DETERMINATION OF MOISTURE CONTENT IN WHEAT BY NEAR-INFRARED DIFFUSE REFLECTANCE SPECTROPHOTOMETRY[1]

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ABSTRACT

A method is described for determining moisture in ground wheat by direct near-infrared reflectance spectrophotometry. Kubelka-Munk values, $F(R'_{\infty})$, were calculated from the spectra at 20 wavelengths between 1.12 and 2.49 μ. Multiple linear regression analysis showed that only the two values at 1.93 and 2.10 μ were sufficient to predict the moisture accurately over a range of 2.8 to 16.5% using the equation: $\log m = 0.966 + 1.620 \log F(R'_{\infty})_{1.93\mu} - 1.628 \log F(R'_{\infty})_{2.10\mu}$. The method is applicable to different wheat types (durum, hard red spring and soft white winter) and is unaffected by a change in mean particle size from 170 to 500 μ.

Several near infrared transmittance spectrophotometric methods for the determination of moisture contents in agricultural seeds and cereal products have been published (1–3). In general, these methods embody the use of methanol extracts or suspensions of the material in methanol or carbon tetrachloride.

Hoffmann (4) drew attention to the benefits of near-infrared diffuse reflectance spectrophotometry to the determination of moisture contents. He established the relations of reflectance at 1.93 μ to moisture content for a range of solid materials including single samples of flour and starch.

Instruments which use the principle of reflectance of near-infrared radiation have been developed specifically for the analyses, including moisture, of cereals and oilseeds (5–10). In a detailed evaluation of these instruments, Williams (10) found that their accuracy in the analysis of wheat was markedly influenced by the variation in particle size of the samples and that the calibration settings were dependent on the type of grinder used to prepare the samples.

The mathematical format of the calibration equations used in these

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instruments varies according to the manufacturer, but essentially all use a linear relation of concentration to apparent absorbance, *i.e.*, log (reflectance of standard ÷ reflectance of sample) measured at several wavelengths (7,8). However, this relation cannot be justified by any of the accepted theories of diffuse reflectance (11).

The most widely accepted theory of diffuse reflectance is that proposed by Kubelka and Munk (cited in 12). For the case of diffuse reflectance from infinitely thick layers the theory proposes,

$$F(R_\infty) \equiv \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{k}{s}$$

where, $F(R_\infty)$ is the Kubelka-Munk (K-M) function or value; R_∞, the absolute reflectance; k, the molar absorption coefficient; and s, the scattering coefficient.

In the case of weak absorption, k may be replaced by 2.30 ϵc where ϵ is the extinction coefficient and c the molar concentration (13); then for constant conditions (particle size, wavelength, temperature, *etc.*), the K-M function is proportional to c:

$$F(R_\infty) \sim \frac{\epsilon c}{s}$$

Small particle size does influence s; however, once particle diameters are above approximately 10 μ, s becomes relatively independent of both particle size and wavelength (11). Hence, a straight line relation between K-M values and concentration for samples of constant particle size or larger particles indicates adhereance to the Kubelka-Munk theory.

This paper presents a method, based on the Kubelka-Munk theory, for the determination of moisture in wheat. However, relative reflectance values designated with a prime (R'_∞) were used instead of absolute reflectance, R_∞. These relative values were obtained in reference to a comparison standard, in which case $R'_\infty = R_\infty$ (sample) ÷ R_∞ (standard). The method is independent of particle size and applicable to a wide range of moisture contents.

MATERIALS AND METHODS

Samples

Calibration. Sound samples of Canada Western (CW) amber durum, CW hard red spring (HRS), and Canada Eastern white winter (SWW) wheat were used with protein contents (Kjeldahl method, N × 5.7) of 12.8, 16.2, and 12.3%, respectively (13.5% moisture basis). Each wheat was ground on three mills: a Hobart model 2040 coffee grinder; a Wiley model 1 cutting mill fitted with a 1.0 mm sieve and a Model CSM-2 Udy cyclone grinder fitted with a 1.00 mm screen. The particle size (root mean square particle diameter) of the resulting nine samples ranged from 170 to 500 μ. Five subsamples obtained from each of the above nine samples were exposed to a range of humidities to produce a range of moisture contents for each wheat grind.

