analyze most of the currently identified volatile constituents in orange juice. Constituents from methyl butyrate to valencene could be quantified at juice concentrations of 0.25 ug/g and above. This is attained without evaporative concentration of the approximately 1ml of methylene chloride remaining after SDE. Coefficient of variation of volatiles ranged from 1.5% to 9.9%. The procedure is useful for quantitative analysis of a wide range of orange juice volatile flavor constituents and should find increased use for recovering minor flavor constituents of fruit juices.

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EVALUATION OF A PORTABLE SPHERE SPECTROPHOTOMETER FOR THE MEASUREMENT OF ORANGE JUICE COLOR

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Abstract. Obsolescence of the electronics of the HunterLab Citrus Colorimeter, originally developed more than 3 decades ago, resulted in the discontinuance of this instrument in the early 1980's. Many are still in use, although the difficulty in finding repair parts for these venerable instruments is slowly forcing their replacement by more modern instruments. Dramatic advances in sensor technology and improvement in complex electronic circuitry led to the development of smaller, accurate and reproducible digital color instrumentation. A compact, hand-held, integrating sphere spectrophotometer, the Minolta Model CM-2002, employing d/0° geometry with the specular reflectance component excluded (SCE) setting, was adapted to 1 inch diameter test tubes to measure X, Y and Z color attributes for about 500 juice samples. The results were subsequently graphically compared with the Citrus Colorimeter values. The data was statistically analyzed to calculate regression equations to express color on a scale equivalent to Citrus Colorimeter color values. The expression for equivalent CN (color number) values was selected as the guide to further evaluate the performance of the Minolta CM-2002 instruments under processing plant conditions.

Introduction

The quality grade orange juice receives includes a substantial portion derived from orange juice color. Current U. S. standards allow up to 40% of the total grade points to be allotted for color (U.S. Department of Agriculture, 1983). Originally, orange juice color was evaluated visually by comparison to a series of orange colored plastic standards under standardized lighting conditions. This method was superseded by an instrumental method relying on the HunterLab Model D45, later the Model D45D2 Citrus Colorimeter (CC), developed nearly 40 years ago (Huggart and Wenzel, 1954,1955; Hunter, 1967; Hunter and Harold, 1987). The CC permitted objective and accurate measurements of color values. The numerical scale employed by the CC was developed to coincide with the quality grade points assigned for the color part of the grading scheme (Huggart et al., 1969). Until late 1985, the CC was the only officially approved instrument for orange juice color measurement (State of Florida, Department of Citrus, 1975, et seq.; U.S. Department of Agriculture, 1983). Discontinuation of the manufacture of the widely used CC brought about testing of a wide variety of mainly reflectance mode colorimeters and spectrophotometers for their suitability for orange juice color measurement (Wagner and Buslig, 1983,1984; Berry et al., 1984; Buslig and

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Wagner, 1984, 1985a,b, 1986, 1988; Buslig et al., 1987; Buslig and Buslig, 1988; Buslig, 1989, 1991, 1992). All were adapted to use one inch diameter test tubes to maintain the sample presentation method used by the CC. Several were found suitable and mathematical equations were developed for each (Buslig and Wagner, 1988; Buslig et al., 1987; Buslig, 1991, 1992). Currently acceptable colorimeters and specific equations developed for each were approved by the USDA Inspection Service (U.S. Department of Agriculture, 1992) and the Florida Citrus Commission (State of Florida, Department of Citrus, 1975 et seq.) as alternatives to the CC.

Continued advances in sensor and computer technology have resulted in dramatic improvements in colorimetric instrumentation. In view of the importance of color in the quality grading process, we maintain an active program both in monitoring the performance of existing instrumentation and refining the mathematical equations in use, as well as testing new or improved colorimeters. The work below describes laboratory results obtained with the Minolta Model CM-2002 portable sphere spectrophotometer.

Materials and Methods

The Minolta Model CM-2002 is a compact portable integrating sphere based reflectance spectrophotometer which uses diffuse illumination and 8° viewing angle from the perpendicular to the specimen surface with a viewing beam width of 7.4°. It has an 8 mm diameter measuring area. Light from a pulsed xenon arc lamp is thoroughly diffused inside the integrating sphere and provides uniform illumination over the area of the sample surface to be measured. Two spectral sensors are used by the meter's double beam feedback system to measure both incident and reflected light. The meter thus detects any slight deviation in the light output by the pulsed xenon arc lamp, and compensates automatically for variations. The spectral output from the sensors is used to calculate values corresponding to the CIE (Commission Internationale de l'Eclairage) Standard Observer Response. The measurements can be displayed in a number of color systems. Data can be converted between color systems or between absolute and difference measurements (Minolta, 1991).

