5) of a standard sugar mix, similar in concentration to the samples analyzed (21). These were found to be 0.02, 0.04, 0.3, and 0.006 %(W/V) for glucose, fructose, sucrose, and myo-inositol respectively. The HPAE/PAD method was used to analyze the sugar content of fresh-squeezed juice from ten early-season citrus cultivars. Results are given in Table 1.

Conclusion

HPLC with amperometric detection can be a useful tool with which to routinely analyze electroactive compounds in citrus juice. A simple, reversed-phase, isocratic HPLC method was illustrated in which vitamin C analysis is complete in less than four minutes. An automated column-switching technique allows the determination of citrus juice folate by direct injection of filtered juice into the HPLC system. Treatment of juices with a conjugase enzyme prior to analysis is recommended for quantitating total folate. Analysis is complete within eight minutes. A high performance anion-exchange method with pulsed amperometric detection can be used routinely to quantitate glucose, fructose, and sucrose, as well as the sugar alcohol, myo-inositol. Run times are less than ten minutes.

The amperometric detection system was found to be rugged and extremely selective, providing superior sensitivity where needed. The methods illustrated are simple and require no sample preparation other than dilution and filtration.

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MODELS FOR SEASONAL CHANGES IN °BRIX AND RATIO OF CITRUS FRUIT JUICE

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Additional index words. Oranges. Forecasting method.

Abstract. **Seasonal changes in °Brix and °Brix/% acid ratio of Florida early season oranges and California 'Washington Navel' oranges were fitted by linear models. The constant term varied with different climatic conditions. The rate of change was 0.0256 °Brix/day and 0.0735 ratio/day for Florida early season oranges and 0.0579 ratio/day for California "Washington Navel" oranges, respectively. An application of the models for early prediction of changes in °Brix and °Brix/% acid ratio throughout the harvesting period was developed.**

Producing high quality products is a common goal of both citrus growers and processors. High quality processed citrus juices must come from high quality fruit. Traditionally, producing high quality fruit is a responsibility of growers. Fruit quality varies with varieties and stages of maturity as well as other factors throughout the season. The processors receive whatever fruit is available as it matures throughout the season and process this into juice

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products. It is often necessary for the processors to blend early and late season juices to achieve optimum quality while utilizing production from the entire season.

Continuous fruit sampling and testing procedures have been practiced to collect seasonal changes in juice yields and quality. These procedures produce the necessary quality information for handling and processing the juice products in day-to-day plant operations. One of the most important quality parameters is the sugar-to-acid ratio. This °*Brix/% acid (B/A) ratio* (hereafter referred to as ratio) is derived from sugar measured as °Brix (by refractometer or hydrometer) and the acid (titratable acidity) measured as citric acid (6). The need to be able to estimate the ratio changes with time throughout the season has been recognized.

Two general approaches have been used to correlate the time required from full bloom to various stages of fruit maturity. One is the heat unit system and the other is the curve-fitting method (by a regression analysis). The former approach was studied by Newman et al. (4), Kimball (2, 3) and others as discussed by Reuther (5). The latter was reported by Tucker and Reuther (7). The heat unit approach has been widely used to predict crop maturity for corn, tomatoes and peas for harvesting and has also been suggested to predict seasonal changes in ratio for practical applications in the citrus industry.

The objective of this work was to investigate the models for early estimation of °Brix and °Brix/% acid ratios of citrus fruit based on the data obtained at the beginning of the citrus season.

Materials and Methods

Empirical models. Twenty-five empirical linear and nonlinear equations commonly used in engineering curve-fitting applications were tested. Computerized curve-fitting technique was used to analyze the goodness of fit. The length of time between April 1 to harvesting dates was used as an independent variable. The day 1 was assumed on April 1 for early season oranges grown in Florida as well as for 'Washington Navel' oranges grown in California.

Data sources. Enormous quality and maturity test data of citrus fruit have been accumulated in the literature. Each set of data was measured for various purposes. Some of the available data were selected for this study. Data of Kimball (3) were selected to represent 'Washington Navel' growing in California. Citrus maturity and yield test data reported by the Florida Dept. of Agriculture and Consumer Services—Florida Agricultural Statistics Service (1) were used for Florida early oranges.

