheat flour. *J. of Near Infrared Spectroscopy* 10(1): 71-76.

Paradkar, M. M., and J. Irudayaraj. 2002. Determination of cholesterol in dairy products by infrared techniques: 2. FT-NIR method. *International J. of Dairy Technology* 55(3): 133-138

Peirs, A., N. Scheerlinck, K. Touchant, and B. M. Micolai. 2002. Comparison of fourier transform and dispersive near-infrared reflectance spectroscopy for apple quality measurements. *Biosystems Engineering* 81(3): 305-311.

Skoog, D. A., F. J. Holler, and T. A. Nieman. 1998. *Principles of Instrumental Analysis*, 5th ed. Chicago, Ill.: Harcourt Brace College Publishers.

Sorvaniemi, J., A. Kinnunen, A. Tsados, and Y. Malkki. 1993. Using partial least-squares regression and multiplicative scatter correction for FT-NIR data evaluation of wheat flours. *J. of Food Science and Technology* 26(3): 251-258.

Williams, P. C. 1997. Recent advances in near-infrared applications for the agricultural and food industries. *Proceedings: International Wheat Quality Conference.* Manhattan, Kans.: Manhattan, Kans., Grain Industry Alliance.

Williams, P. C., and K. Norris. 2001. Method development and implementation of near-infrared spectroscopy in industrial manufacturing processes. In *Near-Infrared Technology in the Agricultural and Food Industries*, 2nd ed., St. Paul, Minn.: American Association of Cereal Chemists.