Volume 52, Issue 2, May 2009

ISSN 0925-5214

ELSEVIER

POSTHARVEST BIOLOGY AND TECHNOLOGY

AN INTERNATIONAL JOURNAL

PBT

Determinants of flavor acceptability during the maturation of navel oranges

David Obenland [a,*], Sue Collin [b], Bruce Mackey [c], James Sievert [b], Kent Fjeld [b], Mary Lu Arpaia [b]

[a] San Joaquin Valley Agricultural Sciences Center, USDA-ARS, Parlier, CA 93648, United States
[b] Kearney Agricultural Center, University of California, Parlier, CA 93648, United States
[c] Western Regional Research Center, USDA/ARS, Albany, CA 94710, United States

ARTICLE INFO

ABSTRACT

Navel oranges of differing maturities were harvested at regular intervals for three successive seasons and evaluated for external color, percent juice, soluble solids concentration (SSC) and titratable acidity (TA). Fruit from harvest dates throughout the season were rated by a sensory panel (12–20 panelists) for flavor likeability (hedonic score), sweetness, tartness and richness (strength of citrus flavor). Gas chromatograpy/olfactometry was used to identify odor-active volatiles present at each harvest date in the final season. Peel color and BrimA, a parameter calculated by subtracting TA times a constant from SSC, were the most closely related quality parameters to the hedonic score and ratings of sweetness, richness and tartness. A predictive equation for hedonic score was developed using stepwise regression that combined peel color, percent juice and BrimA and accounted for 63% of the variation in the data. Year, location and navel strain had only minor effects on the relationship between the quality parameters and the sensory ratings. Nineteen odor-active compounds were identified, of which six were significantly correlated with changes that occurred in the sensory attributes during navel orange maturation. The SSC/TA ratio, the basis for the current minimum maturity standard in California, was not as closely related to likeability as BrimA. At the minimum maturity standard (SSC/TA) of 8:1, the hedonic score calculated from the overall regression equation was 4.4, a value well into the "dislike" range, indicating that the current standard is likely set at too low of a value to satisfy most consumers.

Published by Elsevier B.V.

1. Introduction

Current maturity standards for California navel oranges require a ratio of soluble solids concentration (SSC) to titratable acidity (TA) of 8:1 and yellow-orange color on at least 25% of the peel surface for a minimum of 90% of the lot (California Department of Food and Agriculture, 2003). The SSC/TA portion of the standard, based upon work done by the United States Department of Agriculture, was utilized by the California citrus industry beginning in 1915 (Chace, 1917). A minimum peel color requirement was later added to deal with immature fruit that were able to pass the standard by virtue of a lack of acidity development. The reliability and usefulness of this standard has been contested from its inception (Chace, 1930), and the basis of exactly how the standard was chosen is not clear in the literature. The idea of the "Pritchett Tongue", a graphical representation of SSC/TA versus SSC showing the best combinations for good flavor, was advanced in a report in the mid-1950s to lend support to using a 8:1 SSC/TA ratio as a maturity standard (Baier, 1954). The report, however, contains almost no data or descriptions of the methods by which the data

were acquired. In the 1980s, studies that were conducted using sensory panels in California, Texas, Nevada and New York indicated that consumers preferred oranges above the 8:1 ratio and that raising the ratio might lead to increased purchasing (Ivans and Feree, 1987; Pehrson and Ivans, 1988). Although these studies were formally conducted and utilized actual sensory panels, they were of limited scope and did not address the question of whether other orange quality parameters might be useful as indicators of flavor acceptability.

Even though SSC/TA is currently used to determine the minimum maturity standard in California, it has been recognized that this measurement does not always correlate well with the perception of sweetness or tartness in the fruit (Jordan et al., 2001). One difficulty is that the same ratio may be derived from widely differing levels of SSC and TA, leading to different flavor perceptions for the same ratio (Ishii, personal communication). This problem is dealt with by the Florida grapefruit industry by employing different SSC/TA ratios that depend on the SSC levels (USDA, 2002). Jordan et al. (2001), recognizing that sugar and acid have the opposite effect on flavor and that the tongue is more sensitive to acidity, proposed subtracting TA from SSC after multiplying TA by a constant that differs by fruit type. This measurement index, given the name of BrimA, was found by the authors to be more closely related to flavor than SSC/TA.

* Corresponding author. Tel.: +1 559 596 2801; fax: +1 559 596 2803.
E-mail address: david.obenland@fresno.ars.usda.gov (D. Obenland).

Rind color and firmness are nondestructively measured parameters that are associated with and potentially predictive of maturity (Olmo et al., 2000). Rind color is closely linked to SSC (Sites and Reitz, 1949), but color development is greatly affected by climactic conditions, making it unsuitable as a single measure of maturity. Direct measurement of SSC by near infrared spectroscopy is possible in some fruit, but is difficult in thick-skinned fruit like citrus (Nicolaï et al., 2007).

Volatile constituents have been identified from orange juices that are very important in determining flavor, including hydrocarbons, alcohols, aldehydes and esters (Hinterholzer and Schieberle, 1998; Nisperos-Carriedo and Shaw, 1990). Although important, use of these volatiles as markers to help determine maturity and flavor acceptability is made difficult by the large numbers of volatiles potentially involved and a lack of understanding regarding which of these volatiles are most linked to changes in flavor during navel orange maturation. Prior studies of orange volatiles have primarily utilized purchased oranges of a single and unknown level of maturity, making it impossible to study this relationship. Purchased oranges are also problematic from the perspective that these fruit have most likely been waxed and therefore may have altered flavor due to fruit-handling practices (Baldwin et al., 1995; Obenland et al., 2008).

The objectives of this research were (1) to conduct a comprehensive experiment over different years and locations, using multiple strains of navel oranges, to fully examine the effectiveness of the current California navel orange maturity standard (SSC/TA) in predicting navel orange acceptability; and (2) to determine if other quality parameters, including aroma volatiles, might be also be useful or even superior predictors of acceptability than SSC/TA.