Validation. Forty-nine samples were used to validate the calibration. Thirty-

two of the samples represented eight varieties of hard white wheat grown on four sites in Queensland, Australia, during 1974. The protein contents of the wheats ranged from 12.1 to 18.0%. These samples were ground using a Christy and Norris cyclone grinder fitted with a 1.0 mm sieve, dried at 100°C, and allowed to regain moisture. The remaining 17 were samples of HRS wheat (1975 crop) which were ground on a Hobart model 2040 coffee grinder.

Particle Size Determinations. One-hundred g of the nine ground samples described under 'calibration' were sieved through a series of screens by means of a Rotap mechanical shaker. Particle size (root mean square particle diameter) was calculated from the equation

$$\sqrt{\bar{d}^2} = \sqrt{\frac{\Sigma n_i d_i^2}{\Sigma n_i}}$$

where: n = per cent by weight retained on each sieve, and
d = mean aperture widths (μ) of the through and retaining screens.

Reflectance Measurements. Diffuse spectra were recorded between 1.0 and 2.5 μ using a Cary 171 spectrophotometer and methods described previously (14), with the exception that a pressing made from a mixture of sulfur and powdered polytetrafluoroethylene having an absolute reflectance greater than 95% was used as a reference standard.[3]

Apparent absorbance values, log (standard reflectance ÷ sample reflectance), were recorded at 1.12, 1.20, 1.31, 1.46, 1.57, 1.66, 1.70, 1.75, 1.78, 1.85, 1.93, 2.01, 2.05, 2.10, 2.18, 2.22, 2.29, 2.31, 2.35, and 2.49 μ. These wavelengths corresponded to absorption peaks in the spectra of wheat, starch and gluten, and the valleys in the spectrum of wheat of approximately 10% moisture (14).

After correcting for the effects of the sample holder and cover glass, the recorded data were converted to Kubelka-Munk values, F (R'_∞), using published tables (11,15).

Oven Moisture. The oven moisture contents of the samples were determined by drying in an air oven at 130°C for 1 hr (16). Duplicate determinations were made on the samples used for calibration; in other cases, single determinations were made.

Statistical Analyses. Regression techniques described by Draper and Smith (17) were used. The 5% significance level was used as a criterion for inclusion of variables in the multiple regression equation.

RESULTS AND DISCUSSION

The particle sizes of the samples used for the calibration and their distributions are illustrated in Table I and Fig. 1, respectively. The particle size range was from 170 μ for the SWW sample ground on the Cyclone grinder to 500 μ for the durum sample ground on the Hobart grinder. Assuming that grain hardness increased in the order SWW, HRS, and durum, particle size tended to increase with hardness within each mill type. The exception was the SWW, Hobart grind, where the particle size result appears too high. This may be explained by the greater amount of large bran particles present in this sample as

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compared with other samples from this grinder. Although the particle sizes obtained with the Hobart and Wiley grinders were similar, there were marked differences in their distributions.

The relations of K-M values at 1.93 μ, the most sensitive absorption peak for water (14), to oven moisture contents for the individual samples are illustrated in Fig. 2. Table II lists the parameters and correlation coefficients for the regression lines in Fig. 2. With the exception of the SWW Wiley sample, there is good agreement with the Kubelka-Munk theory. This is in contrast to the finding of Hoffmann (4), who found a curvilinear relation for a single sample of flour. The moisture content range in this earlier study was from 0 to 25%. The variations in the regression lines indicate that no single variable equation is applicable to an individual mill or wheat type. The application of multiple regression analyses to

TABLE I
Particle Size (Root Mean Square Particle Diameter) of Samples Used for Moisture Calibration

Wheat Type	Mill Type		
	Hobart	Wiley	Cyclone
Durum	500 μ[a]	485	199
HRS	443	435	184
SWW	481	377	170

[a]All diameters in microns.