Results and Discussion

Heat unit models

Kimball (2, 3) reported a formula which correlated the ratio development of 'Washington Navel' oranges with the climatic temperature records obtained from weather stations. He developed the following equation:

$$R = H \times S + Y$$

where R is the ratio,
B is the total soluble solids in °Brix,
A is the acid content in percent by weight,
H is the accumulated average temperature (degree-days) from the date just after bloom,
S is the slope of the ratio vs. accumulated degree-days.
Y is the intercept of the ratio vs accumulated degree-days.

The values of H were calculated from weather data and both values of S and Y were empirically determined. S was related to the total harvested crop and Y was correlated to the accumulated maximum temperature from May to August. An attempt to develop a similar formula for California 'Valencia' orange was not successful. It appeared that the correlation equation developed by Kimball was not generally applicable for different varieties. Average seasonal trends of changes in ratio in juices of 'Washington Navel' and 'Valencia' oranges grown in California and Arizona were reported by Tucker and Reuther (7).

Linear models

An analysis of the above reported data by the curve-fitting technique indicated that the rate of change in ratio was fairly constant for the same variety. The data of navel oranges reported by Kimball, was fitted by the following simple linear equation:

$$R = K + 0.0579t$$

where K is an empirical constant and t is time period counting from a given date during the growing season, i.e., from the 1st of April to the date of harvest. By differentiating Eq (2) with respect to time yields:

$$dR/dt = 0.0579$$

where 0.0579 (the slope) is the rate of change per day. By assuming this rate of change was governed by the plant physiological factors and was a constant for every season, Eq (2) was rearranged to solve the constant K (the coefficient) as follows:

$$K = R - 0.0579t$$

The value of K varied from season to season which was used to characterize the difference in climatic conditions for different seasons. By using the measured value of R at the beginning of the citrus season, for example, $R = 10.8$ and $t = 259$ (from April 1st to Dec. 15) for the 1977-78 season, the calculated value of K was -4.196 which was then used in Eq (2) for the estimation of seasonal changes for that particular season.

If July 1 was assumed for day 1 for 'Washington Navel' oranges grown in California, the equation of the curve was:

$$R = K + 0.0581t \qquad (5).$$

The calculated results agreed with those of Eq (2) to within 1%. Thus, any date between April 1 and July 1 can be chosen as day 1 for using the curve-fitting technique.

Florida citrus maturity and yield tests have been conducted by the Florida Dept. of Agriculture and Consumer Services (1) since the early 1960's. The quality and yield statistics of Florida early season oranges for the 1980-81 through 1988-89 seasons are presented in Table 2. The curve-fitting analysis yielded the curve equations for various parameters of quality factors as follows:

Table 1. Measured and calculated °Brix/% acid ratios for 'Washington Navel'.

Season	Month		Measured B/A ratios	Calculated[z] B/A ratios	Estimated[y] B/A ratios
1977-78	Dec		10.8	10.8	10.8
	Jan		12.0	12.5	12.6
	Feb		13.9	14.1	14.4
	Mar		17.3	16.2	16.0
	Apr		17.9	18.0	17.8
		RMS (%) =		3.9	4.9
1978-79	Dec		10.3	10.6	10.3
	Jan		12.4	12.2	12.1
	Feb		13.5	13.7	13.9
	Mar		16.5	15.6	15.5
	Apr		18.2	17.6	17.3
		RMS (%) =		3.7	4.4
1979-80	Dec		10.6	10.5	10.6
	Jan		12.1	12.1	12.4
	Feb		13.4	13.8	14.2
	Mar		15.6	15.5	15.8
	Apr		17.4	17.4	17.6
	May		19.9	19.5	19.3
		RMS (%) =		1.7	3.3
1980-81	Dec		9.0	8.6	9.0
	Jan		10.0	10.2	10.8
	Feb		11.8	11.7	12.6
	Mar		13.5	13.5	14.2
	Apr		15.6	15.5	16.0
	May		18.4	17.6	17.7
	Jun		19.7	20.1	19.5
		RMS (%) =		2.8	5.1
1981-82	Dec		13.0	13.3	13.0
	Jan		14.8	15.0	14.8
	Feb		17.0	16.9	16.6
	Mar		18.9	18.9	18.2
	Apr		20.7	21.1	20.0
		RMS (%) =		1.7	2.8
1982-83	Dec		10.0	8.9	10.0
	Jan		10.9	10.6	11.8
	Feb		12.8	12.3	13.6
	Mar		15.4	14.3	15.2
	Apr		17.1	16.3	17.0
	May		19.3	18.7	18.7
	Jun		21.9	21.2	20.5
		RMS (%) =		6.3	5.2

