APPLICATION OF A TWO-STREAM RADIATIVE TRANSFER MODEL FOR LEAF LIGNIN AND CELLULOSE CONCENTRATIONS FROM SPECTRAL REFLECTANCE MEASUREMENTS (PART 2)

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1. Interpretation of desiccated leaf spectra. Continuing the work described in Part 1, we next sought to understand structures in the dry extracted and derived spectra using calculated reflectances of hypothetical simple two-component mixtures. The reflectances and mixing models used, including the model employed to derive $R_{w\infty}$, ultimately require validation; this has not yet been possible beyond certain qualitative comparisons described here.

In Figure 1 the calculated spectrum $R_{d\infty}$ is compared with lignin and cellulose reflectances (from Elvidge, 1990). A simple interpretation of band position in the desiccated leaf spectrum appears possible in terms of these two end members. We examined this more closely by calculating reflectances of cellulose-lignin and other mixtures and comparing band positions between the hypothetical mixes and $R_{d\infty}$.

Bulk reflectance relationships based on composite scattering and absorption functions were developed from the KM theory for artificial mixtures of dry constituents (and liquid water with dry constituents described here). Many idealized configurations of constituents in single leaves, each individually described by the KM reflectance and transmittance formulae, seem possible. Each has its own macroscopic mixing formula. Some simple possibilities are: (1) single layers comprised of well-mixed pure components, (2) multiple stacked uniform layers of pure end members, and (3) side-by-side compartments of pure end members arranged in single layers. Here we confine attention to (1), lacking a definite basis to pursue another option. Since intrinsic functions of representative major (or minor) pure chemical end members of leaves have not yet been obtained, the development of mixing relations must proceed approximately, in the present case as follows. For two components {1,2} the ratio K_{12}/S_{12}

$$\frac{K_{12}}{S_{12}} = \frac{c_1 \frac{k_1}{s_1} + c_2 \frac{k_2}{s_2} \frac{s_2}{s_1}}{c_1 + c_2 \frac{s_2}{s_1}} \tag{1}$$

of a mixture is $c_1 + c_2 = 1$. Except for the ratio s_2/s_1, the values of the component k/s-ratios are known from the remission function if the spectral diffuse reflectance $R_{j\infty}$ for each component j is known. We will calculate an approximate effective composite ratio K_{12}/S_{12} for the {1,2} mixture by setting $s_2/s_1 = 1$ for all wavelengths, and take the diffuse reflectances of leaf chemical constituents, a number of which have been measured by Elvidge (1990), to estimate k/s-ratios of end-members. In so doing effects of possible impurities, nonuniformity in packing, particle size, and finite sample thickness on reflectances of assumed end members are ignored. The reflectance $R_{12\infty}$ of a two-component mix is calculated from Figure 2 and illustrates application of the model represented by Equation (2) to a mixture of lignin and cellulose, parameterized as the fraction of cellulose (gm/gm) in the mix. Determination of composition in this

$$R_{12\infty} = \frac{1 - \sqrt{K_{12}/(K_{12} + 2S_{12})}}{1 + \sqrt{K_{12}/(K_{12} + 2S_{12})}} \qquad (2)$$

simple dry system might be made from measurement of band position; best resolved and clearest to interpret (although unobservable in the residual spectra from green leaves) is that between 1444 and 1484 nm. This band (reflectance minimum) position is a non-linear function of cellulose fraction f_c, given accurately by $\lambda(f_c) = 1456 + 97.9f_c - 119f_c^2 + 54f_c^3 - 4.5f_c^4$, and is very insensitive to changes in lignin concentration for $.5 \leq f_c \leq 1.0$. For example, suppose the spectral sampling interval $\Delta\lambda$ is that of AVIRIS, 10 nm, and that three perfect spectral band determinations are possible at 1484 and 1474 and 1464 nm. The minimum resolvable difference in lignin concentration Δf_c is approximately 0.75 between the first pair of these and about 0.10 between the second pair. A similar relationship, spectrally less well defined, prevails for the complex of bands between 1650 and 1850 nm.

We return now to interpretation of band positions of $R_{d\infty}$ in Figure 1. From the regression formula for $\lambda(f_c)$ a reflectance minimum at 1460 nm implies a lignin concentration in the two-component dry mix of 94%, and a similar abundance from the band near 1775 nm. This exceeds by far the expected lignin abundance in plant materials of 10 - 35% dry weight (Crawford, 1981).

