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# Remote Sensing of Crop Type and Maturity

**An airborne spectroradiometer was employed to detect a red spectral shift in the chlorophyll absorption edge and, thus, to discriminate crop type and maturity.**

ABSTRACT: *A red-shift in the chlorophyll absorption edge of heading wheat and grain sorghum is clearly visible in high-spectral-resolution measurements made from a low-flying aircraft over Imperial Valley, California. The position of the absorption edge shifts progressively toward the longer wavelengths during the crop growth cycle, reaching a maximum in the fully-headed pre-ripening stage. The red-shift of 7 to 10 nm can be measured by using 10 nm-wide spectral bands, centered at 745 nm and 785 nm. These two bands, plus a band in the pigment absorption region at 670 nm, contain enough information to identify wheat and grain sorghum in the heading stage, to indicate the degree of heading, and to indicate canopy density during the heading stage.*

*A smaller red-shift in the absorption edge is also visible in non-grain crops during maturation. The working hypothesis formed as a result of this study is that the red-shift results from increasing chlorophyll* a *concentration during the growth cycle. The greater concentration produces molecular aggregation by chlorophyll-chlorophyll and possibly chlorophyll-protein interactions. Polymer forms shift the far-red absorption edge by adding closely spaced absorption bands to the far-red shoulder of the main chlorophyll* a *band.*

## INTRODUCTION

THE VITAL GOAL of monitoring wheat crops and other vegetation canopies, based on spectral properties observed by multi-band remote sensing systems, has been an elusive one. Broad-band measurements are sensitive to large and ambiguous spectral variations in reflected radiation, caused by many natural physical and biological variations in extended biomass canopies. As a result, only gross differences in vegetation species or condition can be resolved in the broad-band intensity information. Much of the canopy-induced problem of background variation in radiance measurements has been overcome in the present study by using a discrimination technique based on the spectral position of the far-red chlorophyll absorption edge, which, under varying canopy conditions, remains sensitive to the long-wavelength properties of photon absorption by the plant pigment systems. It appears that, during a crop life cycle and from species to species, the aggregated states of the chlorophyll *a* group of pigments evolve in a consistent and characteristic manner that can be observed as a change in the long wavelength limit of photon absorption on the absorption edge.

High-spectral-resolution data gathered for this study using a specially designed airborne system show for the first time that variations in the spectral position of the far-red absorption edge can be detected in the field with remote sensing techniques. Under spectral resolutions on the order of 2 to 10 nm, shifts in the absorption edge of crop

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spectra are clearly visible to the remote spectral sensor. The shift is progressively toward the longer wavelengths during plant growth and maturation. In wheat and grain sorghum, a very pronounced red-shift occurs during the heading stage. The far-red progress of the shift is sensitive to the degree of heading, which can be discriminated with properly placed narrow bands despite large canopy-induced background variations in other parts of the spectrum. The magnitude of the red-shift distinguishes the headed grains from other non-grain crops in the area surveyed.

The results from the available aircraft spectral data of crops indicate that not only are wheat and grain sorghum clearly identified, but also that, with further development, it may be possible to estimate canopy density and yield during the crucial heading stage based on remote sensor data alone. This information is contained in three spectral bands positioned to measure the near-IR reflection at 785 nm, reflection in the chlorophyll *a* band at 670 nm, and the red-shift at 745 nm.

Changes in the long wavelength limit of photon absorption by chlorophyll and whole quantasome extracts have been observed in laboratory studies. These results are reviewed later in this paper in the discussion of the physicochemical origin of the red-shift. A shift in the spectral position of the chlorophyll absorption edge of whole leaf samples has also been reported by Gates *et al.* (1965). Their laboratory measurements of white oak leaves show a progressive shift toward the longer wavelengths as the leaves mature. The *in vivo* properties of the red-shift or its application to remote sensing have not, however, been reported previously. The present study of plant canopies using airborne remote sensing techniques (1) examines the problem of ambiguous background variations that effect remote radiance measurements and analysis of vegetation canopies; (2) presents the red-shift phenomenon observed *in vivo* with the airborne remote sensing system, and discusses the potential use of the red-shift to improve remote sensing analysis of vegetation canopies—grain crops in particular; and (3) discusses a working hypothesis for the origin and behavior of the observed red-shift phenomenon.

## DATA COLLECTION AND INSTRUMENTATION

The airborne survey was conducted in Imperial Valley, California in May and September, 1975. The data were collected between 11:00 a. m. and 12:30 p. m. with clear skies and low haze conditions. More than 300 fields in plots ¼ mile and ½ mile (400 and 800 meters) on a side, sectioned in an orthogonal pattern, were surveyed. The main crops growing in the survey sites were wheat, alfalfa, cotton, sugar beets, sudan grass, and milo. All crops in the area are grown under flood irrigation. The Imperial Valley sites were chosen because of the variety of crops and different stages of growth available simultaneously. Flight lines were flown over selected areas in a 5 mile long east-west pattern parallel to the ground sectional pattern. The data and the survey area are documented in more detail in Ungar *et al.* (1977).

The instrumentation used is a 500 channel spectroradiometer with 1.4-nm wide bands, sensitive in the 400-nm to 1100-nm spectral region. The system employs a parallel input optics and detector array design, which gives optimum band-to-band registration of the ground target from a moving platform, and high sensitivity at rapid data acquisition rates. The system acquires 500 channel spectra at the rate of 2.5 spectra per second. The data are digitized and stored on computer-compatible magnetic tape. The instrumentation is described fully in Collins (1976) and Chiu and Collins (1978).