[z] Kimball (2).
[y] This work. Note: RMS = root mean square error.

for °Brix,

$$B = K + 0.0256t$$

for °Brix-to-% acid ratio,

$$R = B/A = K + 0.0735t$$

The simple linear equations obtained by the curve-fitting technique were adequate for navel and early season oranges but more complex models might be needed for 'Valencia' oranges (7).

A comparison of models

The accuracy of the calculated values were checked by comparing them against the measured values. The differences between the calculated and the measured values are expressed as the root mean square error (RMS) which is defined as:

$$\text{RMS } (\%) = 100^{x} \sqrt{\Sigma(Y_{cal} - Y_{mea})/Y_{mea}]^{2}/(N-1)}$$

where N = number of points.

A comparison of measured and estimated ratios for navel oranges grown in California is presented in Table 1.

Table 2. Statistics of maturity and yield test results for early season oranges grown in Florida from the 1980-81 through 1988-89 seasons.

Parameter	Month	Average	Range	Std. Dev.	c.v.
% acid (A)	Oct 1	1.29	. – .	0.16	12.5
	Nov 1	1.02	. – .	0.12	11.9
	Dec 1	0.89	. – .	0.10	11.0
	Jan 1	0.85	. – .	0.08	9.1
% soluble solids (B)	Oct 1	9.45	. – .	0.28	3.0
	Nov 1	10.19	. – .	0.25	2.4
	Dec 1	11.13	. – .	0.39	3.5
	Jan 1	11.80	. – .	0.38	3.2
B/A ratio	Oct 1	7.60	. – .	1.00	13.1
	Nov 1	10.33	. – .	1.20	11.6
	Dec 1	12.69	. – .	1.30	10.2
	Jan 1	14.17	. – .	1.05	7.4
Pounds juice/box	Oct 1	48.54	. – .	0.75	1.5
	Nov 1	51.05	. – .	0.48	0.9
	Dec 1	51.65	. – .	0.85	1.6
	Jan 1	50.28	. – .	2.14	4.2
Pounds solids/box	Oct 1	4.59	. – .	0.15	3.2
	Nov 1	5.20	. – .	0.11	2.1
	Dec 1	5.69	. – .	0.14	2.5
	Jan 1	5.94	. – .	0.40	6.7

Data Source Florida Department of Agriculture and Consumer Services (1).
Note: c.v. = coefficient of variation

The root mean square errors ranged from 1.7 yo 6.3% and 2.8 to 5.2% for Eq (1) and Eq (2), respectively. The goodness of fit for both the heat unit and the linear models was fairly close.

A comparison of measured and estimated °Brix and the ratio for early season oranges grown in Florida is presented in Table 3. The root mean square errors were in

Table 3. Comparison of measured and calculated °Brix and °Brix/% acid (B/A) ratios for Florida early season oranges.

