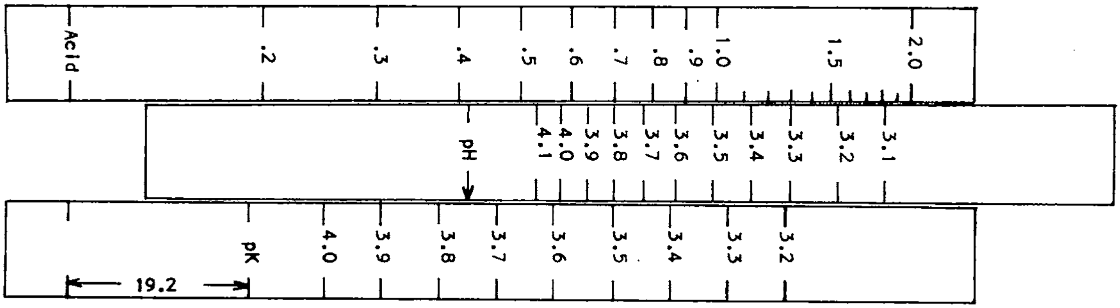
Figure 6.

Nomograph for Titratable Acid Using pK and pH Values.



measured pH value and noting the acid value that abuts this reading. In Figure 6, the pH value of 3.59 is adjacent to an acid value of .88%. The pH value of 3.35 is adjacent to the acid value 1.21%. These correspond to juice samples No. 5 and No. 6 in Table 2.

A special electronic circuit could be easily devised to perform this calculation. All that is involved is the addition of a constant, the log function of the signal from a cation electrode-calomel pair, and the log of the signal from a glass electrode-calomel pair. This could be indicated or recorded as titratable acidity in the juice. This method of measurement could be used on either a batch or continuous basis. Placing three standard electrodes in a flowing juice stream and connecting the appropriate pair to amplifier instruments, putting the output of the amplifiers through the computer circuit, would give a continuous measurement af acidity in a flowing stream of citrus juice.

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COLOR CHANGES IN CITRUS FRUIT AS MEASURED BY LIGHT TRANSMITTANCE TECHNIQUES

Otto L. Jahn[1] and M. B. Sunday[2]

Introduction

Color measurement by instrumental means has many advantages over visual methods, including greater accuracy, flexibility, and speed. Many instruments, using various techniques, have been developed for this purpose. For the measurement of color of intact fruits, however, the selection of equipment is limited. Some instruments measure color using light reflected from the sample; this system is being used commercially for the color sorting of some fruits and vegetables. This method measures the surface color of the product. To evaluate internal characteristics as for the detection of defects or measuring some quality index, light transmittance may be used. By this technique, a selected beam of light is directed through the intact fruit, and its absorbance characteristics are then related to previously established standards to determine the level of quality or the presence of defects.

Light-transmittance procedures have been tested on a number of fruits and vegetables. Birth and Olsen (5) have shown that water core may be detected in intact apples, and quality separations based on chlorophyll content have

[1]Agricultural Research Service, U. S. Department of Agriculture, Orlando, Florida.
[2]The late M. B. Sunday was formerly Bioloical Laboratory Technician, Market Quality Research Division.

been made (13). Light transmittance has also been used to make measurements of peaches (9, 11) and other stone fruits (6, 9, 10, 12), tomatoes (4), and potatoes (2). In Murcott Honey oranges, Long (7) found a good correlation between chlorophyll measurement by light transfittance and taste panel preferences. Seasonal changes in chlorophyll content in the fruit were also measured (7, 8).

Much of the earlier work with light transmittance was done with relatively cumbersome procedures. With the development of simplified instrumentation and the initial promise shown with citrus, further investigation was undertaken. The present studies were concerned with the evaluation of this instrumentation for measurements of chlorophyll in citrus.

Materials and Methods

Studies were made through the 1963-64 and 1964-65 seasons using fruit of Hamlin and Valencia oranges and Marsh grapefruit. The same trees were used as the source of fruit throughout both seasons. The fruit was washed, and random samples were taken, except that exceptionally scarred or discolored fruits were excluded.

In 1963-64 each test included 4 lots of 20 fruits each in a combined study of degreening and storage temperatures. Two lots were degreened with ethylene for 40 hours before storage, and the other two lots were placed directly into storage at 32° and 60° F. The degreening room was run at 85° and 90-95 percent humidity. Oranges were held for a total of 2 weeks and grapefruit 3 weeks. For each variety, tests were run at approximately monthly intervals. In 1964-65 similar studies were made at about 6-week intervals. In addition, a second series of tests was included to give more detailed information on seasonal changes in fruit color. For these, 20-fruit samples of the 3 varieties were obtained at 2-week intervals. Only date-of-harvest color readings were taken in these expirements.