The measuring unit was equipped with a 1 inch tube adapter, designed to swing out of the way for white tile calibration. During these experiments, the units were calibrated each morning with the lock-on white calibration cap (white tile) supplied with the instruments and were rechecked periodically with an OJ4 tube. The systems were recalibrated with the white calibration cap after each 24 measurements. Two CM-2002 instruments were used to determine instrument to instrument reproducibility. Results were read directly as the CIE X, Y and Z values and were graphically compared with the analogous CC values.

A HunterLab Model D45D2 CC was used as the experimental reference device. This instrument uses illuminant C and four broad-band filters corresponding to the tristimulus response functions X (constructed from X_A and X_B), Y and Z, with 45°/0° source/observer geometry. Results for orange juices are normally obtained in CR (citrus red), CY (citrus yellow) and CN (color number) units, but X, Y and Z values are also available on this instrument. The relationship between CR, CY, CN and the tristimulus X, Y and Z values are shown in Table 1. The CC is normally calibrated with an OJ4 orange plastic standard tube, whose values are assigned by the USDA Inspection Service during a yearly instrument calibration. During these experiments, the CC was recalibrated with the OJ4 tube after each 24 measurements.

A total of 499 orange juice samples, ranging in CN from 32.1 to 42.2, were measured with each instrument. The color values obtained with the CC were used as the dependent variables to generate regression equations with values obtained from the CM-2002 instruments. All statistical calculations were performed with the MSTAT-C statistical package (Michigan State University, 1988). Graphics were created by the Axum[™] graphics package (Trimetrix, 1993).

Results and Discussion

Since the CC operates with an illuminant C source, the CM-2002 was calibrated under that illuminant setting. Comparability of sample presentation was assured with the tube adapter. Since the CM-2002 is capable of providing output in CIE X, Y and Z tristimulus values, these were directly compared with the analogous values measured with the CC.

To determine instrument to instrument reproducibility, the raw data for each measured variable from the CM-2002 instruments were plotted against each other. Figs. 1, 2 and 3 show graphical comparisons of X, Y and Z values. The correlation coefficients (r) for the comparable color values were 0.996, 0.996 and 0.997 for X, Y and Z respectively. The minimal observed offset between the scales on all curves indicated good instrument to instrument reproducibility. When the X/Y and the Z/Y ratios were calculated, plotting these values from each CM-2002 against the other (Figs. 4 and 5) showed a slight improvement in the correlation coefficient. The correlation coefficients were 0.997 and 0.999 for the ratios X/Y and Z/Y, respectively.

Since CN measured with the CC was derived from CR and CY values and these in turn are related to X/Y and Z/Y as shown in Table 1, the analogous ratios calculated from the CC data were used to graphically compare these values with each of the appropriate ratios from the CM-2002 instruments. Figs. 6 and 7 show these comparisons. The correlation coefficients comparing X/Y between the CC and the two CM-2002's were 0.920 for both, while Z/Y showed correlation coefficients of 0.923 and 0.922. It is obvious that these regression lines, both between X/Y and Z/Y values of the CC and the CM-2002, exhibited considerable scatter. From past work with other colorimeters, it was apparent that a possible correction factor may be needed (Buslig, 1991,1992). The luminance correction in the form of 1/Y improved the correlation for X/Y only slightly from

Table 1. Citrus Colorimeter color scales

CR = 200[(1.277X - 0.213Z)/Y - 1] CY = 100(1 - 0.847Z/Y) CN = 22.51 + 0.165CR + 0.111CY CN = 0.61 + 42.14X/Y - 16.43Z/Y

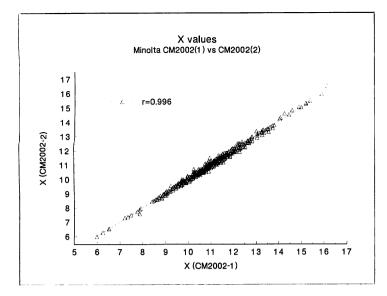


Fig. 1. Correlation analysis for X values (2 Minolta CM-2002's)

