

NOTE

Sensitivity of Near-Infrared Absorption to Moisture Content Versus Water Activity in Starch and Cellulose¹

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ABSTRACT

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Near-infrared (NIR) diffuse reflectance spectra of wheat starch and microcrystalline cellulose were gathered at water activity (a_w) levels of 0.43 and 0.53 attained through adsorption or desorption. The primary interest was whether NIR absorption was more directly sensitive to a_w or to moisture content (MC). Results indicate that NIR spectroscopy can discriminate between different MCs at the same a_w but is much less

sensitive to different a_w at the same MC. This suggests that separate models are not required when using NIR spectroscopy to estimate MC of carbohydrates that have reached equilibrium along vapor adsorption and desorption pathways. However, the use of NIR spectroscopy to determine the susceptibility of starch and cellulose to a_w -related deterioration processes may be confounded by their sorption history.

Near-infrared (NIR) spectroscopy is commonly used to estimate the moisture content (MC) of wheat and other small grains (Law and Tkachuk 1977, Williams et al 1985). High accuracy, minimal sample preparation (usually only grinding is required), and rapidity of analysis are reasons for the widespread use of this technique. NIR spectroscopy has also been proposed as a method for determining physicochemical properties of foods (Wetzel 1983). The success of this technique in examining water carbohydrate behavior depends on a better understanding of how water is detected during NIR absorption.

Water activity (a_w) is directly related to the chemical potential of water and hence to the occurrence of biological reactions that cause degradation of carbohydrates. However, a_w and MC do not follow a one-to-one relationship in carbohydrates. At a given a_w , adsorbed materials (i.e., materials equilibrated to a given a_w through adsorption) have a lower MC than do desorbed materials (those equilibrated to the same a_w through desorption) (Labuza 1975, Kapsalis 1981, van den Berg 1981, Wolf et al 1984). The effect of this hysteresis on carbohydrate degradation has not been extensively studied. Scott (1957) stated that microbial growth was more dependent on a_w than on MC. More recently, Labuza and coworkers (Labuza et al 1972a,b; Chou et al 1973; Chou and Labuza 1974) found that at a given a_w , the rates of lipid oxidation and growth of certain microbes were higher in desorbed foods than in adsorbed foods. This finding was attributed to a higher

level of chemical and enzymatic reactivity in desorbed foods due to their higher MCs. However, these effects varied greatly among mold species.

The objective of this study was to determine whether NIR can discriminate between MCs of materials equilibrated by adsorption and desorption to the same a_w , and, conversely, between the a_w of materials equilibrated to the same MC. Experiments were conducted on wheat starch and microcrystalline cellulose (MCC). The results were the basis of a recommendation as to whether separate MC regressions are necessary for adsorbed and desorbed materials, and whether the storability of grains (presumably related to a_w) as determined by NIR spectroscopy is confounded by the sorption history.

MATERIALS AND METHODS

Samples of unmodified wheat starch (Sigma Chemical Co.) and MCC (Avicel PH101, FMC Corp.) at room temperature (25°C) were initially equilibrated to either near total dryness or near saturation. Approximately 100 g of material was placed on an elevated tray inside a desiccator containing either desiccant (molecular sieve type 4A) or distilled water. After 44 days, when sample mass changed less than 2 mg in two weeks, the materials were loosely packed into nylon rings with an internal diameter of 38 mm and a depth of 8 mm. The bottom of each ring was fitted with an infrared transmitting quartz window 1.27 mm thick. Sample masses were 3.5 g for dried and humidified MCC and humidified wheat starch, and 5.0 g for dried wheat starch. Each packed ring was placed in one of two controlled humidity chambers containing different saturated salt solutions. Water activity values (Greenspan 1977) were 0.43 and 0.53 and were chosen to maximize the difference in MCs at the same a_w and to yield similar MCs at different a_w (Delwiche 1990). Samples were allowed to equilibrate for an additional 20 weeks at 25°C. Once equilibrated, the open end of each sample ring was capped with a rubber stopper equilibrated to the same a_w as the sample.

Diffuse reflectance readings were collected at 0.4-nm wavelength

¹Mention 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 products not mentioned.

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increments over a wavelength range of 1,000–2,636.8 nm using a modified Cary model 14 prism-grating spectrophotometer with lead sulfide detectors (Norris et al 1976). The instrument bandpass was nominally 7 nm. Sample reflectance readings were referenced against powdered polytetrafluoroethylene (type G-80, Allied Chemical Co.) packed to a density of 1.0 g/cm³ (Weidner and Hsia 1981). Moisture content was determined by oven drying 2 g of each sample at 130°C for 1.5 hr (ISO 1985). Due to the small mass of each equilibrated sample, only one MC determination was made per sample.