The instrument was flown at 610 m above the ground and at 200 km per hr ground speed. The target measurements were taken with an 18 meter square field-of-view and in a contiguous one-dimensional sequence along the ground track. Fifteen to forty spectra were obtained in each field, dependent on field size, giving a complete cross-sectional sampling of the field. The data were calibrated channel-by-channel for radiance received at the entrance aperture. The calibrated spectral data have been processed in order to obtain individual reflection curves (in spectral radiance) and differential spectral information in the cross-sectional sample (traverse) of individual fields (standard and percent standard deviation). Discrete wider band ratios have been calculated for field and entire flight line traverses by integrating over selected portions of the spectral curves.

## INTERPRETATION OF AIRCRAFT SPECTRAL DATA

### SPECTRAL VARIATIONS IN EXTENDED NATURAL CANOPIES

In order to appreciate the importance of the spectral information obtainable from the

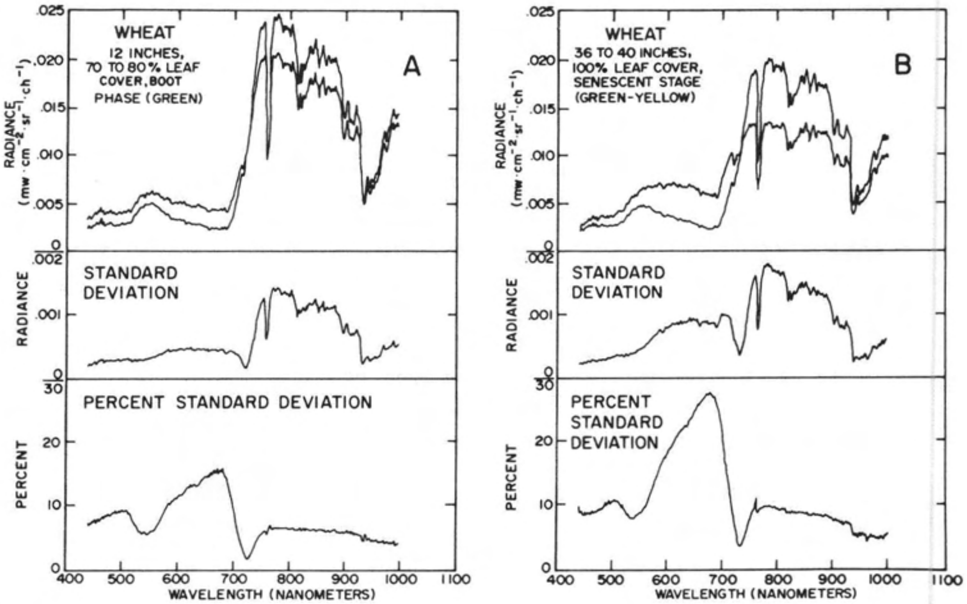

FIG. 1. Reflected spectral radiance and deviation spectra of wheat from two fields in different stages of growth. The top curves show the spectral extremes in each field based on the ratio of near-IR reflection at 785 nm to chlorophyll absorption at 670 nm.

position of the chlorophyll absorption edge, it is necessary to understand the physical effects responsible for the vegetation canopy spectra. It is necessary in particular to establish the nature of the canopy-induced spectral variations inherent in the aircraft remote sensor measurements, which are individually integrated over extended, nonhomogeneous fields-of-view and collectively gathered over terrain with varying canopy conditions.

A combination of different energy-matter interactions in the visible (400 to 750 nm) and near IR (750 to 2000 nm) are responsible for the characteristic vegetation spectra shown in Figure 1 and elsewhere in this study. In the near IR, leaf material is transparent to the long wavelength radiation. This radiation is scattered by multiple reflections at optical density boundaries within the mesophyll structure (Gates *et al.*, 1965; Gates, 1970). Therefore, the near IR reflectivity of a vegetation canopy is dependent on development of the mesophyll structure in individual plants and on the vertical density (up to the light penetration limit) of the overall canopy. Laboratory measurements presented by Gates *et al.* (1965) and Gates (1970) show increasing near-IR reflectance in white oak leaves during the mesophyll development stage of plant growth. Increased reflectance from multiple leaf layers is demonstrated by Myers *et al.* (1970). Laboratory measurements by Gates (1970) also show a decrease in the IR reflectivity in matured plants in the senescent stage where dehydration occurs and the mesophyll structure breaks down.

Radiation interactions with the chlorophylls and auxiliary pigments in the visible region are far more complex. Photon absorption bands of individual chlorophyll pigments are on the order of 25 nm or less in width. In a living plant, however, the interactive effects of the photon absorbing pigments broaden the absorption bands causing considerable overlap. In addition, large changes in the refractive indices for wavelengths near the pigment absorption frequencies (anomalous dispersion) cause wavelength-selective losses of radiation by scattering (French, 1960). This "apparent absorption" also tends to widen the photon absorption region and increase the overlap among individual bands. The result is a wide absorption area in the visible region with only a small rise in the green part of the reflection spectrum at 550 nm where the overlap is not quite complete.

Although the enhanced reflectivity in the IR and the absorption in the visible spectrum are due to different processes of energy-matter interaction, they are related insofar as chlorophyll production and mesophyll development are interdependent functions of the plant growth and vigor.

Under field conditions, unfortunately, variations in relative reflectivity between the near-IR region and the red chlorophyll absorption band can be caused by several (sometimes overlapping) plant or canopy conditions. For instance, the spectral reflection variations due to the ground surface showing through a healthy green canopy are similar to the spectral variations produced by chlorosis.

*Nature of canopy related variations in the aircraft data.* Spectral variations due to canopy density effects and ripening in two different wheat fields from the Imperial Valley study are shown in Figure 1. Spectral reflection curves show the two most different spectra in a single field. The difference criterion is the ratio difference between the near-IR plateau and the chlorophyll absorption band at 670 nm. The lower curves show the standard deviation and percent standard deviation among all spectra in the individual fields. The deviation spectra are calculated from 15 to 40 spectral measurements depending on the field width along the aircraft traverse. The spectral variation in the field of young green wheat with areas of sparser leaf cover (figure 1A) are similar, except for degree, to the spectral variations seen in a wheat field in the senescent (ripening) stage (figure 1B). In the case of soil showing through the canopy and senescence, the decrease in chlorophyll absorption is accompanied by a drop in the IR reflection.