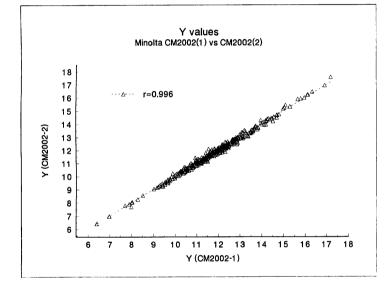


Fig. 2. Correlation analysis for Y values (2 Minolta CM-2002's)

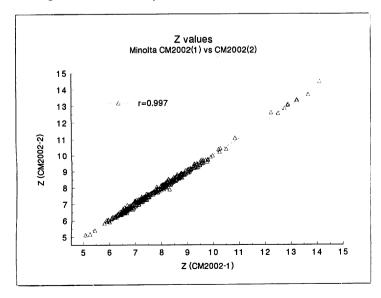


Fig. 3. Correlation analysis for Z values (2 Minolta CM-2002's)

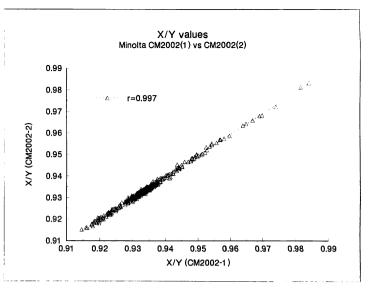


Fig. 4. Correlation analysis for X/Y (2 Minolta CM-2002's)

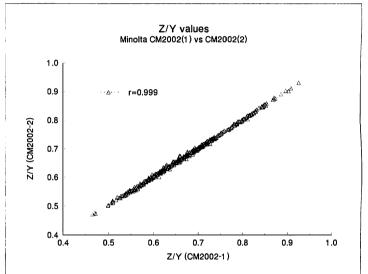


Fig. 5. Correlation analysis for Z/Y (2 Minolta CM-2002's)

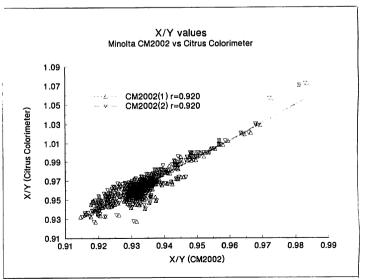


Fig. 6. Correlation analysis for X/Y(CC) vs X/Y(Minolta CM-2002)

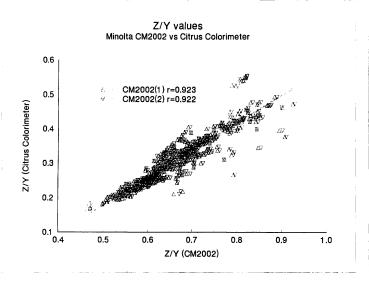


Fig. 7. Correlation analysis for Z/Y(CC) vs Z/Y(Minolta CM-2002)

0.920 for each to 0.926 and 0.925, respectively, for the individual CM-2002's. However, for Z/Y the improvement was from 0.923 and 0.922 to 0.991 and 0.988, respectively. As with other instruments tested (Buslig, 1991, 1992), this factor was included in the calculation of the regression equations for CN. The data from both CM-2002 instruments was combined to calculate the expression equivalent to the CC values for CN. The combined regression equation fell mid-way between the equations calculated from the results of each individual CM-2002's and the values obtained from the CC. The regression coefficients were rounded to obtain the preliminary equation shown in Table 2. This equation was used to calculate CN values from the CM-2002 data. The CN values calculated for each CM-2002 were plotted against each other to determine inter-instrument agreement with a correlation coefficient of 0.999 (Fig. 8). Plotting these calculated CN values vs the CN values read from the CC gave the graph in Fig. 9. The graph indicated good agreement between the two types of instruments for the most part, yielding correlation coefficients of 0.993 for both CM-2002 instruments. The combination of both sets of data showed a slightly lower correlation coefficient of 0.992, with only slight increase in the standard error. Of the 998 values calculated from the CM-2002 data, 68 values deviated more than ± 0.3 CN values from those measured with the CC. At this time, no explanation can be offered for these deviations. However, the importance of differences between geometry of the 0/45° CC and the possibility of non-linear response of the integrating sphere CM-2002 at extreme values cannot be excluded.