2. Materials and methods

2.1. Fruit

The experiment was conducted over three seasons, beginning in 2003 and ending in 2006. In the first two seasons, navel oranges (*Citrus sinensis* (L.) Osbeck) were harvested weekly from a navel strain research plot at the University of California Lindcove Research and Extension Center (LREC) near Exeter, CA, from mid-September until mid-November, and then subsequently bi-weekly until early to mid-March. All trees were grafted on Carrizo citrange rootstock. To enable a comparison of the effect of maturation date on quality and sensory characteristics, early-maturing ('Beck Early'), mid-maturing ('Parent Washington') and late-maturing ('Palmer') navel orange strains were harvested at each date. Selection of strains to be used for the experiment was primarily based upon there being an abundance of fruit present on these strains and that they were common strains used by the California citrus industry. In the third season, fruit were harvested from three separate commercial sites and one research site (LREC) in central California (Kern and Tulare Counties): (1) Kern County site 1, strains 'Parent Washington' and 'Atwood'; (2) Kern County site 2, strains 'Beck Early' and 'Thompson Improved'; (3) Tulare County site 1, strain 'Parent Washington'; (4) Tulare Country site 2 (LREC); strain 'Parent Washington'. Comparison of mature trees of the same strain ('Parent Washington') across three of the four locations allowed a determination of the effect of location. Harvest sites were visited on a 3-week cycle beginning on September 20 with site 1 and ending on January 17. In all 3 years, fruit was harvested by size from random locations in the tree canopy from multiple trees. After harvest, fruit were transported to the Kearney Agricultural Center in Parlier, CA, where they were held for up to 3 d at 5 °C and 90–95% RH until the fruit was evaluated by the sensory panel.

2.2. Sample preparation

The fruit to be tasted for each day were taken from cold storage and allowed to stand overnight at room temperature. After being washed and dried, the fruit were visually rated for external color using a pictorial color chart and given a rating from 3 (dark green) to 13 (orange). The color chart was developed by researchers at the University of California, Riverside, and a rating of 5 corresponded to the "A" rating, which is part of the California state maturity standards (California Department of Food and Agriculture, 2003). Ratings were carried out by the same person each time except for the very few times when that person was not present. The fruit were then cut lengthwise and the top and bottom third cut away and discarded, leaving a 2.5-cm section from the center of the fruit. One half of the fruit was peeled and then cut into six bite-sized wedges for presentation to the sensory panelists. The other half was used for juicing for quality analysis. After weighing, the fruit were juiced by hand using a commercial table-top juicer (Model 932, Hamilton-Beach, Washington, NC, USA). The juice was weighed and the percent juice calculated by dividing the juice weight by the weight of the unpeeled portion. The juice was then filtered through a screen sieve and placed into a 15-mL centrifuge tube for quality factors determination. The juice samples were either kept at 5 °C until analysis or frozen at −12 °C if it was necessary to store the juice for more than a few days.

In the third year of the experiment, juice samples for volatile analysis were collected from the tasted fruit in a similar manner as for the quality analysis. In this case, the rind was carefully cut away prior to juicing in order to minimize the presence of peel oil in the resulting juice. The juice was placed into 23 mm × 75.5 mm (20 mL) glass vials sealed with a Teflon-coated septum and frozen at −20 °C until analysis. Seven vials, each from an individual fruit, were collected at each harvest from the Parent Washington strain only.

2.3. Quality and sensory analysis

SSC was measured in filtered juice by using a temperature-compensated refractometer (AO Scientific, Model 10423, Buffalo, NY, USA) and TA by titration with 0.1 mol L^{-1} NaOH to an end point of pH 8.2 using a Radiometer TitraLab 80 Titration System (Lyon, France). Acidity was expressed as percent citric acid. Panelists were served individual fruit wedges to taste in white, 30-mL soufflé cups that were identified with a unique three-digit number. For each test, 12–20 panelists were available. These panelists were mainly employees at the Kearney Agricultural Center and could be considered as being semi-experts due to their familiarity with tasting citrus from numerous prior sensory panel studies with oranges. Samples were presented in random order, with each panelist receiving them in a different order to minimize order effects. Panelists were provided with distilled water and were directed to rinse their palate between samples. Individual, three-sided white booths that had a small doorway through which to receive the sample trays were used for the tasting. Light fixtures with SP30 fluorescent bulbs (General Electric, Fairfield, CT, USA) mounted over the evaluation area to provide standardized lighting. Eight samples were evaluated by each panelist for each tasting session. Each individual fruit was tasted by up to six panelists, with eight fruit being tasted per strain for each harvest date. Fruit from each harvest date was tasted over a 2–3-day period following harvest. Panelists gave each sample a hedonic flavor score ranging from 1 (dislike extremely) to 9 (like extremely). Also, the samples were rated for the degree of sweetness, tartness and richness of flavor by drawing a line on separate 150-mm scales. The measured distance from the 0-point indicated the intensity of the three sensory attributes, with a greater number indicating more sweetness and richness

(desirable flavor characteristic of oranges), but less tartness. Prior to the evaluation, panelists were given instructions regarding definitions of the attributes and how to utilize the line scales.