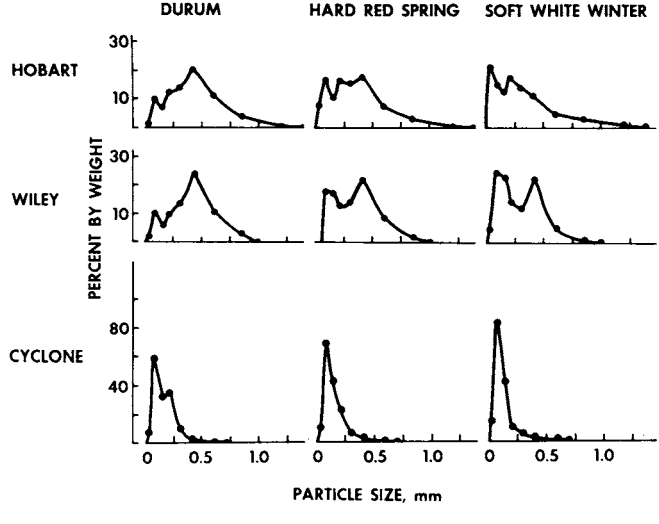

Fig. 1. Particle size distributions of the samples used for the calibration of the reflectance method. Areas under the curves were normalized.

the pooled data using both an 'as-is' and 'common log' format yielded the following relation as the most significant, as measured by the lowest coefficient of variation:

$$\log m = 0.966 + 1.620\ (\pm 0.038)\ \log x_1 - 1.628\ (\pm 0.040)\ \log x_2$$

TABLE II
Parameters of the Regression Equations $F\ (R'_\infty)_{1.93\mu} = a + bm$, for Samples Used for Calibration

Sample	Intercept a	Slope b	Correlation Coefficient
Hobart			
Durum	0.20	0.18	0.99
HRS	0.06	0.14	0.99
SWW	0.27	0.06	0.99
Wiley			
Durum	0.22	0.14	1.00
HRS	0.00	0.07	0.98
SWW	0.32	0.02	0.91[a]
Cyclone			
Durum	0.00	0.08	1.00
HRS	0.00	0.06	1.00
SWW	0.08	0.03	1.00

[a]Not significant.

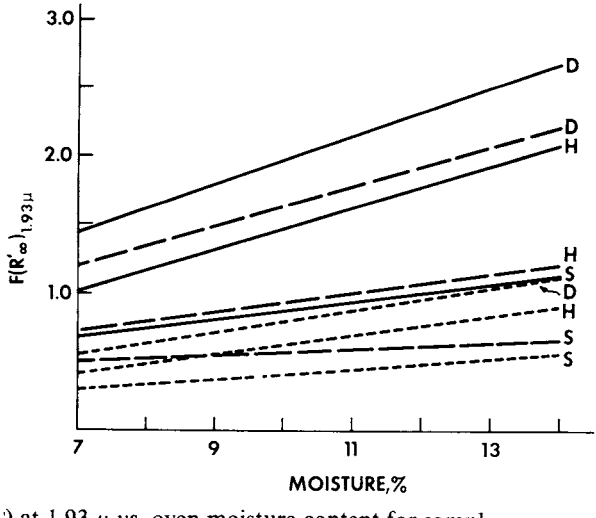

Fig. 2. $F(R'_\infty)$ at 1.93 μ *vs.* oven moisture content for samples representing three wheat types × three mills. D = durum, H = hard red spring, S = soft white winter. ———— Hobart; — — — — Wiley; - - - - - - - - - - Cyclone mill.

where: m = per cent moisture,
$x_1 = F(R'_\infty)$ at 1.93 μ,
$x_2 = F(R'_\infty)$ at 2.10 μ.

The relation of the predicted reflectance moisture content to experimental oven moisture content is illustrated in Fig. 3. The coefficient of variation of 1.5%

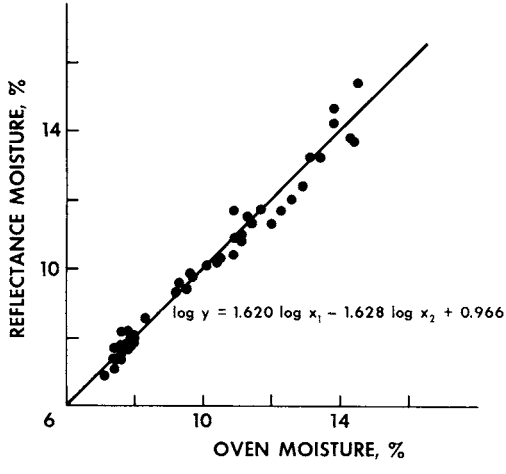

Fig. 3. Moisture content determined by reflectance *vs.* oven moisture content for 45 samples used to derive the calibration equation. $x_1 = F(R'_\infty)$ at 1.93 μ; $x_2 = F(R'_\infty)$ at 2.10 μ.