In addition to these spectral variations, independent fluctuations occur in both the chlorophyll band and the near-IR plateau in healthy plant canopies with total leaf cover. Variation in the IR plateau in fields of alfalfa and cotton, shown in Figures 6B and 7, are not accompanied by a sympathetic variation in the chlorophyll band. Similarly, the variation in the chlorophyll band in the alfalfa field of Figure 6A is not accompanied by an IR plateau fluctuation. These independent spectral variations compound the already large uncertainty inherent in using the relative height of the IR plateau and depth of the chlorophyll band as an indication of plant species, canopy condition, or state of stress.

### SPECTRAL VARIATION ON THE CHLOROPHYLL ABSORPTION EDGE

The far-red absorption edge between 700 nm and 750 nm has been considered a transition region that, when using wide spectral bands on the order of 50 nm or more, does not contain information useful in remote sensing of vegetation canopies (Tucker and Maxwell, 1976). This is understandable because broad bands straddling the absorption edge are in a position to be sensitive to the intensity variations in both the chlorophyll absorption region and the near-IR plateau of high reflectivity in green canopies. Therefore, radiance measurements in bands covering the entire 700 to 750 nm region would be a convoluted function of the canopy variables affecting the spectral regions on both sides of the absorption edge. The problems of background canopy-induced variations become more complex when using broad bands in the absorption edge region.

Under the wavelength resolution achieved in the airborne system, however, the absorption edge region contains unique spectral information about the location of the far-red pigment absorption bands. This is the only region in the vegetation spectrum where the sides of the pigment absorption bands are unobstructed and can be used to extract spectral information that may indicate the physicochemical states of the pigment systems. Furthermore, with properly placed narrow bands in this region, the broad-band problems of canopy-induced background "noise" variations are greatly reduced.

*The red-shift.* In the aircraft data from Imperial Valley, the absorption edge in spectra of crop canopies shifts toward the longer wavelengths as a function of both crop type and stage of growth (Figure 2). The largest spectral shift, 7 to 10 nm toward the longer wavelengths, occurs consistently in the spectra of wheat crops during the green, headed stage. A red-shift of similar magnitude is present in the reflected spectra of grain sorghum (milo), also in the green, headed stage.

Green alfalfa and green wheat are among the "confusion" crops, with respect to their broad-band spectral characteristics. Individual spectra of these crops, compared in Figure 2, show a typical example of the distinctive red-shift phenomenon as it develops in the green wheat spectrum during the heading stage. The red-shift occurs along the entire length of the absorption edge. It is most pronounced on the shoulder at ≈740 nm.

The difference and percent difference spectra for the two spectral curves in Figure 2 are shown in Figure 3. A maximum relative difference of 15 percent occurs on the absorption edge at 725 nm. The absolute difference is greatest on the shoulder at 740 nm. The width of the difference peaks is ≈50 nm at the half power points. Among the more than 300 crop fields surveyed, the spectral

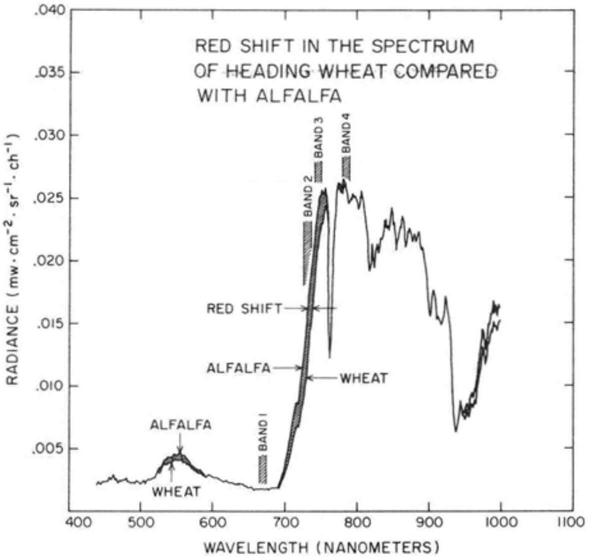

FIG. 2. The reflected spectral radiance of wheat in the green, headed stage compared with the spectrum of mature, green alfalfa clearly shows the nature of the red-shift phenomenon.

shift of this magnitude and toward the longer wavelengths is an unambiguous indicator (1) of grain crops in the green, headed stage as opposed to grain crops in pre-heading (boot) or ripening stages; and (2) of green, headed grain crops as opposed to green, non-grain crops.

*Narrow band ratios for canopy discrimination.* For analyzing large numbers of spectra, the aircraft data have been reduced to the four 10-nm wide bands shown in Figure 2. The 10-nm bands are simulated by integrating the 1.4-nm instrument channels over the selected spectral regions. Band 1, at 670 nm, is at the center of the chlorophyll *a* absorption region. Bands 2 and 3, near the difference maxima in Figure 3, are centered at 735 nm and 745 nm; they are shifted toward the longer wavelengths to avoid the effects of intensity variations in the 670 nm

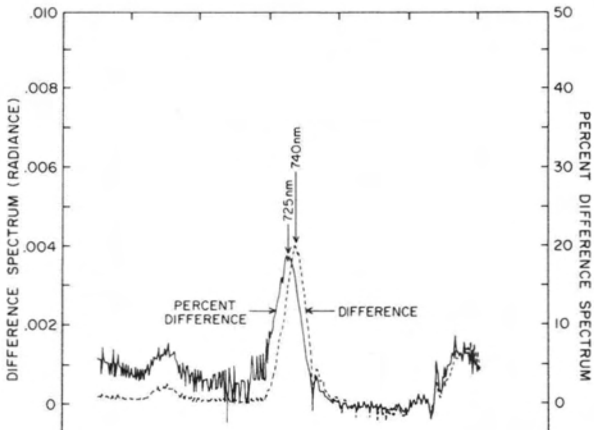

FIG. 3. Difference spectra of wheat and alfalfa.

chlorophyll region. The crossover, quasi-isobestic point, between the major effects of pigment absorption in the visible region and enhanced reflectivity on the near-IR plateau, is indicated by the dip in the deviation curves at 730 nm (e.g., Figure 1B).