2.4. Volatile analysis

Six vials (representing six individual fruit) were thawed and pooled from each harvest, with each of the resulting six vials containing 6 mL (final sample volume). No salt was added to the juice, as preliminary experimentation had not found any advantageous benefit of its addition (data not shown). The vials were placed back into storage at −20 °C until analysis. Just prior to analysis, the juice from each vial was thawed by partial immersion of the vial for 15 min in a 40 °C water bath. Volatiles were then trapped from the headspace of the vial using solid phase microextraction with a 75-μm carboxen/polydimethylsiloxane fiber while maintaining the juice at 40 °C. During the 30-min trapping period, the juice was slowly stirred by means of a stir bar. Fiber phase, trapping time and temperature had been previously optimized to provide a large quantity and wide range of odor-active volatiles (Obenland et al., 2008). Analytical conditions for gas chromatography of the volatiles are as detailed in Obenland et al. (2008). Effluent exiting the chromatography column was split between a flame ionization detector (250 °C) and a SGE ODO II sniffer port (Austin, TX, USA). Quantification of the FID peaks of interest was performed using standards curves that were generated by the addition of standards to deodorized orange juice, whereas identification was based upon retention times, retention indices and odor of the peak. Mass spectrometry was used to confirm the identifications, using the system described in Obenland et al. (2008). The standard curve for heptanal was used to provide quantification for compounds with an unknown identity.

Sniffing of the column effluent was performed by three panelists that had been extensively trained on detection and identification of different aromas from citrus juice. When an odor was detected, the panelist would slide a lever on a self-made variable potentiometer for which the amount of movement reflected the intensity of the odor. This information, in the form of peaks outputted to the Chem-Station software (Agilent, Palo Alto, CA), could be overlaid over the data from the FID detector and used to determine which of the FID peaks were aroma-active and potentially contributing to flavor. Samples from each harvest date were run six times by each of the panelists. For a component to be considered aroma-active, it had to be detected by at least two of the panelists in at least three out of six runs. These were the criteria that we had developed through prior experimentation to ensure that the detected components were valid. Peaks generated by the olfactory potentiometer were normalized by setting the highest value equal to 100 to adjust for differences among the panelists.

2.5. Statistics

Sensory data were analyzed using the hedonic and attribute means across panelists for each fruit. Panelists were considered to be a random effect representing just one panel that differed slightly from time to time but with the same core people and analyses were conducted using different panels as a single group. Stepwise regression with the sensory attributes as the dependent variables was performed using PROC General Linear Model (SAS Institute, Cary, NC) with a significance cutoff of $P \leq 0.15$ for inclusion of variables into the model. Analysis using PROC REG (GLM, SAS) were performed using site, location or year as fixed effects and the quality parameters as continuous explanatory variables, including possible interactions. Transformations were conducted as needed prior to either the regression or GLM analyses. Comparisons of R^2 values between the stepwise regression and GLM analyses were used to determine the influence of site location and year on the various models. Pearson's correlation coefficients between the sensory attributes and quality parameters were performed using SAS. Regressions and correlations were conducted across all 3 years since analyses had shown no large between-year effects (data not shown). Volatile data were collected from pooled ($n = 6$) individual fruit that had been tasted from each harvest date. Analysis was conducted using the GLM (SPSS, Chicago, IL) with harvest date as a fixed effect. Mean separations were performed at the 5% level of significance using the Bonferroni test. Pearson's correlation coefficients between the sensory attributes and volatiles were calculated using SPSS. Equations to best fit the relationships between hedonic score and either SSC/TA or BrimA were determined by using the curve estimation parameter of the SPSS regression procedure.

3. Results

3.1. Relationships between quality and sensory attributes

Pearson's correlation coefficients derived from 3 years of combined data indicated that peel color and BrimA were the quality parameters most closely related to the hedonic flavor score, sweetness, richness and tartness over the course of the entire season (Table 1). In the case of tartness, TA was also an important quality parameter. Percent juice had a very low correlation with hedonic score for any of the sensory attribute ratings. Stepwise linear regression was used to develop equations to predict hedonic score, tartness, sweetness and richness from combinations of the quality attributes (Table 2). Values of R^2 from these predictive equations ranged from 0.53 for richness to 0.68 for sweetness.

3.2. Effect of strain, location and year

During the initial 2003/2004 season, the navel orange strain Beck Early reached the legal harvest maturity standard for California of 8:1 (SSC/TA) by the October 20 harvest, while Parent Washington and Palmer reached this standard on November 3 and November 17, respectively. Statistical analysis were conducted for each of the sensory rating attributes, using quality factors as explanatory variables, with and without strain as a fixed effect in the model, to test whether or not strain had a significant effect in that season (Table 3). Although strain was statistically significant ($P \leq 0.05$) for hedonic score and ratings of sweetness and tartness, the R^2 values for models with and without strain for all four sensory attributes were nearly identical, indicating that strain was not an important factor in describing the relationship of quality and sensory attributes.

Similar results were obtained in experiments designed to test the effect of location. Washington navels were harvested from four separate sites in Tulare and Kern counties in Central California from September 2005 until mid-January 2006 and the same type of analysis performed as was done for strain, except that location

Table 1
Pearson's correlation coefficients between sensory and quality attributes using three seasons of combined data.

	Color	% Juice	SSC	TA	SSC/TA	BrimA
Hedonic score	0.73	0.30	0.59	−0.55	0.61	0.74
Sweetness	0.76	0.28	0.59	−0.61	0.68	0.78
Tartness	0.69	0.20	0.44	−0.70	0.72	0.70
Richness	0.68	0.28	0.60	−0.42	0.52	0.68

Color = external rating of the peel using the 3–13 color scale developed by the University of California, Riverside; % Juice = weight of the juice as a percentage of the total weight of the fruit; SSC = soluble solids concentration; TA = titratable acidity expressed as percent citric acid; BrimA = SSC − 3(TA). For tartness, a higher rating indicated less tartness.

Table 2
Equations to predict hedonic score, tartness, sweetness or richness from quality attributes obtained using stepwise linear regression from three seasons of sensory and quality data.