RESULTS AND DISCUSSION

Desorbed wheat starch samples at 13.4% MC (dry basis) equilibrated to 0.43 a_w and at 14.8% MC (0.53 a_w), were 0.9 and 1.3 percentage points higher in MC than were the corresponding adsorbed samples (12.5% MC [0.43 a_w] and 13.5% [0.53 a_w]). Comparable MCs were obtained (within 0.1 percentage points) between the desorbed sample at 0.43 a_w and the adsorbed sample at 0.53 a_w . For MCC, the desorbed samples (5.9% MC [0.43 a_w] and 6.6% MC [0.53 a_w]) were higher than the adsorbed samples (5.4% MC [0.43 a_w] and 6.2% MC [0.53 a_w]) by 0.5 and 0.4 percentage points, respectively. The equivalency of MC of the 0.43 a_w desorbed sample and the 0.53 a_w adsorbed sample (0.3 percentage points difference) was not quite as good as that for wheat starch but was still useful for the purpose of analysis.

The spectra of adsorbed and desorbed wheat starch and MCC at each of the two levels of a_w are presented in Figure 1. Two scales were used for the vertical axes of each material for the purpose of clarity; the left corresponds to adsorbed samples, the right to desorbed samples. For wheat starch within a given sorption mode, the 0.53 a_w spectrum (Fig. 1, curves a or c) appears to overlap the 0.43 a_w spectrum (curves b or d, respectively) except in the water absorption band regions of 1,900–2,000 nm, 1,400–1,500 nm, and beyond 2,550 nm. Similar behavior is observed for MCC with the exception that the adsorbed samples

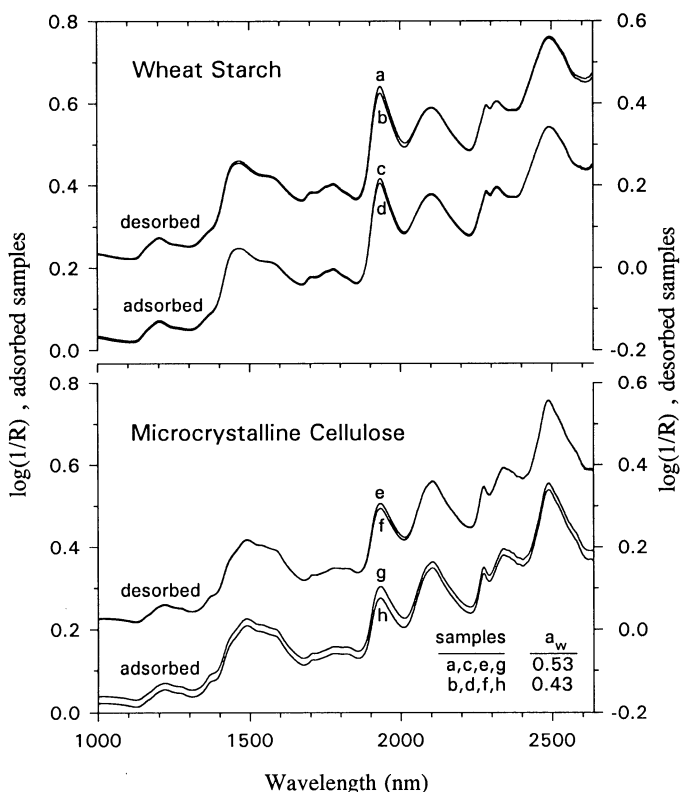


Fig. 1. Diffuse reflectance spectra of wheat starch and microcrystalline cellulose equilibrated to 0.43 and 0.53 water activity (a_w) over paths of adsorption and desorption. The left vertical scales apply to the adsorbed samples; the right scales to the desorbed samples.

(curves g and h) are offset from each other throughout the entire wavelength range due to differences in sample packing density (discussed later). Comparing within a_w and across sorption mode (a vs. c, b vs. d, e vs. g, f vs. h), the adsorbed and desorbed spectra have the same general appearance. This is not surprising if the premise of van den Berg et al (1975) is accepted; hysteresis in starch primarily affects the proportion of starch-starch to water-starch hydrogen bonds. Such changes often give only subtle changes in the NIR spectra.