Season	Month		Measured[z] °Brix	Estimated[y] °Brix	Measured[z] B/A ratio	Estimated[y] B/A ratio
1984-85	Oct 1		9.60	9.60	8.49	8.49
	Nov 1		10.43	10.39	12.17	10.70
	Dec 1		10.95	11.16	13.25	12.97
	Jan 1		11.90	11.96	14.64	15.18
		RMS (%) =		1.2		7.4
1985-86	Oct 1		9.34	9.34	8.82	8.82
	Nov 1		9.99	10.13	11.85	11.03
	Dec 1		10.62	10.90	13.98	13.30
	Jan 1		11.48	11.70	15.40	15.51
		RMS (%) =		2.1		7.3
1986-87	Oct 1		9.53	9.53	7.49	7.49
	Nov 1		10.28	10.32	9.99	9.70
	Dec 1		10.95	11.09	14.28	11.97
	Jan 1		11.86	11.89	14.99	14.18
		RMS (%) =		1.1		10.0
1987-88	Oct 1		9.79	9.79	6.80	6.80
	Nov 1		10.23	10.58	8.85	9.01
	Dec 1		11.31	11.35	12.13	11.28
	Jan 1		12.22	12.15	14.21	13.49
		RMS (%) =		2.0		4.5
1988-89	Oct 1		9.54	9.54	6.76	6.76
	Nov 1		10.46	10.33	9.49	8.97
	Dec 1		11.23	11.10	11.53	11.24
	Jan 1		12.26	11.90	14.21	13.50
		RMS (%) =		2.0		4.5

[z] Data source Florida Department of Agriculture and Consumer Services (1).
[y] This work.
Note: RMS = root mean square error.

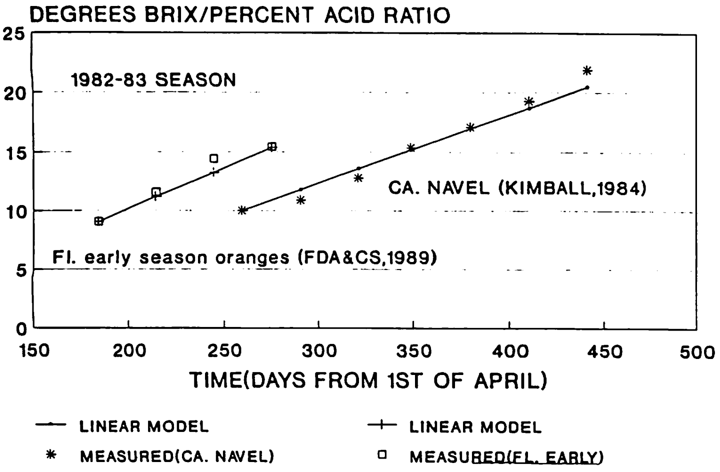

Fig. 1. A comparison of measured and calculated values of degrees Brix/percent acid ratio for citrus fruits.

the range of 1.1 to 2.1% °Brix and 4.5 to 10% for the ratio, respectively. It appeared that the early prediction is more reliable for the °Brix change than for the ratio.

A comparison of measured and calculated ratios of California 'Washington Navel' and Florida early season oranges for 1982-83 season is shown in Fig. 1. It should be noted that the data of early season oranges were a composite of different citrus varieties presumably primarily 'Hamlin', but some 'Parson Brown' and other varieties as well. Better results could be expected if data of the same variety grown in the same area were available for correlation.

The close agreement in predicted results between the linear model and the heat unit model suggested that the simpler linear model can be used advantageously over the heat unit model for early prediction of seasonal changes in °Brix and ratios.

Forecasting applications

The linear models contain only one unknown constant K which can be determined at the beginning of the season using the test data of °Brix and ratio, respectively. Conversely, the assumed values can be used to determine the constant K's which can be used in respective equations for forecasting applications. In late September, 1990, some Florida growers reported °Brix ranging from 9.2 to 9.6 and unusual high ratios ranging from 18.3 to 18.6, respectively, for navel oranges. Table 4 shows the prediction of °Brix changes with time at different initial values for early season oranges grown in Florida. Table 5 shows the prediction of °Brix/% acid ratio changes with time at different initial values for early season oranges grown in Florida. By measuring °Brix and ratio at dates during September and October to determine the initial values, the predicted corresponding subsequent changes can then be found from the above tables. It should be noted that the predicted values were based on the averaged values of all early season oranges derived from 1980-1989 seasons. There are no reported data for seasonal changes in °Brix and ratio for gift fruit varieties. More research work should be directed to collect data of each variety and to develop the rate constant for the specific variety.