Y	Regression equation	R^2
Hedonic score	$Y = 0.142(\text{Color}) - 12.290(\text{BrimA}) + 0.001(\% \text{ Juice}) + 4.283$	0.63
Tartness	$Y = 31.233(\text{SSC/TA}) + 2.698(\text{Color}) - 190.613(\text{BrimA}) + 3399.051(\text{SSC}) - 16.549$	0.63
Sweetness	$Y = 3.144(\text{Color}) - 239.649(\text{BrimA}) + 0.011(\% \text{ Juice}) + 37.404(\text{SSC/TA}) + 22.082$	0.68
Richness	$Y = 2.728(\text{Color}) - 97.652(\text{BrimA}) + 0.009(\% \text{ Juice}) - 1537.666(\text{SSC}) + 73.193$	0.53

Color = external rating of peel color using a color chart; BrimA = SSC − 3(TA); % Juice = weight of the juice as a percentage of the total weight of the fruit; SSC = soluble solids concentration; TA = titratable acidity expressed as percent citric acid.

Table 3
Effect of navel strain, location or year on the relationship between sensory and quality attributes as determined by values of R^2 calculated from statistical models including or excluding navel strain, location or variety.

Sensory attribute	Fixed effect in model					
	Navel strain[v]		Location[w]		Year[x]	
	Excluded[y]	Included[z]	Excluded	Included	Excluded	Included
Hedonic score	0.69	0.70	0.79	0.81	0.63	0.67
Sweetness	0.75	0.76	0.84	0.87	0.68	0.73
Tartness	0.65	0.66	0.79	0.82	0.63	0.67
Richness	0.60	0.61	0.66	0.70	0.53	0.57

All quality attributes were included.
[v] Data from 2003–2004 season.
[w] Data from 2005–2006 season using the 'Parent Washington' strain.
[x] Data from all three seasons combined.
[y] Excluded from model. Stepwise regression analysis used for R^2 calculation.
[z] Included in model. General linear model used for R^2 calculation.

rather than strain was the fixed effect in the analysis. Location was a significant effect in the analysis with regard to the hedonic score ($P \leq 0.01$), but inclusion of location into the model resulted in only small increase in R^2 values, indicating that location was not an important effect (Table 3). Similarly, location also had little influence on sweetness, tartness and richness.

The data from all 3 years were combined and also subjected to the same analyses as were performed for strain and location to determine if year was a significant factor in determining hedonic score and the ratings of sweetness, tartness and richness. Although year was statistically significant for hedonic score ($P \leq 0.04$) and

tartness ($P \leq 0.02$), the comparisons of R^2 values for the different sensory attributes (Table 3) indicated that there was little increase in R^2 due to the inclusion of year in the model, showing that year had a relatively small impact.

The above-mentioned analyses were conducted using a combined analysis with all of the quality factors together. Additional analyses done for SSC/TA and BrimA separately obtained very similar results as the combined analyses (data not shown) and confirmed that strain, location and year had only a minor impact on the relationship of the sensory attributes with each of the quality factors.

Table 4
Aroma-active volatiles present in 'Parent Washington' navel oranges harvested at time points throughout the 2005/6 season as determined by GC olfactometry.

Compound	Aroma descriptor	Harvest number[x]				
		1	4	7	10	13
Unknown 1 (U1)	Alcohol, sweet	1.76a	1.19a	2.18a	6.16b	6.92b
Unknown 2 (U2)	Metallic	0.21a	0.18a	0.29a	0.91b	1.42c
Pentanal (PEN)	Sour, pungent	31.93a	46.47ab	57.49b	96.69c	52.42ab
Unknown 3 (U3)	Sour	2.31a	2.69a	2.64a	3.66b	3.81b
Hexanal (HEX)	Grassy	7.00a	22.12ab	23.25ab	86.90c	40.55b
Ethyl butanoate (EB)	Fruity	ND	ND	0.63a	8.16b	15.30c
Heptanal (HEP)	Fatty	4.70a	6.21a	8.92b	17.27c	9.33b
α-Pinene (PIN)	Spicy	7.61b	7.63b	8.07b	3.22a	6.07ab
1-Octen-3-one (OCT)[y]	Mushroom	0.36a	0.52ab	0.72bc	1.35d	0.84c
Unknown 4 (U4)	Fatty, lemony	1.17a	1.54a	1.59a	1.64a	2.38b
β-Myrcene (MYR)	Fatty, musty	311.69c	277.69c	264.96bc	79.34a	196.03b
Ethyl hexanoate (EH)	Fruity	0.29a	0.28a	1.11b	3.08c	5.21d
Octanal (OCT)	Fatty, lemony	4.43ab	4.15a	5.48b	9.26c	4.79ab
Limonene (LIM)	Minty	7433.85b	7715.82b	7259.61b	2544.69a	6979.71b
γ-Terpinene (TER)	Citrus	0.85a	1.28b	1.76c	2.55d	1.48bc
Linalool (LIN)	Citrus	44.85a	50.55a	48.55a	71.60b	40.05a
Unknown (U5)	Cereal, fatty	0.67	0.71	0.71	0.67	0.64
(E)-2-Nonenal (NON)	Fatty	2.00a	3.11ab	4.50c	6.64d	3.89bc
Ethyl octanoate (EO)	Fruity, floral	0.75a	1.17cd	1.37d	1.13bc	0.92ab

Fruit were not waxed after harvest and were juiced within 3 d of harvest.
Values presented are in μg L^{-1}. Different letters following the values indicate a statistically significant difference ($P \leq 0.05$) among harvests within a compound, $n = 6$. ND = not detectable.
[x] Harvest number 1 = September 19; 4 = October 10; 7 = October 31; 10 = November 28; and 13 = January 9.
[y] Tentative identification based upon retention index and aroma.

Table 5
Pearson's correlation coefficients between aroma-active compounds and sensory attributes as determined from a series of five harvests throughout the 2005/6 navel orange season.