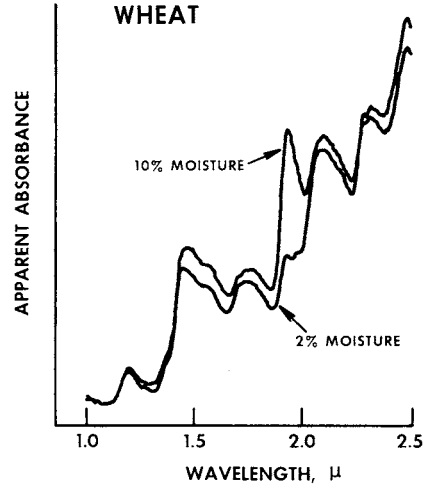

Fig. 4. Reflectance spectra for ground red spring wheat containing 2 and 10% moisture.

is the same as that quoted for the determination of moisture by the Neotec Grain Analyzer when a single wheat type and mill were used (10).

The presence of $F(R'_\infty)$ at 1.93 μ in the multiple regression was predictable as this wavelength is the most sensitive to changes in moisture concentration. However, the inclusion of the value at 2.10 μ as the sole additional significant variable in the regression was unexpected. The absorption peak at 2.10 μ arises from the carbohydrate components (14) (Fig. 4). Norris and Hart (3), who carried out transmission near-infrared spectrophotometry on slurries of ground wheat in carbon tetrachloride, found two wavelengths, similar to the two above, that could be used to predict moisture content. These authors found a curvilinear relation between the optical density difference, Δ o.d. (1.94 − 2.08) μ and oven moisture values. Variations in protein content would be expected to influence the above relation due to absorption at 1.98, 2.05, and 2.18 μ. Because values at these wavelengths were not significant in the regression suggests that (a) absorption at 2.10 μ may be unaffected by the variation in protein content, or (b) protein has a similar effect on absorption at 1.93 and 2.10 μ.

The similarity of the regression coefficients of x_1 and x_2 suggests that an equation of the form, $\log m = a + b \log x_1/x_2$ would be equally applicable to the data. This was shown to be the case; however, the equation is not presented, as the format applies an unnecessary construction to the calibration.

The accuracy of the calibration is illustrated in Fig. 5. The most notable feature is the accuracy below 7.1% and above 14.5%, which were the lowest and highest moisture contents used for calibration. It is obvious that the 45° line is not the 'best fit' and that there is a bias toward underestimation for the Australian samples and overestimation for the Canadian samples. However, the mean

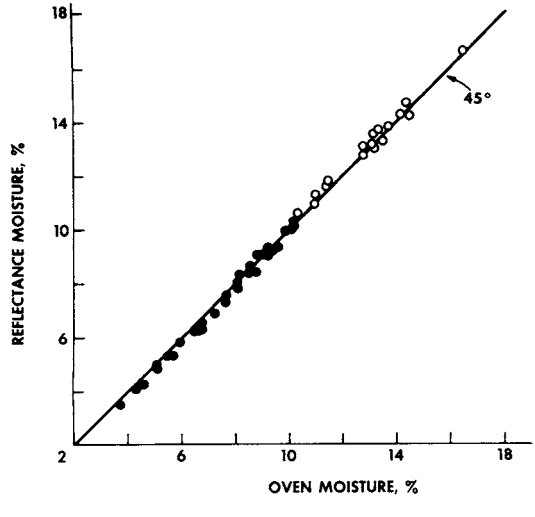

Fig. 5. Moisture content predicted from the equation: $\log m = 1.620 \log F(R'_\infty)_{1.93\mu} - 1.628 \log F(R'_\infty)_{2.10\mu} + 0.966$ *vs.* oven moisture for 32 Australian (•——•) and 17 Canadian (o——o) samples.

differences, −0.14 and + 0.16, are not of sufficient magnitude to detract from the utility of the method.

In summary, the results provide a near-infrared reflectance method for the determination of moisture in wheat which is independent of particle size and applicable to different wheat types with a wide range of moisture contents. Accordingly, this method allows for the development of instruments for the analysis of moisture which can be calibrated with reflectance standards rather than samples of known composition.

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