Light-transmission measurements were made with a difference meter (3) (ASCO Ratiospect). This instrument measures the difference in optical density of the fruit between light of the measuring wavelength and the reference wavelength. In these studies, the measuring wavelength was 695 nm and the reference 740 nm, a system developed for the measurement of chlorophyll (green pigments). This represents a modification of the earlier procedure used on citrus (7, 8). The instrument used previously, a horticultural spectrophotometer, scanned the spectrum of transmitted light. Desired information was then read from the recording rather than directly from a meter as with the difference meter. Measurements with the difference meter are more rapid, but the instrument previously used yielded more information.

On the difference meter two measuring systems were compared, the direct path (DP) and an integrating sphere (IS). In the first system, light is restricted to a 1⅛-inch diameter path on entering and leaving the fruit. With the integrating sphere, light enters the fruit as in the DP system but may leave in any direction. With both systems, the light path was parallel to the fruit axis with the light entering by the stem-end in the DP system and stylar-end in the IS system. This difference was due to the reversal of the direction of the light beam in the two systems.

Results and Discussion

Seasonable Changes.—Data from the DP system showed a rapid loss of chlorophyll in both oranges and grapefruit during October and November 1963 (Fig. 1). Readings, recorded as ΔOD, are positively related to the amount of chlorophyll present (1, 13). The rate of change was similar in all fruits tested but occurred approximately a month later in Valencia oranges. Some regreening of grapefruit occurred in March, and this was supported by visual observations.

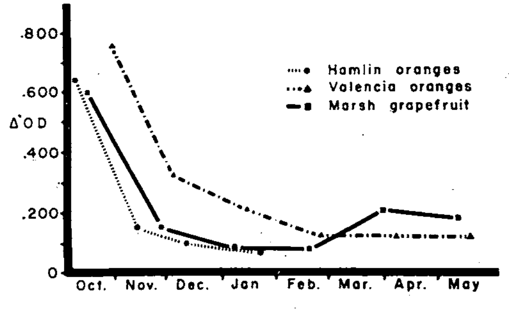

Figure 1.—Seasonal changes in chlorophyll level (ΔOD readings) of intact citrus fruit during the 1963-64 season, Direct Path Difference Meter ratings.

Results of the 1964-65 studies show changes in color more clearly (Fig 2). Again Hamlin oranges changed color rapidly during October. In comparison, Valencia oranges showed a later and somewhat more gradual loss of chlorophyll. The color change tended to be more gradual on grapefruit than on Hamlin oranges. Again regreening was detected in grapefruit in March. Some regreening was shown in Valencia oranges this season also. These data obtained with the DP system show that color changes in citrus can be readily followed with nondestructive instrumental methods.

Data for the 1964-65 season using the IS system (Fig. 3) indicate essentially the same seasonal pattern as with the DP system (Fig. 2). The same calibration was used for both systems. However, slight differences between the light paths in the two systems resulted in somewhat higher readings with the IS. The regreening shown by the DP system is not as apparent here since the IS system is not as sensitive to localizen green areas, particularly when these are at the stem end as in regreening. Pigment at the point of light entrance into the fruit may have a major effect on the reading obtained with the IS system, but variability from this source was minimized by using the more uniformly colored stylar end for this purpose. Such differences in sensitivity may result from other variations in the distribution of chlorophyll as well as regreening.

Since the DP system is restricted to spot measurements of the rind, there is a greater problem of orientatiton of fruit for repeated

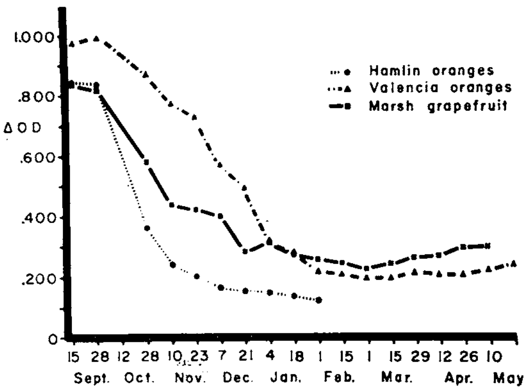

Figure 3.—Seasonal changes in chlorophyll level (△OD readings) of intact citrus fruit during the 1964-65 season, Integrating Sphere Difference Meter ratings.

measurements. This was shown in two tests where coefficients of variability of 2.75 and 2.57 percent were found for the DP system and 0.90 and 1.01 percent for the IS system. Though small, this difference indicates that the IS system would be better for the measurement of rind chlorophyll in citrus.