Compound	Aroma descriptor	Sensory attribute			
		Hedonic	Sweetness	Tartness	Richness
Unknown 1 (U1)	Alcohol, sweet	0.87*	0.83*	0.83*	0.77
Unknown 2 (U2)	Metallic	0.88*	0.89*	0.86*	0.79*
Pentanal (PEN)	Sour, pungent	0.59	0.61	0.45	0.46
Unknown 3 (U3)	Sour	0.89*	0.91*	0.83*	0.76
Hexanal (HEX)	Grassy	0.64	0.67	0.50	0.48
Ethyl butanoate (EB)	Fruity	0.86*	0.87*	0.85*	0.78
Heptanal (HEP)	Fatty	0.66	0.67	0.53	0.53
α-Pinene (PIN)	Spicy	−0.55	−0.57	−0.41	−0.37
1-Octen-3-one (OCT)[x]	Mushroom	0.74	0.75	0.62	0.61
Unknown 4 (U4)	Fatty, lemony	0.87*	0.88*	0.91*	0.83*
β-Myrcene (MYR)	Fatty, musty	−0.71	−0.73	−0.58	−0.55
Ethyl hexanoate (EH)	Fruity	0.91*	0.92*	0.91*	0.85*
Octanal (OCT)	Fatty, lemony	0.45	0.46	0.31	0.34
Limonene (LIM)	Minty	−0.43	−0.45	−0.28	−0.28
γ-Terpinene (TER)	Citrus	0.65	0.66	0.52	0.55
Linalool (LIN)	Citrus	0.13	0.15	−0.04	−0.02
Unknown (U5)	Cereal, fatty	−0.52	−0.52	−0.53	−0.48
(E)-2-Nonenal (NON)	Fatty	0.68	0.69	0.56	0.58
Ethyl octanoate (EO)	Fruity, floral	0.25	0.25	0.22	0.28

A star following a correlation coefficient indicates statistical significance ($P \leq 0.05$).

[x] Tentative identification based upon retention index and aroma.

3.3. Aroma volatiles, harvest date and sensory attributes

Using GC-olfactometry, it was possible to consistently smell 19 different odor-active compounds in the orange juice samples (Table 4). All of these compounds produced peaks quantifiable by the FID detector. Fourteen of the compounds were identified by use of retention indices, aroma characteristics, comparison to standards and mass spectrometry. Fatty, fruity and citrus were the most common aroma descriptors noted. Significant changes in amount due to time of harvest were observed in almost all of the compounds. Five of the compounds (U1, U2, U3, EB and EH) increased in amount throughout the season, while six (PEN, HEX, HEP, OCT, TER and NON) increased until harvest 10 (November 28) and then deceased thereafter. Four of the compounds (PIN, LIM, LIN and U5) showed no clear pattern of change. Changes in the hedonic score during the season were significantly correlated with changes in four unknown compounds (U1, U2, U3 and U4), as well as for ethyl butanoate (EB) and ethyl hexanoate (EH) (Table 5). The same pattern with aroma volatiles was observed for the sensory attributes sweetness and tartness. Changes in richness were significantly correlated with changes in U2, U4 and EH (Table 5).

3.4. Relationship of SSC/TA, BrimA and hedonic score

Current minimum maturity standards for California are primarily based upon SSC/TA and so comparisons were made to determine how SSC/TA related to the hedonic flavor scores given by the panelists over the 3-year period of the study. A quadratic function was found to best fit the relationship between SSC/TA and hedonic score (Fig. 1A), while BrimA, a variant of SSC/TA derived from subtracting TA from SSC (BrimA = SSC − k(TA)), was related in a linear manner to hedonic score (Fig. 1B). We modified the formula for BrimA suggested by Jordan et al. (2001), substituting their recommended constant (k) of 5 with a value of 3 in order to eliminate the generation of negative BrimA values. We found k factors of 3, 4 or 5 to provide nearly identical values of R^2 as calculated from the linear regression of hedonic score versus BrimA, with BrimA calculated using a k of 4 being slightly superior predictor of flavor ($R^2 = 0.5646$) than that calculated from a k of 3 ($R^2 = 0.5555$) or 5 ($R^2 = 0.5604$). Hedonic scores calculated from the quadratic equation for SSC/TA versus hedonic score (Fig. 1A) at various SSC/TA values and the cor-

responding value of BrimA are given in Table 6. At a SSC/TA value of 8.0 (8:1), the current minimum maturity standard in California, the calculated hedonic score was 4.4, which is well into the dislike range. Not until SSC/TA was 13.0, did the hedonic score reach 6.0 (like slightly).
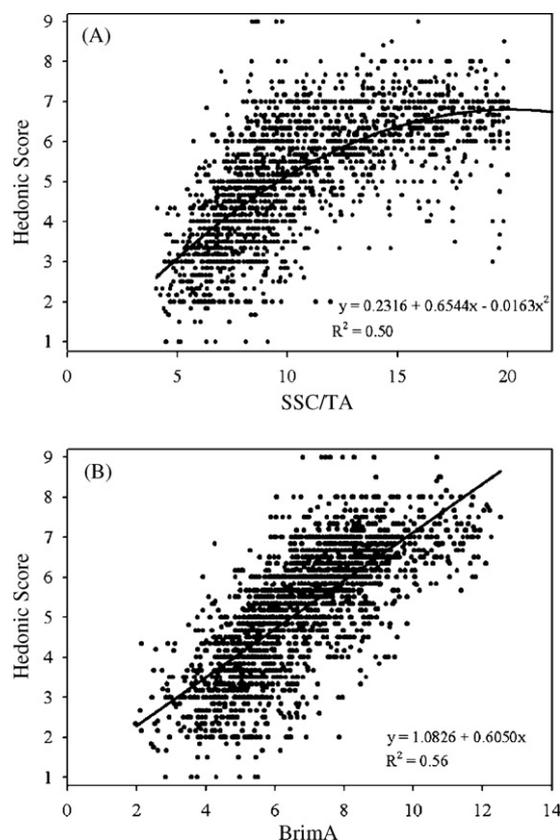
Fig. 1. Relationship between hedonic score and SSC/TA (A) or BrimA (B). BrimA = SSC − 3(TA). Points indicate individual fruit (n = 2124) that were tasted and measured for SSC and TA over three seasons. Listed equations were those that best fit the data.