Table 4. Prediction of °Brix changes with time at different initial values for early season oranges grown in Florida.

Time week	°Brix										
0	9.0	9.1	9.2	9.3	9.4	9.5	9.6	9.7	9.8	9.9	10.0
1	9.2	9.3	9.4	9.5	9.6	9.7	9.8	9.9	10.0	10.1	10.2
2	9.4	9.5	9.6	9.7	9.8	9.9	10.0	10.1	10.2	10.3	10.4
3	9.5	9.6	9.7	9.8	9.9	10.0	10.1	10.2	10.3	10.4	10.5
4	9.7	9.8	9.9	10.0	10.1	10.2	10.3	10.4	10.5	10.6	10.7
5	9.9	10.0	10.1	10.2	10.3	10.4	10.5	10.6	10.7	10.8	10.9
6	10.1	10.2	10.3	10.4	10.5	10.6	10.7	10.8	10.9	11.0	11.1
7	10.3	10.4	10.5	10.6	10.7	10.8	10.9	11.0	11.1	11.2	11.3
8	10.4	10.5	10.6	10.7	10.8	10.9	11.0	11.1	11.2	11.3	11.4
9	10.6	10.7	10.8	10.9	11.0	11.1	11.2	11.3	11.4	11.5	11.6
10	10.8	10.9	11.0	11.1	11.2	11.3	11.4	11.5	11.6	11.7	11.8
11	11.0	11.1	11.2	11.3	11.4	11.5	11.6	11.7	11.8	11.9	12.0
12	11.2	11.3	11.4	11.5	11.6	11.7	11.8	11.9	12.0	12.1	12.2

Note: Initial °Brix determined at dates between mid-September and mid-October

Table 5. Prediction of °Brix/% acid ratio changes with time at different initial values for early season oranges grown in Florida.

Time week	°Brix/% acid ratio										
0	18.0	18.1	18.2	18.3	18.4	18.5	18.6	18.7	18.8	18.9	19.0
1	18.5	18.6	18.7	18.8	18.9	19.0	19.1	19.2	19.3	19.4	19.5
2	19.0	19.1	19.2	19.3	19.4	19.5	19.6	19.7	19.8	19.9	20.0
3	19.4	19.5	19.6	19.7	19.8	19.9	20.0	20.1	20.2	20.3	20.4
4	19.9	20.0	20.1	20.2	20.3	20.4	20.5	20.6	20.7	20.8	20.9
5	20.4	20.5	20.6	20.7	20.8	20.9	21.0	21.1	21.2	21.3	21.4
6	20.9	21.0	21.1	21.2	21.3	21.4	21.5	21.6	21.7	21.8	21.9
7	21.4	21.5	21.6	21.7	21.8	21.9	22.0	22.1	22.2	22.3	22.4
8	21.8	21.9	22.0	22.1	22.2	22.3	22.4	22.5	22.6	22.7	22.8
9	22.3	22.4	22.5	22.6	22.7	22.8	22.9	23.0	23.1	23.2	23.3
10	22.8	22.9	23.0	23.1	23.2	23.3	23.4	23.5	23.6	23.7	23.8
11	23.3	23.4	23.5	23.6	23.7	23.8	23.9	24.0	24.1	24.2	24.3
12	23.8	23.9	24.0	24.1	24.2	24.3	24.4	24.5	24.6	24.7	24.8

Note: Initial °Brix and % acid determined at dates between mid-September and mid-October.

The importance of developing an accurate and reliable forecasting system for fruit maturity has been well recognized, especially for fresh fruit market. The simple linear model yielded useful approximation for proper scheduling and planning for just-in-time operation for the season. Further research and development are needed to develop more accurate prediction methods.

Conclusion

Simple linear models were capable of correlating the change in °Brix and sugar-to-acid ratio of Florida early season oranges as well as the ratio of California 'Washington Navel' oranges throughout the growing season. The constant term varied from season to season which accounted for the difference in climatic conditions. The rate of change with time during the maturation period for each quality parameter was relatively constant which appeared to depend on the physiological factors. The models allowed the use of data obtained at the beginning of the citrus season for early estimation of seasonal change in °Brix and ratio with accuracy to within 2% and 4-10% standard deviations, respectively. The accuracy of the linear models was comparable to that of the conventional heat unit system.