Other chemical constituents in addition to lignin and cellulose make spectral contributions to the desiccated foliar reflectance, and will alter by dilution the relative abundances of lignin and cellulose present. The nature of the spectral contributions so introduced will be described qualitatively using hypothetical two-component systems, cellulose-starch and cellulose-protein (D-ribulose 1-5-diphosphate carboxylase), illustrated in Figures 3 and 4. Combinations with other plant chemical constituents might be worked out from spectral data given by Elvidge (1990). The admixing of starch with cellulose displaces the 1485-nm cellulose band to shorter wavelengths, similar to lignin. The 1775-nm band position is largely unaffected. The admixing of protein with cellulose produces displacements opposite (but of comparatively small magnitude) to those of both starch and lignin at 1485 nm and to shorter wavelengths at 1775 nm, also similar to that of lignin. Thus both protein and starch mimic spectrally the presence of lignin in mixes with cellulose, especially at 1775 nm. The isolation of lignin concentration from band position alone without knowledge of other end member concentrations thus seems problematical.

2. Mixing of desiccated and liquid water components. Mixing relationships employed in the present application of KM theory together with spectral reflectances of mixtures based thereon have been worked out to isolate signatures of supposed desiccated leaf components and to aid interpretation of spectral signatures of derived reflectance residuals. The theory applied to leaf reflectance awaits detailed experimental validation but offers another set of relationships that suggests its usefulness. We used the intrinsic k- and s-functions of Figure 1 in Part 1 of this article together with Equations (1) and (2) to calculate for sweetgum the spectral reflectance of intermediate mixtures of wet and dry components. These calculations are illustrated in Figure 5. A comparison with single leaf reflectance data as a function of relative water content given by Hunt and Rock (1989) is suggestive.

3. Reflectance retrieval from AVIRIS. The previous analysis leading to plots of residuals given in Figure 4 in Part 1 was based on diffuse spectral reflectance

measurements made under idealized conditions with a laboratory spectrometer. The largest spectral variations in these residuals amount to approximately 2 % in the 1700-nm region. Reflectance variations are also present below this level. Under field conditions, using measurements of the upwelling radiance at AVIRIS, an atmospheric model is ordinarily required to retrieve an effective surface (Lambertian) reflectance, unless ground targets can be used (Elvidge, 1988). Noise arising from spatial fluctuations or uncertainties in atmospheric properties and from AVIRIS will contribute uncertainty to the reflectance values so derived. We carried out numerical experiments with the LOWTRAN 7 (Kneizys et al., 1983) radiative transfer model to estimate uncertainties due to atmospheric variations. It proves advantageous to recalibrate AVIRIS in-flight using local surface targets to eliminate channel-to-channel variations in radiance that are thought to originate from changes in the radiometric calibration coefficients between laboratory and in-flight conditions.

For homogeneous, plane-parallel atmospheric conditions over uniform ground of Lambertian surface reflectance ρ_s, the radiance at AVIRIS is represented approximately as

$$L(\mu,\mu_0,\tau) = \frac{F_{\odot}}{4\mu}\left[S(\mu,\mu_0,\tau) + \frac{4\rho_s}{1 - \rho_s\bar{s}}\,\mu\mu_0 T(\mu,\mu_0,\tau)\right] . \tag{3}$$

In Equation (3) $\pi F_{\odot}$ is the solar irradiance, $S(\mu,\mu_0,\tau)$ is the atmospheric scattering function, $T(\mu,\mu_0,\tau)$ is the two-way diffuse plus direct atmospheric transmittance, $\bar{s}$ is the hemispherical backscatter function, μ and μ_0 are cosines of the zenith angles of viewing and solar incidence directions respectively, and τ is optical depth. Spectral dependence of the atmospheric and surface quantities is implied. An in-flight calibration experiment redefines the radiometric calibration in terms of in-flight coefficients Φ^* given by

$$\Phi^* = \frac{(L_M)_c}{(DN-DN_0)_c} \tag{4}$$

where DN and DN_0 represent instrument and dark current response for the conditions of calibration, and $(L_m)_c$ is the radiance at AVIRIS obtained from a radiative transfer model (LOWTRAN and/or MODTRAN) using measured atmospheric conditions. $(L_m)_c$ is given approximately by

$$(L_m)_c = \left[\frac{S_c}{4\mu_c} + (\mu_0)_c T_c R_c + (\mu_0)_c T_c \bar{s}_c R_c^2\right]F_{\odot} \tag{5}$$