The NIR sensitivity to MC or sorption mode may be examined more closely using spectral subtraction. Desorbed minus adsorbed $\log(1/R)$ spectra for wheat starch are depicted in Figure 2. Using the curve nomenclature developed in Figure 1, curve (a-c) in Figure 2 represents the case of spectral differences caused by MC rather than by a_w , since a_w was 0.53 in both spectra. Similar results occurred for the 0.43 a_w wheat starch difference spectrum (not shown). In contrast, curve (b-c) represents the case when MC is approximately equal (0.1 percentage points actual difference), while allowing the a_w of the component spectra to differ. The greater departure from zero for curve (a-c) compared to (b-c), especially in the water-absorption regions centered at 1,450 nm and 1,930 nm, indicates that the NIR spectra were more sensitive to different MCs at the same a_w than to different a_w at the same MC. This suggests that hysteresis-induced differences in the starch spectrum are attributable to MC rather than to a_w .

Difference spectra for MCC are depicted in Figure 2. Again, curve (e-g) represents different MCs at 0.53 a_w , and curve (f-g) represents different a_w at near equivalent MC (within 0.3 percentage points). As in the case of wheat starch, the peaks in curve (e-g) at the locations of the water bands indicate that MC rather than a_w is detected in MCC. The difference curves

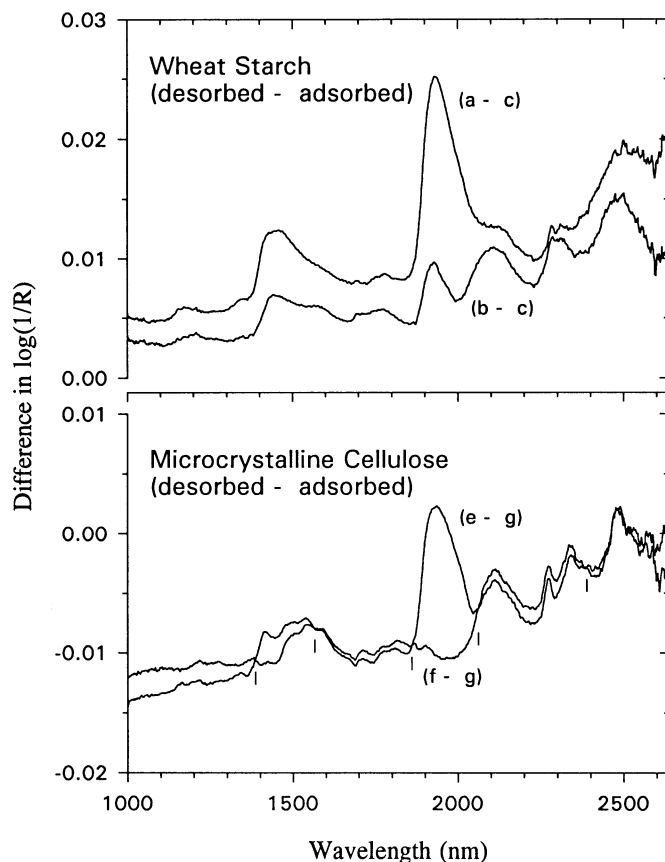


Fig. 2. Difference (desorbed minus adsorbed) $\log(1/R)$ spectra of wheat starch and microcrystalline cellulose. Curves (a-c) and (e-g) each represent the case of holding water activity constant while varying moisture content. Curves (b-c) and (f-g) hold moisture content approximately constant while varying water activity. In the 1,000–2,400-nm region of the microcrystalline cellulose spectra, vertical marks directly below the curves indicate cross-over points.

are less than zero throughout most of the wavelength range. This can be attributed to the slightly greater packing density of the desorbed samples compared to the adsorbed sample, which led to a greater level of overall surface reflectance and hence a decrease in absorbance of NIR energy.

CONCLUSIONS

Spectral differences between materials of similar a_w but different MC were greater than the spectral differences of materials of similar MC but different a_w . Therefore, we propose that NIR absorption in starch and cellulose is more directly sensitive to MC than to a_w . This suggests that separate MC calibration models are not required for adsorbed and desorbed samples of starch and cellulose.

On the other hand, the use of NIR to determine a_w of starch or cellulose as an indicator of susceptibility to deterioration processes may be confounded by their sorption history. Food quality analysts who use NIR for these purposes should be cognizant of this limitation when evaluating deterioration factors that are more strongly dependent on a_w than on MC.

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