Band 4, on the near-IR plateau at 785 nm, is the reference point for relative measurement of apparent chlorophyll absorption in band 1 and the red-shift in bands 2 and 3. Band 4 is placed on the absorption shoulder, close to the difference maxima, in order to minimize possible noise effects of wide-band variations in the near-IR region, i.e., canopy effects, instrument factors, atmospheric effects. The four bands for discrimination have been tested by varying the positions and widths. The present configuration gives optimum contrast of relative variations in the chlorophyll absorption region and on the absorption edge.

*Red-shift in wheat.* The band 4/3 ratios have proven the most sensitive to the red-shift. The 4/3 and the 4/1 ratios for 10 wheat fields in various stages of maturity are shown in Figure 4. The band ratios are plotted with respect to the sequence of spectral measurements along the traverses of selected fields from three adjacent flight lines. All spectral data presented in Figure 4 were taken within a 15-minute interval at midday, which amounts to a 2 degree change in solar elevation at that time and location.

The red-shift among wheat spectra follows a very consistent trend over the crop life cycle. The absorption edge shifts progressively into the far-red (4/3 ratios increase) during the green growth stage. The shift reaches a maximum when the heads are fully emerged and green. The ratios, for 24-inch wheat, increase from 1.15 for the unheaded wheat to 1.25 for the field of 24-inch wheat with heads emerged. The incremental nature of the increase is probably an artifact of the data: no early stages of heading occurred in the area. The wheat heads in the 24-inch headed field are not quite fully emerged (90 percent emerged). The ratios for the following two fields in the fully headed stage go well above 1.30. The band 4/3 ratios decline steadily in the senescent (ripening) stage and go below 1.10 as ripening progresses.

Although the band 4/1 ratios follow a general upward trend in the green growth stage, the variations within fields and among fields, which can be considered the canopy-induced noise, range between 7.0 and 13.0 for headed and non-headed (booted) wheat alike. In contrast, the 4/3 ratios increase from 1.150 to greater than 1.250 with only a ±0.025 canopy-induced noise variation. The red-shift, measured by the magnitude of the 4/3 ratios, is an unambiguous indicator of heading in the green wheat. Furthermore, the large canopy-induced noise variations affecting the 4/1 ratios do not have the same

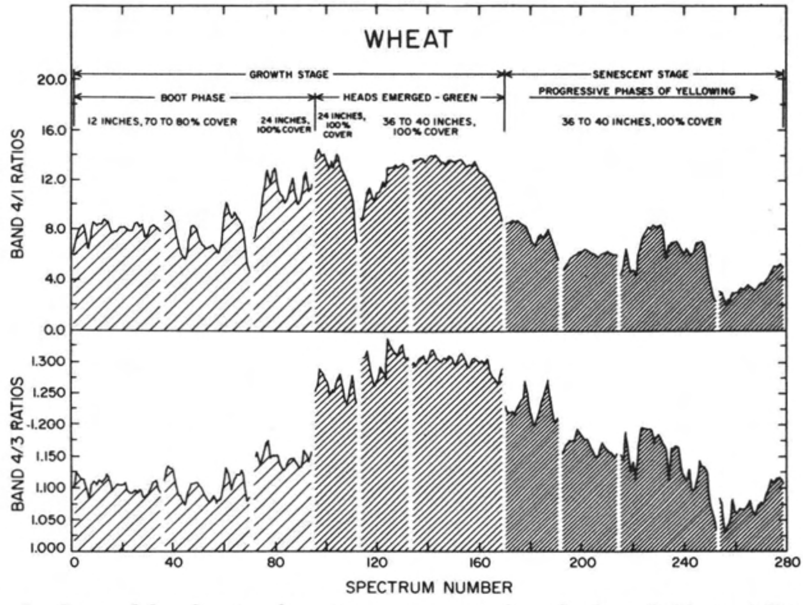

FIG. 4. Spectral band ratios from traverses over selected wheat fields in different stages of growth. The ratio curves are constructed from the 15 to 40 measurements taken in a continuous sequence along aircraft traverses of each field.

signal degradation effect on the 4/3 ratios. The decrease in the 4/1 ratios toward the edges of the fields, where the canopies are generally thinner, is not reflected in the 4/3 ratios.

The red-shift is also very sensitive to the degree of heading, as indicated by the lower ratios (≈1.250) in the field of 24-inch wheat with the heads only 90 percent emerged. The average 4/3 ratios of fully headed fields are higher by twice the noise factor than the heading field. This difference is not visible among the 4/1 ratios of the heading and fully-headed fields. These relationships demonstrated in the sample fields of Figure 4 hold true for all wheat crops observed in 72 aircraft traverses of 49 individual wheat fields in the survey sites.

The ripening fields presented in Figure 4 are in the earlier stages of turning green-yellow. The first yellowing tint is barely perceptible to the eye in the field centered at spectrum 180. The 4/1 ratios drop very quickly in the senescent stage, probably as a result of dehydration at the onset of senescence. The 4/3 ratios indicate that the absorption edge shifts back toward the shorter wavelengths in the senescent wheat.