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QUALITY CHANGES DURING HARVESTING AND HANDLING OF 'VALENCIA' ORANGES

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Additional index words. citrus, mechanical damage, acid, Brix, ethanol, storage.

Abstract. **External and internal quality of 'Valencia' oranges was monitored at 7 stages of the commercial harvesting and handling process. The greatest amount of external damage was found in fruit collected at the pallet bin and at packinghouse departure. Mechanical damage incurred at harvest was largely removed during grading, but additional damage occurred in the packinghouse. No further external damage occurred after this point. Peel and pulp temperatures, monitored during transport from the packinghouse to the warehouse, decreased 1°F/hr over a 20 hr transportation period. Pulp temperatures were always greater than the peel during this time. Percent acid, measured in fruit initially collected after each marketing event and after 4 weeks storage at 50°F, 90% RH, declined significantly only in stored fruit late in the handling sequence. Brix of initially evaluated and stored fruit increased significantly after harvest and remained high during handling. Waxing with a solvent-based wax had no significant effect on % acid or °Brix. Juice ethanol increased in stored fruit collected at packinghouse departure and increased only slightly thereafter; whereas, a significant increase in non-stored fruit occurred only in fruit collected at simulated consumer storage.**

The Florida citrus industry produces a high quality fresh fruit crop for domestic and international markets. Fruit destined for fresh market are subject to a variety of handling events that can ultimately affect the external appearance and internal quality of the fruit. Hand harvesting of round oranges has often resulted in a variety of external damages, the highest percentage of which were plugged fruit (2, 8, 10). Although packinghouse grading removed any fruit with external defects, a high percentage of fruit which had plugging damage (stem-end tears) passed through the packinghouse unnoticed and were found in the final packed carton. No further increase in external damage was found during later handling events. Decay was not detected until the retail and consumer marketing channels (2).

Internal quality can also be affected by harvesting and handling events. Whereas external damage occurred primarily at harvest, internal quality of 'Hamlin' oranges was most affected during later handling events (2). A rapid and significant decline in % acid and °Brix was measured in stored fruit originally collected at packinghouse departure. Acid and Brix remained low but unchanged throughout the remainder of the marketing sequence. A sharp increase in % juice ethanol, an indicator of anaerobic metabolism (3), was also measured during the later portion of the marketing sequence. Although the data suggested that packinghouse treatment, such as wax application, resulted in change in internal quality (2), measurements were only performed on stored fruit and not on those initially brought from each marketing event. Thus, the effect of time of storage and handling event could not conclusively be separated.

A study was initiated in 1989 to provide additional data on the effects of harvesting and handling on external and internal quality of 'Valencia' oranges. Internal quality was assessed directly after fruit collection and after storage to clarify the effects of handling and storage. Seven sampling points were chosen along the commercial harvesting and handling sequence, and the effects of waxing on internal quality was also assessed.

Materials and Methods

Plant material. 'Valencia' oranges (*Citrus sinensis* Linn. Osbeck) were harvested in April from an established grove in central Florida. Fruit were hand harvested simultaneously by a commercial grove crew (commercial fruit) and by a selected crew from the Citrus Research and Education Center, Lake Alfred, FL (control fruit). Only fruit of size 125 (fruit/carton) were harvested. Fruit from 7 specific points along the commercial harvesting and handling sequence (Table 1) were evaluated. After each harvesting and handling point, commercial fruit were divided into 2 subsamples, each containing 2 cartons. One subsample was evaluated for external quality immediately and then internal quality determined as described below; the other was stored at 50°F, 90% RH for 4 weeks, and then analyzed. Control fruit were harvested directly into cartons and transported to the LA-CREC. Fruit were divided into 4 subsamples, each containing 2 cartons. Each subsample was washed and 1000 ppm TBZ applied. Two subsamples

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