Table 6
Hedonic flavor score obtained from a given SSC/TA ratio, the corresponding BrimA, and the average date over three seasons that this SSC/TA ratio occurred on.

SSC/TA	Hedonic score[x]	BrimA[y]	Average date[z]
6	3.6	4.2	September 26
8	4.4	5.5	October 18
10	5.2	6.8	November 8
12	5.7	7.6	November 30
13	6.0	8.1	December 10
14	6.2	8.5	December 21
16	6.5	9.0	January 11

[x] Hedonic flavor score calculated from quadratic equation from Fig. 1A.
[y] BrimA calculated from linear equation from Fig. 1B.
[z] Three-year average calculated from linear regression of SSC/TA and date.

Data were sorted into four classes based on range of TA concentrations (1 = 2.53–1.51; 2 = 1.50–1.11; 3 = 1.10–0.71; 4 = 0.70–0.28) and linear correlations of SSC/TA and BrimA with hedonic score run within each TA class to determine the effect of TA on these relationships (Fig. 2A). Class ranges were derived from an attempt to equally separate the data into four separate classes. Values of R^2 were very similar between the hedonic score and SSC/TA or BrimA for classes 1–3, while R^2 values differed between the two quality factors for class 4 (low acidity). Both SSC/TA and BrimA had low R^2 values in class 4, but BrimA was more closely related to the hedonic score in class 4 than was SSC/TA. The similarity of SSC/TA and BrimA at higher values of acidity (classes 1 and 2) and the lesser similarity

Fig. 2. Linear correlation of SSC/TA and BrimA with hedonic score (A) and correlation of SSC/TA with BrimA by TA class (B). TA classes: 1 = 2.53–1.51; 2 = 1.50–1.11; 3 = 1.10–0.71; 4 = 0.70–0.28.

at low acidity (class 4) were also clearly visible in linear regressions of the two quality factors (Fig. 2B).

4. Discussion

Even though SSC/TA is the current standard in California for determining minimum maturity and legal time of harvest, we found both peel color and BrimA to be more closely related to the flavor of the fruit over the course of the season (Table 1). Sweetness and richness, being components of flavor, were also strongly correlated with these two quality attributes. Although peel color is presently an element of the California maturity standard, it functions more as a means to prevent early-season, low-acid fruit from being certified as mature, rather than a direct measure of maturity (Chace, 1917). Color development is strongly affected by temperature and, as a result, would likely not be a good sole means by which to determine maturity. Our findings support the suggestion by Jordan et al. (2001) that BrimA is a better predictor of flavor than SSC/TA. Recent consumer testing with navel oranges at the University of California, Davis, has also found similar results with regard to SSC/TA and BrimA (Ishii, personal communication). In agreement with the findings of Jordan et al. (2001), who presented data for grapes and grapefruit, our results showed BrimA to have both a higher degree of correlation (Table 1) and a greater linearity in the relationship with flavor (Fig. 1) than SSC/TA. As was also noted by these authors, the advantage of BrimA over SSC/TA is most pronounced in low-acid fruit (Fig. 2). When acidity is low, SSC/TA becomes excessively high relative to BrimA due to SSC/TA being calculated as a ratio, rather than in a subtractive calculation as is BrimA. In our data of three seasons, we observed low acidity to be primarily a phenomenon of late season fruit. Out of 560 low-acid fruit that could be placed into our lowest acidity class (class 4; TA 0.28–0.70), only 14 (2.5%) were harvested during the early part of the season (September and October) that would have had sufficient color development to have met the California maturity standard. This suggests that most of the benefit to be obtained by switching to a standard based on BrimA rather than SSC/TA occurs late in the season at a time when maturity standards are not currently utilized. It cannot be discounted, however, that there are certain lots of navel oranges that have higher proportions of low-acidity fruit during the early season that would be positively impacted by this change in the maturity standard.

Stepwise linear regression analysis identified BrimA, external color and percentage juice as being the combination of quality attributes most predictive of the hedonic flavor score over the entire course of the season (Table 2). It is questionable, however, whether the increase in the R^2 value from 0.56 to 0.63 as a result of the addition of peel color and percentage juice to the selection model would add enough additional precision to warrant the extra effort in data collection. Given that oranges with a very dry texture (low % juice) are unlikely to be acceptable to consumers, however, it is likely that there exists a minimum level of percentage juice that is needed for acceptability

Our data analysis showed that navel orange strain, location and year have little impact on the relationship between the quality and sensory attributes. Although it cannot be ruled out that there could be changes due to these three parameters under other circumstances, this conclusion indicates that the results are applicable over a wide range of conditions.