*Red-shift in other crops.* The spectral band ratios for some non-grain crops and for grain sorghum (milo) are shown in Figure 5. Although the 4/1 ratios vary widely in these crops, due mostly to canopy density variations, the 4/3 ratios follow consistent trends. The non-grain crops occur in various stages of growth and canopy condition throughout the survey region, but the absorption edge does not shift into the far-red region beyond a maximum 4/3 ratio of 1.15 in any non-grain field. The ratios range between 0.95 for bare soil to 1.15 for a mature green canopy. The red-shift in grain sorghum spectra, however, follows a trend similar to the one in the wheat cycle. The heading stage is accompanied by a high 4/3 ratio that drops in the ripening stage. The non-grain form of sorghum (sudan grass) does not develop a red-shift.

Selected spectra from some of the fields used in Figure 5 are shown in Figures 6 and 7. The two individual spectra for each field are those with the maximum difference in the 4/1 ratio. The spectral variation within a species is far greater than any difference among them, except in the position of the far-red absorption edge, which can hardly be discriminated by eye in the spectral plots.

The small variations that occur on the absorption edge of non-grain crops can be observed in the sensitive 4/3 ratios. These absorption edge variations, which, on a much reduced scale, behave similarly to those ob-

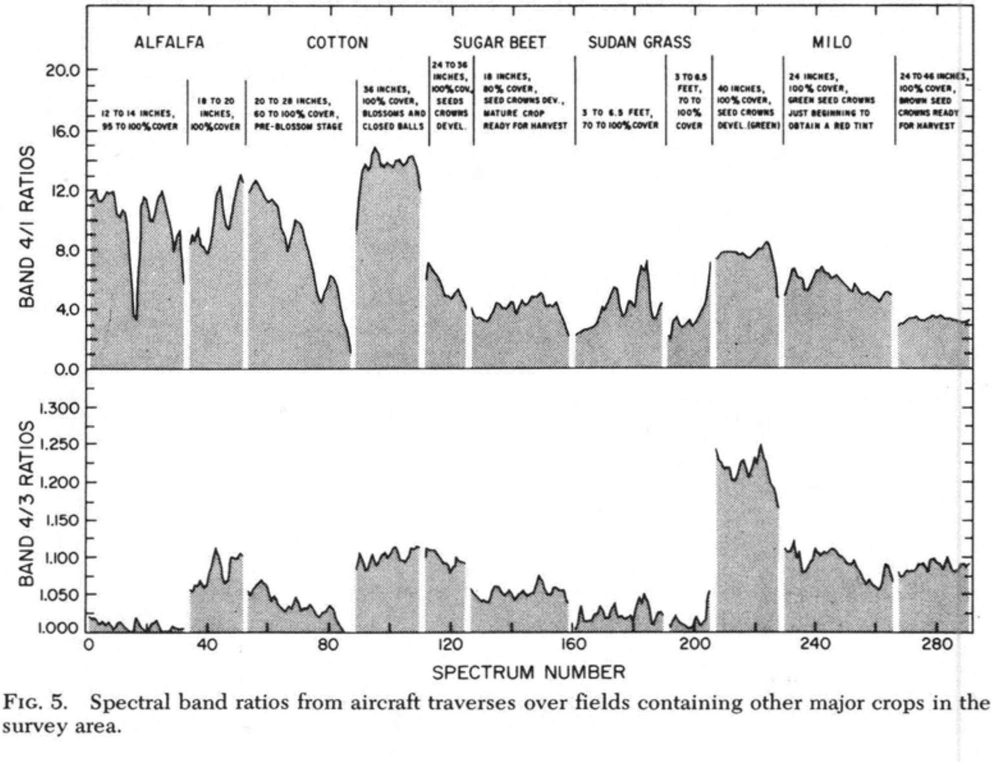

FIG. 5. Spectral band ratios from aircraft traverses over fields containing other major crops in the survey area.

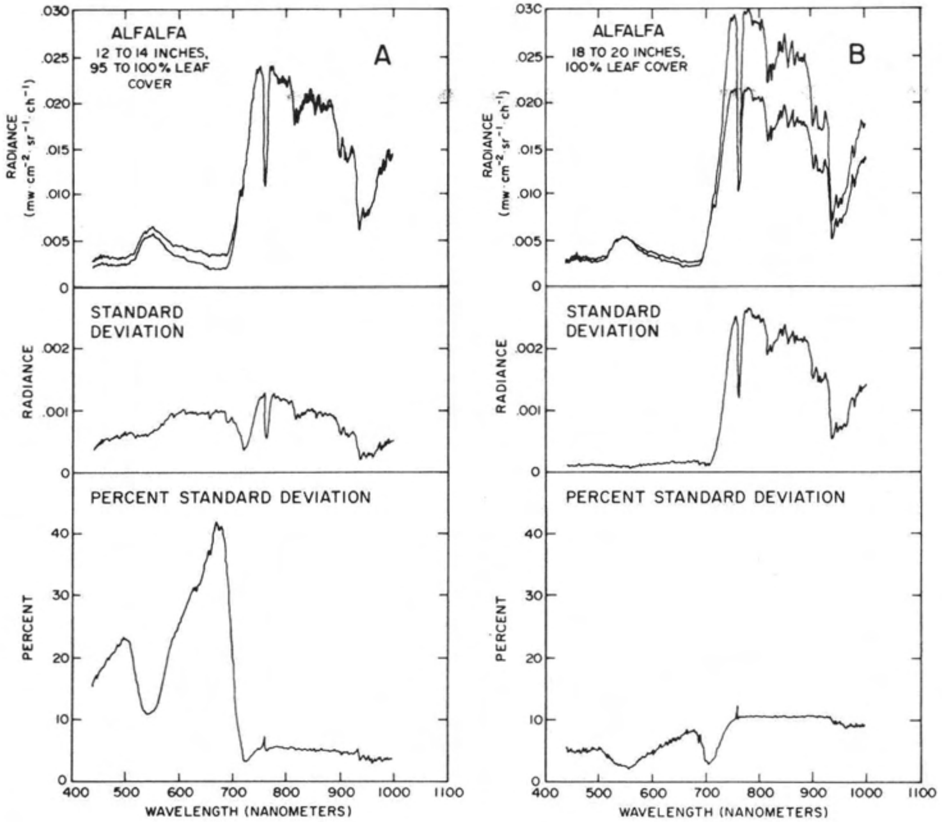

FIG. 6. Reflected spectral radiance and deviation spectra from two alfalfa fields with differing variance characteristics.