Degreening and Storage Changes.—The color changes occurring during degreening are similar to the natural seasonal changes. As shown in Figure 4, degreening Hamlin oranges for 40 hours caused a rapid loss of chlorophyll. Other tests during the past 2 seasons have shown similar results. As the season advanced, the color change resulting from 40 hours degreening usually was proportional to the initial color of the fruit (Fig. 5). However, even visually

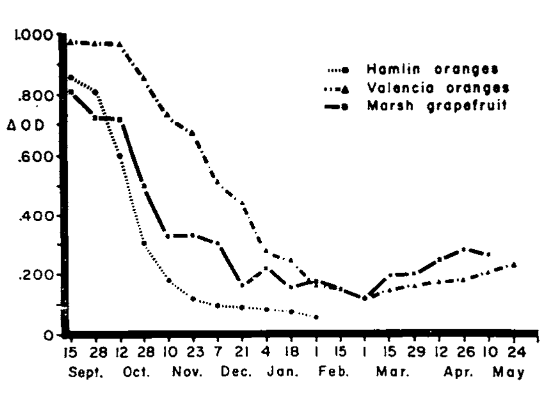

Figure 2.—Seasonal changes in chlorophyll level (△OD readings) of intact citrus fruit during the 1964-65 season, Direct Path Difference Meter ratings.

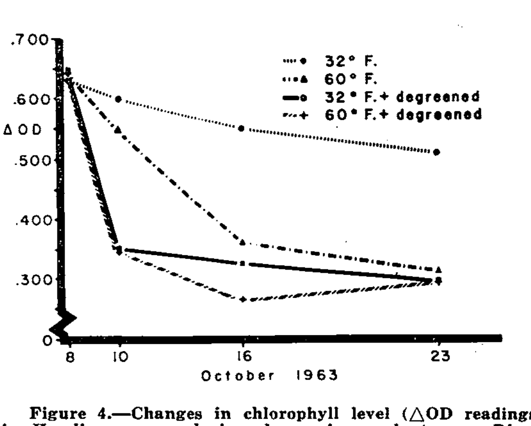

Figure 4.—Changes in chlorophyll level (△OD readings) in Hamlin oranges during degreening and storage, Direct Path Difference Meter ratings. October 1963.

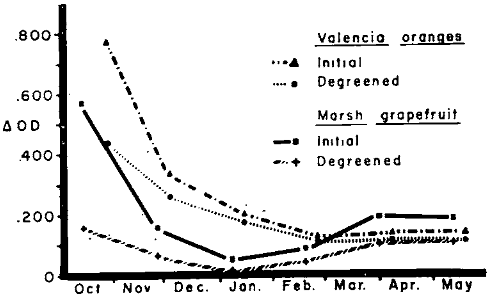

Figure 5.—Changes in chlorophyll level (ΔOD) readings in citrus fruit with degreening in relation to the initial color of the fruit, Direct Path Difference Meter ratings. 1963-64 season.

well-colored Valencia oranges and March grapefruit frequently showed a measurable response to ethylene.

The effects of storage temperature on color changes in Hamlin oranges are also shown in Figure 4. At 60° F., the loss of chlorophyll was much more rapid than at 32°. Other studies indicate that most of this loss at 32° resulted from the warming of fruit while measurements were being made. However, long-term storage studies have shown a measurable loss of chlorophyll at this temperature. After degreening, the rate of change in treated fruit returned to a level similar to that of the non-degreened fruit. The apparent increase in chlorophyll recorded for the 60°-degreened fruit at the last date was due to the presence of some stem-end decay. This decay is picked up by the DP system especially, at which time it is also readily visible.

Results of these studies show that chlorophyll levels and changes in citrus can be measured with light-transmittance procedures. The seasonal changes are similar to those shown by Long, Sunday, and Harding with a horticultural spectrophotometer (8), but with the difference meter chlorophyll measurements are simpler to make. In its present form, this technique is used as a research tool. With further study of measurement procedures and quality relationships, this procedure may be developed as a nondestructive method for mechanical sorting of citrus.

Summary

Data from 2 season's studies on Hamlin and Valencia oranges and Marsh grapefruit show that seasonal changes in chlorophyll level can be determined with light-transmittance techniques. The earliest color change occurred in Hamlin oranges and the latest in Valencia oranges. The chlorophyll level in Marsh grapefruit declined more gradually than in Hamlin oranges. The difference meter was effectual in measuring the rapid changes in chlorophyll content that occurred during degreening. Effects of storage temperature were also shown with changes at 60° being more rapid than at 32° F. Although the data show similar trends with both sample presentation systems, the integrating sphere appears to be more suitable for estimating the chlorophyll pigment in citrus than the direct path system because the integrating sphere is sensitive to light from a greater proportion of the surface area of the fruit, as well as providing more precise measurements.

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