With the in-flight calibration factors, the ground reflectance R_g is

$$R_g = -\frac{A}{B} - \bar{s}\left(\frac{A}{B}\right)^2 + \left[1 + 2\bar{s}\left(\frac{A}{B}\right)\right]\frac{\Phi^*}{B}(DN - DN_0) - \bar{s}\frac{\Phi^{*2}}{B^2}(DN - DN_0)^2 \tag{6}$$

where $(DN - DN_0)$ represents the dark-current corrected in-flight instrument response, and

$$A = \frac{SF_{\odot}}{4\mu}, \qquad B = \mu_0 TF_{\odot}$$

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The expression for R_g, Equation (6), is independent of the solar irradiance, but use of the in-flight calibration coefficients Φ^* has introduced additional variables pertaining to atmospheric conditions during calibration and also the calibration target reflectance R_c. We applied standard error propagation formulas to Equation (6) to evaluate a fractional uncertainty σ_{R_g}/R_g from fluctuations in all the atmospheric parameters (taken equal for both calibration and observation experiments) and from the AVIRIS response parameterized as the signal/noise ratio. The LOWTRAN model evaluated was midlatitude summer, rural aerosols, surface meteorological range 25 km, surface reflectance 0.50, and solar zenith angle 22°.179. The calculated uncertainty as a function of AVIRIS signal/noise ratio at 1700 nm with prescribed atmospheric uncertainties, written collectively as σ_a/a to represent σ_S/S, etc., is shown in Figure 6. Values of σ_{R_g}/R_g less than a few percent are achieved only for uniform atmospheric conditions ($\sigma_a/a < .01$) and high signal/noise ratios (> 100).

4. Summary. We used the Kubelka-Munk theory of diffuse spectral reflectance in layers to analyze influences of multiple chemical components in leaves. As opposed to empirical approaches to estimation of plant chemistry, the full spectral resolution of laboratory reflectance data was retained in an attempt to estimate lignin or other constituent concentrations from spectral band positions. A leaf water reflectance spectrum was devised from theoretical mixing rules, reflectance observations, and calculations from theory of intrinsic k- and s-functions. Residual reflectance bands were then isolated from spectra of fresh green leaves. These proved hard to interpret for composition in terms of simple two component mixtures such as lignin and cellulose. We next investigated spectral and dilution influences of other possible components (starch, protein). These components, among others, added to cellulose in hypothetical mixtures, produce band displacements similar to lignin, but will disguise by dilution the actual abundance of lignin present in a multicomponent system. This renders interpretation of band positions problematical. Knowledge of end-members and their spectra, and a more elaborate mixture analysis procedure may be called for (see, for example, Kortum, 1969, p. 303). Good observational atmospheric and instrumental conditions and knowledge thereof are required for retrieval of expected subtle reflectance variations present in spectra of green vegetation.

6. References.

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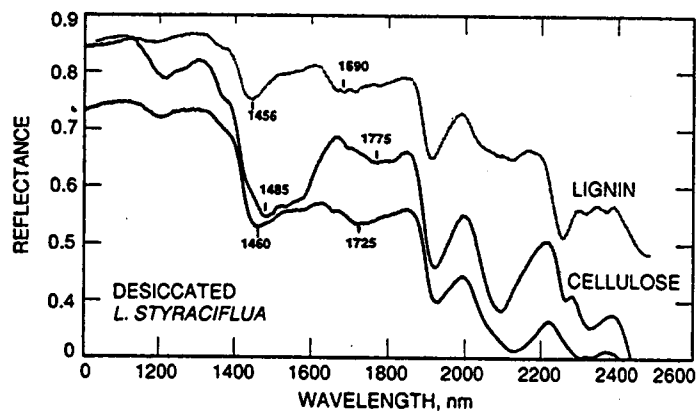
Figure 1. Reflectances of lignin, cellulose, and desiccated
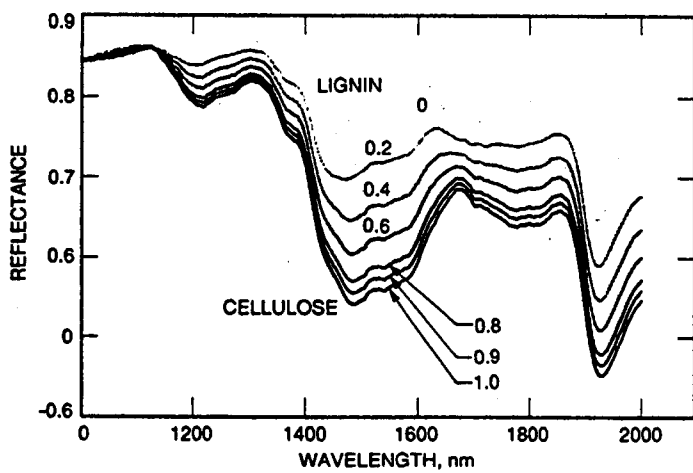*L. styraciflua.*