served in the wheat growth cycle, may be indicative of maturation within these species. The higher 4/3 ratios for alfalfa and cotton in Figure 5 occur in the taller or more mature fields. The lower ratios for sugar beets occur in the post growth stage: ready for harvest. As further example, the deviation curves for the shorter alfalfa crop (Figure 6A) indicate a uniform canopy with varying chlorophyll content, suggesting the pigment development stage. Compared with Figure 5, the red absorption edge is well toward the shorter wavelength region, also indicating a young, developing pigment system. In the taller crop, the chlorophyll is very uniformly developed (Figure 6B), and the absorption edge has shifted toward the far-red in Figure 5. This is probably the order of magnitude signal that will be important in the analysis of non-grain crops and other types of vegetation. Noise filtering may be required to further analyze these smaller red-shifts.

*Wheat discrimination based on the red-shift.* The obvious and vital application of the red-shift in grain crops is toward monitoring growth conditions in the vast wheat fields of the Midwest and other areas of the world. With further experimentation and quantification of the information available in the 4/3 and 4/1 ratios, the potential for identifying wheat and estimating grain yield based on spectral remote sensing techniques may improve significantly.

Ratio plots for the data in one continuous aircraft traverse of ten fields are shown in Figure 8. The crops covered in this traverse include wheat in various stages, alfalfa, and sugar beets. High 4/1 ratios indicate thick canopy development in three fields containing wheat and alfalfa. The high 4/3 ratios clearly distinguish the two headed wheat fields from the alfalfa, which has very low 4/3 ratios. The 4/2 ratios also separate headed wheat from the other fields, but the contrast is not as clear as in the 4/3 curve. The slightly lower 4/3 ratios in the headed wheat field near the end of the flight line (spectra 240 to 260) indicate that heading has not progressed as fully as in the field with 4/3 ratios exceeding 1.30. Ground-truth substantiates that the wheat heads in the field

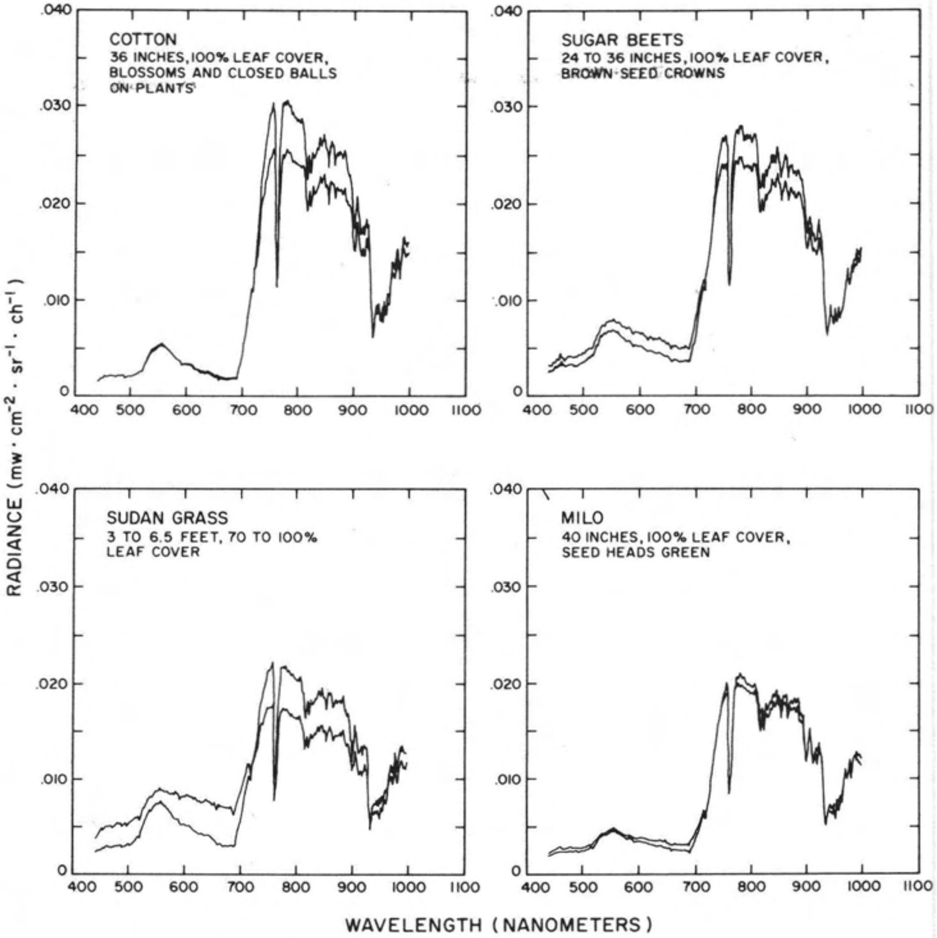

FIG. 7. Reflected spectral radiance curves showing the extremes of spectral variation in four fields used in Figure 5.

with slightly lower 4/3 ratios have not yet fully emerged. The sharp shoulders on the 4/3 ratio curves of the headed wheat indicate that heading has occurred, or is uniformly in progress, across the fields. The rounded shoulders on the 4/1 ratio curves, however, indicate that these crops have thinner canopies on one side of the field.

The identification of wheat and indication of the degree of heading are a critical part of the information required for grain yield estimates. The high 4/3 ratios also indicate that the canopy is in the mature, green stage, which removes the ambiguity introduced in bands 1 and 4 by the effects of underdeveloped pigment systems in young canopies or chlorosis in senescent canopies. Given the information that the canopy is green and mature, canopy density estimates based on the 4/1 ratio values should definitely improve.