These results will be used to calculate CN values with data being currently accumulated under processing plant conditions. The data will be further reevaluated with non-

Table 2. Minolta CM-2002 preliminary regression equation

$$CN = 56.5X/Y - 18.4Z/Y + 48.2/Y - 8.57$$
$$r = 0.002 \text{ s.e.} = 0.211$$

$$1 = 0.992$$
 s.e. $= 0.211$

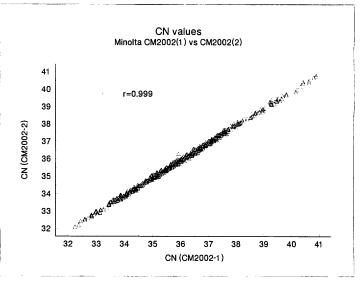


Fig. 8. Correlation analysis for CN values (2 Minolta CM-2002's)

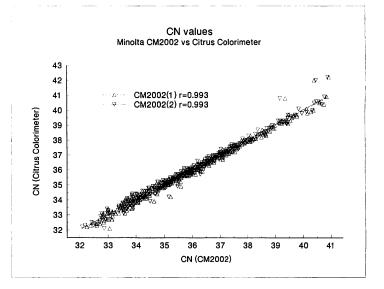


Fig. 9. Correlation analysis for CN(CC) vs CN (Minolta CM-2002)

linear statistical methods to possibly reduce the differences observed between CC values and calculated CN from the CM-2002 instruments.

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harvest treatments of fruits to reduce these losses have

proven to be effective by delaying fruit ripening and de-

gradation caused by hydrolyzing enzymes, resulting in loss

of firmness, increased susceptibility to damage and the

weakening of the texture of fruits. (Basiouny and Woods,

1993; Marinos, 1962, Huber, 1983). Calcium has been ef-

fective in maintaining texural strength of fruits (Huber, 1983; Dey and Brimson, 1984; Poovaiah 1986). Rossignol

et al. (1977) reported that about 60% of calcium is as-

sociated with cell wall fractions. The middle lamella-cell wall area is rich in pectinacious materials that interact with

Ca⁺² to form Ca-pectate, thereby enhancing cell to cell

of 400 ppm. A 0.5% Nufilm-17 solution (Miller Chem. and

Fertilizer Corporation) was added to enhance penetration.

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CALCIUM-MEDIATED POSTHARVEST CHANGES IN STORAGEABILITY AND FRUIT QUALITY OF PEACHES

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Additional index words. Postharvest physiology, ethylene evolution, ominooxyacetate, cold storage, firmness.

Abstract. The shelf life and quality attributes of mature-green and mature-ripe peaches [Prunus persica cv. 'Surecrop'] were determined following pre- and postharvest applications of CaCl2 (2,000 ppm), Nutrical [8% soluble Ca solution] (2,000 ppm) and an ethylene inhibitor, aminooxyacetate (400 ppm). Periodic samples were taken from fruits stored at 3° C over a period of 7 weeks. Calcium increased fruit firmness and delayed ripening in fruit harvested at two stages of development. TSS, acidity and pH varied at different sampling intervals.

Harvested fruits undergo a series of processes before reaching the consumer. These processes include precooling, grading, packaging, transportation, and storage. If not performed properly, these processes may exert considerable strain on the texture of the fruit, resulting in cracking, bruising and/or fungal attack. Consequently, the shelf life of fruit is reduced culminating in waste, loss of income to producers, and higher prices to consumers. Pre- and post-

cohesiveness (Dey and Brimson, 1984). Conway et al.(1987) reported that Ca reduced ethylene production, polygalacturonase and cellulase activities. These enzymes, among others, are thought to be responsible for cell wall and cutin degradation. The objective of this study was to determine the effects of pre- and post-harvest calcium treatments on quality and shelf life of peach fruits. **Materials and Methods** Twelve peach trees (Prunus Persica cv 'Surecrop'), spaced 20 ft by 20 ft and growing on sandy loam soil in Chilton County, Alabama, were used in this study. Trees received a preharvest application of Ca Cl₂ (2,000 ppm), Nutrical (NC) (8% soluble Ca, CSI Chemical Corp.) at a rate of 2,000 ppm, and aminooxyacetate (AOA) at a rate