Figure 2. Reflectances of hypothetical mixes of cellulose
and lignin. Curves are for cellulose fractions of
1.0 (pure cellulose), 0.9, 0.8, 0.6, 0.4, 0.2,
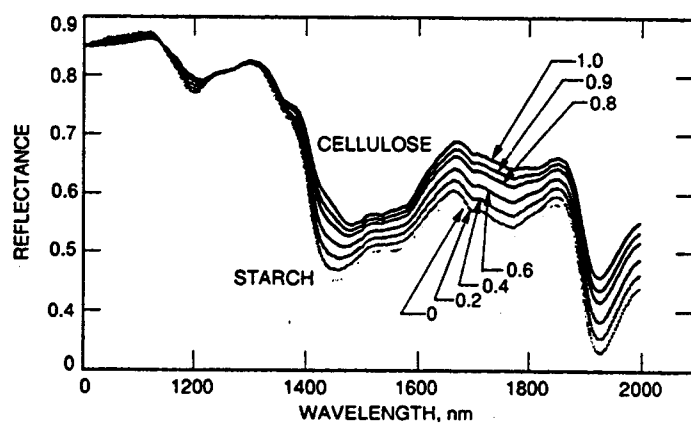and 0.0 (pure lignin).

Figure 3. Reflectances of hypothetical mixes of cellulose
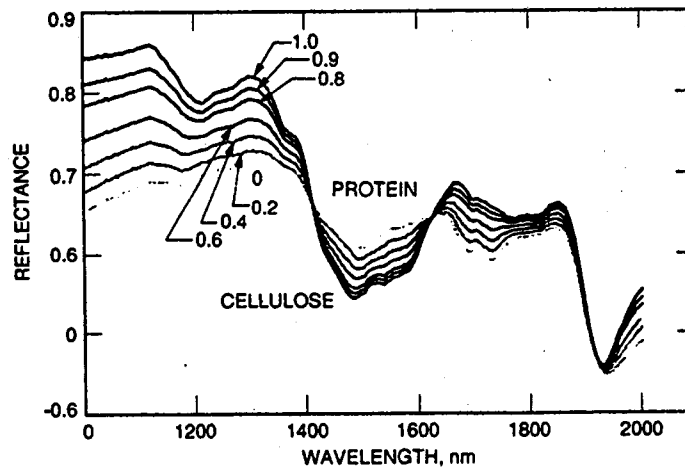and starch. See caption Figure 2 for curve
assignments.

Figure 4. Reflectances of hypothetical mixes of cellulose
and protein. See caption Figure 2 for curve
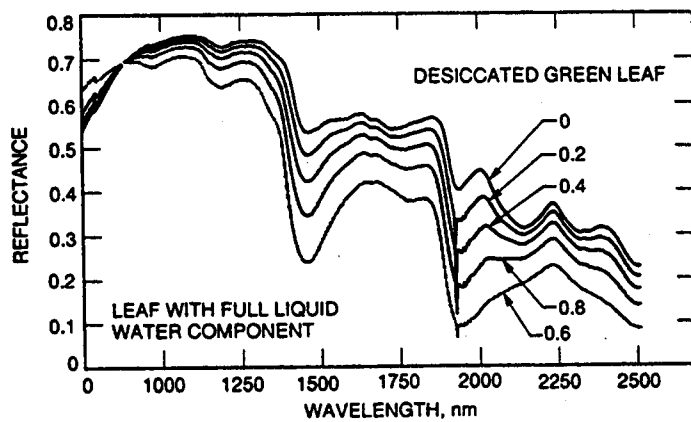assignments.

Figure 5. Reflectances of hypothetical combinations of
desiccated *L. styraciflua* and leaf liquid water
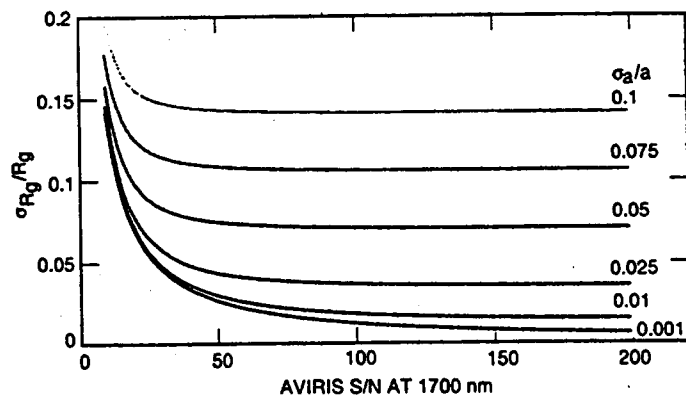components.

Figure 6. Calculated uncertainties in retrieved surface
reflectance for AVIRIS S/N and atmospheric
variability.