## PHYSICOCHEMICAL ORIGIN OF THE RED-SHIFT

The red-shift in the absorption edge of white oak spectra, observed by Gates (1965), was interpreted as a response to variation in chlorophyll content. Evidence from the literature on photosynthesis research substantiates this interpretation. However, the physicochemical states of the pigment systems responsible for increased photon absorption at longer wavelengths are only partly understood; they result from a very complex system of bioenergetic and biochemical processes that are difficult to resolve, especially in living plants.

In the green plants, an undetermined number of pigments interact in a specific ordered sequence to energize the photosynthetic reaction. Chlorophyll *a*, which is the pigment present in all green plants, is the end member in the ordered sequence. Photon absorption by this pigment deter-

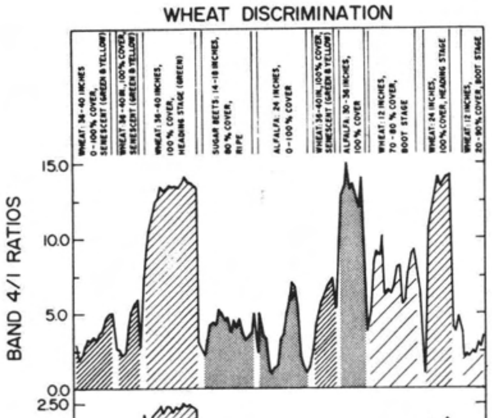

FIG. 8. Continuous aircraft traverse of ten crop fields. The ratio combinations of band 4 with bands 1, 2, and 3 are plotted in the measurement sequence along the flight path.

mines the position and shape of the far-red absorption edge in the reflectance spectrum. The chlorophyll *a* group absorbs in a variable band that is nominally 30 nm wide and centered at about 675 nm. This band contains the two most abundant forms of chlorophyll *a*: chl *a* 670 and chl *a* 680. Photon energy absorbed by the accessory pigments at shorter wavelengths (mainly chlorophyll *b* and the carotogens) is passed on to the chlorophyll *a* group.

### TWO PIGMENT SYSTEMS

The interacting pigments in a bioenergetic chain are defined as a photosynthetic unit. Although the details of the interactions within a photosynthetic unit are controversial, the general biophysical process is well documented. Two distinct bioenergetic systems of pigment interaction occur simultaneously in green plants (Govindjee and Govindjee, 1975). The two types of photosynthetic units (Figure 9) apparently perform photosynthesis by somewhat different processes using different relative amounts of accessory pigments, chl *a* 670, and chl *a* 680 to gather energy for sensitizing photosynthesis. (The numbers 670 and 680 indicate the central absorption wavelength.)

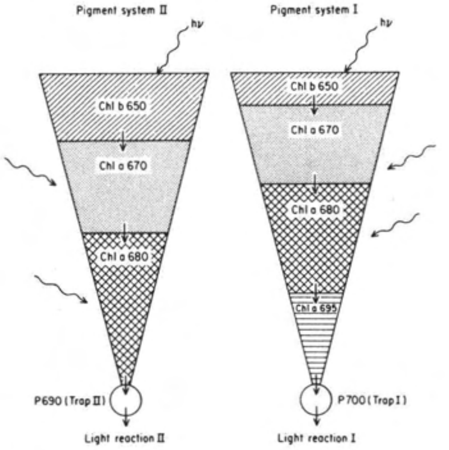

FIG. 9. Schematic diagram of the two pigment system model of green plant photosynthesis (from Rabinowitch and Govindjee, 1969).

The two pigment systems are distinctive in that they transfer energy to different long wavelength chlorophyll forms (chl *a* 690, chl *a* 695, and chl *a* 700) at the termini of the dual bioenergetic chains. These longer wavelength pigments, although they absorb photon energy, apparently are not important energy contributors for the photosynthetic process. They serve rather as the critical "energy trap" for photon energy absorbed by pigments farther up the chain (Rabinowitch and Govindjee, 1969). The photosynthetic reaction is energized in these vital longer wavelength forms of chlorophyll, which function as the reaction center.

### POLYMERIZATION

The multiple forms of chlorophyll *a* absorbing beyond the far-red limit of the main chlorophyll *a* band at 675 nm can be explained by polymerization of the single molecule form. Aggregation of chlorophyll *a* molecules in highly concentrated solutions broadens the absorption band and also shifts it toward the far-red (Brody and Brody, 1963). The absorption spectrum of a chlorophyll *a* extract from bacteria shows a red-shift of up to 12 nm in the dimeric form relative to the absorption spectrum of the monomer (Sauer, 1975). A study by Dratz *et al.* (1967) on whole quantasome extracts of barley indicates that about half of the chlorophyll *a* is aggregated, and much of it may be in a higher form than the dimer. The absorption band of the partially aggregated chlorophyll *a* shows component peaks at 673 nm, 683 nm, and 695 nm. The two longer wavelength peaks are due to absorption by the aggregated chlorophyll forms. The resultant absorptance curve peaks at 678 nm and has a broadened shoulder on the far-red side.

Methods of derivative spectroscopy have been used to resolve the longer wavelength forms of polymeric chlorophyll *a* that develop progressively from the monomeric form. Litvin and Sineshchekov (1975) show that as concentration of chlorophyll *a* increases, resulting in more aggregation (chlorophyll-chlorophyll interactions and probably chlorophyll-protein interactions), the apparent broadening of the absorption band actually is due to the addition of narrowly spaced bands appearing in the far-red shoulder. The new bands result from the splitting of the allowed energy levels in the excited electronic states of the more complex polymer molecules. The discrete nature of the bands indicates selection rules of quantum mechanics in the physicochemical bonding of aggregate states. Litvin and Sineshchekov conclude that chlorophyll *a* forms between 665 nm and 676 nm are probably dimeric with increasing interaction or packing density toward 676 nm. The longer wavelength forms are higher order polymers.