The data scatter visible in the relationship between both SSC/TA and BrimA with the hedonic flavor score (Fig. 1A and B) is at least partly due to the difficulty in trying to describe the flavor of fruit solely using TA and SSC, which excludes the important role of volatile compounds. Volatiles, which were determined to be odor-active and potentially have an impact on flavor, were quantified at different stages of maturation to estimate the influence of these compounds on flavor development. The increases in
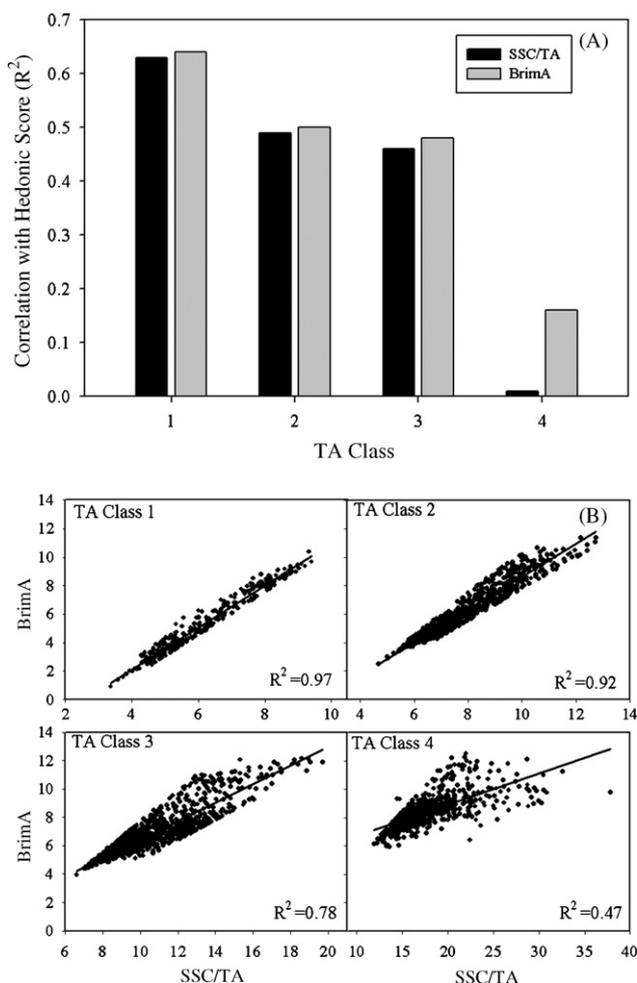
amount during the progression of the season that occurred with the majority of the volatiles likely incrementally enhanced their overall contribution to flavor (Table 4). Some of the volatiles later declined in abundance, but the amounts still generally exceeded those from the first harvest. The compounds, including aldehydes, esters, hydrocarbons, an alcohol and a ketone, were higher in all but one case in juice concentration than the odor threshold values previously published (Buettner and Schieberle, 2001; Moshonas and Shaw, 1994), indicating a possible role for each in flavor. Use of published odor thresholds, however, must be regarded with caution, since they are generally performed in water and neglect the potential matrix effect (Plotto et al., 2004). Also, the interactive effects of the components on each other undoubtedly alter the impact of each individual volatile component. The amounts of these compounds were often less than had been previously reported (Buettner and Schieberle, 2001; Moshonas and Shaw, 1994), but this could be attributable to differences between the studies such as juice extraction technique, fruit origin, fruit postharvest handling procedures and volatile analytical techniques.

Correlations were conducted between the volatiles and sensory attributes to obtain an estimate of the overall impact of each individual volatile on flavor across all harvests. Two of the six compounds that had a significant correlation with the hedonic flavor score (Table 5) were EB and EH, esters with a fruity, sweet odor. Both have been identified as contributors to orange flavor (Ahmed et al., 1978; Buettner and Schieberle, 2001). EB, due to its low odor threshold, is believed to be especially important (Hinterholzer and Schieberle, 1998). We could not detect any EB until the third harvest at the end of October, after which it greatly increased in amount, indicating that this compound may be especially closely tied to the enhancement of flavor during navel orange maturation. The other four compounds that had significant correlations with the hedonic flavor score could not be conclusively identified even though a measureable peak was present on the FID chromatogram generated from the GC olfactory runs. Aromas of these compounds were described by panelists as being alcoholic, sweet (U1), metallic (U2), sour (unknown 3), and fatty, lemony (U4). Although the odors of these compounds were generally unpleasant on their own, the increasing amounts during the season could be interacting with other volatile as well as nonvolatile flavor components to help give the characteristic orange flavor. Identification of these odor-active compounds would aid in a determination of their importance.

In agreement with prior reports (Ivans and Feree, 1987; Pehrson and Ivans, 1988), we found the current California maturity standard based upon a minimum SSC/TA ratio of 8:1 to be set too low to provide good eating quality navel oranges to consumers. On average, panelists in this study rated fruit with this ratio well into the "dislike" range of the hedonic flavor scale, most likely due to sourness (Pehrson and Ivans, 1988; Ishii, personal communication). This study confirmed this finding in a much more rigorous manner than had previous work, performing sensory evaluations over three separate seasons, using multiple strains and growing locations. A much smaller study that we conducted in the 2004/2005 season using 16 employees of Sunkist Inc., a California citrus cooperative (data not shown), found nearly an identical degree of dislike for fruit at 8:1 SSC/TA as did the large study presented here. Similar results have been found from consumer testing of navel oranges by the University of California, Davis (Ishii, personal communication). We recognize that the KAC panel had shortcomings as a consumer panel due to the relatively small size of our panel and its familiarity with navel oranges, yet these additional studies give reassurance to our findings in terms of their relevance to consumer acceptance.

Another consideration regarding what ratio that the maturity standard should depend on is that commercially the measurements of SSC and TA are done on pooled, randomly selected, 30-fruit sam-ples (California Department of Food and Agriculture, 2003). Since levels of SSC and TA found in individual fruit can vary within an orchard and even within different locations within the canopy of individual trees (Sites and Reitz, 1949, 1950), this practice can lead to fruit that have ratios lower than the maturity standard reaching the marketplace. Ivans and Feree (1987) reported that in a mid-November sampling of oranges from markets in six different counties in California, 39% of the fruit were below the minimum level, with some being as low as 5:1. In this study, it was observed that in 30-fruit samples that averaged 8:1, there would be individual fruit well below 6:1, and that it was not until the lots reached and exceeded an average of 10:1 that individual fruit with ratios below 8:1 were not found (data not shown). Fruit with very low SSC/TA ratios such as 5 or 6:1 are very sour and were strongly disliked by our panelists (Fig. 1A). Raising the minimum SSC/TA ratio required for harvest would help lessen the number of these low-ratio fruit from entering the marketplace.