Preferred polymeric bonding states, therefore, would explain the persistence of certain far-red peaks commonly observed at 685 nm, 695 nm, 700 nm, and 707 nm. These peaks become progressively weaker; however, only small red-shifts in the absorption peak can give the edge variation seen in wheat. Ke and Sperling (1967) show that a 2 nm red-shift in the absorption maximum of polymerized chlorophyll *a* results in a 15 percent peak in the difference spectrum. Their results very closely match the red-shift seen in Figure 2 and the difference spectrum of wheat and alfalfa in Figure 3.

### RED-SHIFT HYPOTHESIS

The physicochemical mechanism of the red-shift, from the latest experimental evidence, is most likely polymerization, or other forms of aggregation, of chlorophyll *a*. The biochemical and physiological events in the plant cycle that could affect polymerization, however, are not resolved. A change in activity between the two separate photosynthetic systems could determine the relative amounts of long wavelength pigments. On the other hand, concentration of chlorophyll *a* would determine the degree of polymerization, in which case, relative activities of the two bioenergetic chains would have to adjust according to the concentration of the long wavelength forms of chlorophyll *a*. The events that determine chlorophyll *a* concentration could begin farther down the biochemical chain where thermochemical reactions controlled by plant enzymes produce protochlorophyll. The protochlorophyll is rapidly converted to chlorophyll by a photochemical reaction in the presence of visible radiation in the shorter wavelength region. The slower thermochemical reactions, therefore, may also control the events observed on the far-red absorption edge by controlling the rate of chlorophyll *a* production.

## DISCUSSION

The airborne spectroradiometer study of Imperial Valley agricultural fields reveals the red-shift phenomenon as it occurs in the crops and under the growing conditions in the survey sites. Extensive additional research will be required to explain fully the *in vivo* characteristics of this biological phenomenon, namely, its dependence on crop variety, irrigation practices, fertilization, health and vigor, disease, and many other environmental factors and management practices. The experimental results thus far obtained, however, indicate that the position and shape of the far-red absorption edge is potentially a very important diagnostic in remote sensing of vegetation canopies.

The red-shift phenomenon is all the more interesting because it can be observed independently of background canopy-induced variations that confuse the information in other spectral regions. The large background variations induced by canopy effects are especially overwhelming in agricultural and forestry applications aimed at detecting subtle states of plant condition or stress. In remote surveillance of crops and forests, it is desirable to detect the smallest possible spectral reflectance variations in order to evaluate growth and vigor or to detect the earliest phases of disease and insect infestation. In order to be useful in remote sensing, the subtle spectral variations indicating abnormal plant conditions or different phases of growth must be uniquely different from the canopy-induced background variations in biomass canopies, and detectable even in the presence of the very large canopy-induced "noise" in remote spectral measurements.

Based on the ratio plots of Figures 5 and 4, it can be concluded that the young non-grain crops are very low in far-red pigments. Even under full canopy conditions, the 4/3 ratios stay below 1.05. Maturity in the non-grain crops affects a small red-shift, but the ratios do not exceed 1.15. The large red-shift develops only in the heading grains. They are identified by 4/3 ratios greater than 1.20. If these or similar limits persist under field testing, discrimination based on the upper limits, especially of the headed grains, will be unique.

The upper limits of variation in the 4/3 band ratios are uniquely determined by the position of the absorption edge. The common environmental noise factors operate on the 4/3 ratios in the opposite direction from the red-shift. For example, large amounts of soil showing through the canopy will depress the 4/3 ratio signal. The 4/3 ratios for bare soil in the survey region are in the range of 0.97 to 0.95. Increasing atmospheric interference should have minimal effect on the 4/3 ratios. Atmospheric effects are broadband and relatively small in the red and far-red region; they are further minimized by the close band spacing. Those atmospheric effects that are seen, will tend also to depress the 4/3 ratios because of higher back scattering in the shorter wavelengths (band 3) and greater absorption in the longer wavelengths (band 4). Lower 4/3 ratios, therefore, can be ambiguous; but the higher 4/3 ratios uniquely identify vegetation canopies with far-red absorbing pigments.

Variations in the position or shape of the absorption edge, other than the red-shift associated with maturing pigment systems, have been observed. Laboratory measurements by Keegan *et al.* (1956) show a rounding effect on the shoulder of the absorption edge in the near-IR spectra of plants suffering from wheat rust. It is not clear from their data if the rounding on the shoulder is associated with the pigment absorption properties and a shift in the spectral position of the absorption edge. If the long wavelength limit of photon absorption changes in stressed plants with decreased chlorophyll productivity, it would be expected to shift toward the shorter wavelengths. This kind of absorption edge change has been detected in the spectra from a forest canopy growing over copper-lead-zinc sulfide mineralization (Collins *et al.*, 1977). The forest canopy data, collected with the same airborne system used in the Imperial Valley study, show a small absorption edge shift toward the blue end of the spectrum of stressed trees growing in soil with high heavy metal concentrations. The forest study is very encouraging for geobotanical and other studies of stressed canopies, and it substantiates the present working hypothesis for the red-shift.

Narrow bands placed at 745 nm and 785 nm should theoretically be very effective in satellite applications. These bands are in a spectral region of good atmospheric transmittance, and the close spacing minimizes the relative atmospheric noise effects. The practical limitation is one of obtaining sufficient signal strength in such narrow bands. The width and position of the spectral bands for monitoring the absorption edge are critical. The positions of bands 3 and 4 have been tested by simulating shifted bands, but their present positions yield optimum sensitivity to the red-shift as measured by the band ratios. Increasing the width of band 3 also has the effect of decreasing the ratio sensitivity. The outside limits of band 3 width are the oxygen absorption band at 760 nm and the crossover region at 730 nm. The 730 nm limit is especially critical because the background band 1 variations are two orders of magnitude greater than the band 3 signals.

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