Due to the need to taste and determine quality parameters of individual oranges, it was not possible to exactly reproduce in this study the juice extraction and SSC determination methods used by the industry. Preliminary results from our laboratory indicate that SSC determined by using a pressure-actuated citrus press and hygrometer (industry method) is slightly higher than that determined by using a Hamilton-Beach press and refractometer, as was done in this study. This difference is potentially due to the greater inclusion of extraneous soluble solids by use of the citrus press and means that the industry SSC and SSC/TA values are likely somewhat inflated and that the true hedonic score for fruit from the industry at 8:1 is even further into the dislike portion of the hedonic scale than we have indicated.

In conclusion, results from this extensive study indicate that the current California maturity standard of SSC/TA for oranges does not correlate with flavor well when the fruit have low acidity and that BrimA is a superior predictor of flavor under these circumstances. Although low-acidity fruit is primarily a feature of the late season when the maturity standard is not in use, the navel orange industry in California may be better served by using BrimA as a maturity standard rather than the current standard SSC/TA in order to lessen the possibility of low-acid, poor-tasting fruit entering the marketplace. For a flavor quality standard spanning the entire season, BrimA would definitely be recommended over SSC/TA. An additional problem with the current maturity standard that has been highlighted by this research and noted by others (Ivans and Feree, 1987; Pehrson and Ivans, 1988) is that the minimum SSC/TA ratio is set too low for acceptable flavor to be consistently obtained in the early season. The minimum SSC/TA ratio, or BrimA value, needs to be raised to a level that will prevent consumers from purchasing excessively sour fruit. A further point demonstrated by this research is that flavor is not fully described by SSC and TA alone and that aroma volatiles are changing in concert with the observed changes in flavor during navel orange maturation. Further characterization of these aroma volatiles and determination of how to integrate knowledge of the relative levels of these compounds into decisions regarding maturity standards and general fruit quality would be worthy goals of future research.

References

Ahmed, E.M., Dennison, R.A., Dougherty, R.H., Shaw, P.E., 1978. Flavor and odor thresholds in water of selected orange juice components. J. Agric. Food Chem. 26, 187–191.

Baier, W.E., 1954. The Pritchett Tongue. Calif. Citrogr. 39, 442.

Baldwin, E.A., Nisperos-Carriedo, M., Shaw, P.E., Burns, J.K., 1995. Effect of coatings and prolonged storage conditions on fresh orange flavor volatiles, degrees brix, and ascorbic acid levels. J. Agric. Food Chem. 43, 1321–1331.

Buettner, A., Schieberle, P., 2001. Evaluation of aroma differences between hand-squeezed juices from Valencia Late and Navel oranges by quantitation of key odorants and flavor reconstitution experiments. J. Agric. Food Chem. 49, 2387–2394.

California Department of Food and Agriculture, 2003. Title 3, Division 3, Chapter 1, Subchapter 4, Article 22, Section 1430.36.

Chace, E.M., 1917. Maturity standard for Washington navel. Calif. Citrogr. 2, 7 and, 17.

Chace, E.M., 1930. Maturity data on the California Washington navel orange. Calif. Citrogr. 15 534, 569.

Hinterholzer, A., Schieberle, P., 1998. Identification of the most odour-active volatiles in fresh, hand-extracted juice of Valencia late oranges by odour dilution techniques. Flav. Fragrance J. 13, 49–55.

Ivans, E., Feree, M., 1987. Early-season navel oranges may be too sour for consumers. Calif. Agric. (January–February), 20–21.

Jordan, R., Seelye, R., McGlone, A., 2001. A sensory-based alternative to brix/acid ratio. Food Technol. 55 (6), 36–44.

Moshonas, M.G., Shaw, P.E., 1994. Quantitative determination of 46 volatile constituents in fresh, unpasteurized orange juices using dynamic headspace gas chromatography. J. Agric. Food Chem. 42, 1525–1528.

Nicolaï, B.M., Beullens, K., Bobelyn, E., Peirs, A., Saeys, W., Theron, K.I., Lammertyn, J., 2007. Nondestructive measurement of fruit and vegetable quality by means of NIR spectroscopy: a review. Postharvest Biol. Technol. 46, 99–118.

Nisperos-Carriedo, M.O., Shaw, P.E., 1990. Comparison of volatile flavor components in fresh and processed orange juices. J. Agric. Food Chem. 38, 1048–1052.

Obenland, D., Collin, S., Sievert, J., Fjeld, K., Doctor, J., Arpaia, M.L., 2008. Commercial packing and storage of navel oranges alters aroma volatiles and reduces flavor quality. Postharvest Biol. Technol. 47 (2), 159–167.

Olmo, M., Nadas, A., García, J.M., 2000. Nondestructive methods to evaluate maturity level of oranges. J. Food Sci. 65, 365–369.

Pehrson, J.E., Ivans, E.M., 1988. Variability in early season navel orange clone maturity and consumer acceptance. In: Proceedings of the Sixth International Citrus Conference, Tel Aviv, Israel, pp. 1631–1635.

Plotto, A., Margaría, C.A., Goodner, K.L., Goodrich, R., Baldwin, E.A., 2004. Odour and flavour thresholds for key aroma components in an orange juice matrix: terpenes and aldehydes. Flav. Fragrance J. 19, 491–498.

Sites, J.W., Reitz, H.J., 1949. The variation in individual valencia oranges from different locations of the tree as a guide to sampling methods and spot-picking for quality. Part I. Soluble solids in the juice. Proc. Am. Soc. Hort. Sci. 54, 1–10.

Sites, J.W., Reitz, H.J., 1950. The variation in individual valencia oranges from different locations of the tree as a guide to sampling methods and spot-picking for quality. Part II. Titratable acid and the soluble solids/tiratable acid ratio of the juice. Proc. Am. Soc. Hort. Sci. 55, 73–80.

USDA, 2002. Oranges, grapefruit, tangerines, and tangelos grown in Florida; change in the minimum maturity requirements for fresh grapefruit. Federal Register, Vol. 67, No. 232, 7, CFR Part 905.