

Results obtained in evaluating fruit for degree of cleanliness, by the two methods previously described, are illustrated in Figures 3 and 4. Figure 3 is a photograph of pads after filtering rinse water from each station during one sampling. From visual observation unwashed fruit carried a heavier load of soil up through station 4. Commencing with station 5, soil was about equal between the two processes and remains fairly constant up to the point of extraction.

Figure 4 is a graph showing the light transmission values obtained from rinse water. Data for washed and unwashed fruit are the average of 7 test runs. The higher transmission values indicate less opacity and, thus, less soil rinsed from the sample of oranges. Oranges sampled from the truck, whether subsequently washed or unwashed, showed almost identical Lumetron readings. This establishes that fruit used for the two processes was equal in initial soil load. The results also show that initially washed fruit is markedly cleaner up to the brush washer (station 5) than unwashed fruit, but only slightly cleaner from this point to the extractors.

In checking on the efficiency of the first grading operation, it was noted that more boxes were culled when unwashed fruit entered the bins (Table I). One assumption might be that the graders discarded more sound oranges than unsound oranges when fruit was dirty than when it was clean. The final graders (fruit to process) showed no significant difference in number of boxes culled between washed and unwashed fruit. In the course of this investigation, it was observed that recording the number of culls after the

final grading operation is an excellent method of checking grading efficiency. In this particular study a record was kept of the culls graded by each shift. It was noted that when the initial graders "fell down on the job," the final graders culled more fruit. Also, in one instance when the percentage of culls graded was exceptionally high it was found that the final graders were over grading. Keeping a record of these culls also gives a more accurate basis for figuring yields at the plant.

The data presented in this paper show that washing fruit prior to bin storage has no beneficial effect in reducing fruit surface contamination, but it does result in fruit handling equipment remaining in a more sanitary condition. This is especially true in the bins where soil and other debris ordinarily accumulate. The initial graders also stated that it was easier to grade washed rather than unwashed fruit.

#### Summary

Oranges washed prior to bin storage, in addition to regular sanitizing after bins, decreases surface contamination immediately after the initial wash operation. Otherwise, initially washed fruit was not significantly different in contamination from the regular fruit handling procedure. Washed fruit is cleaner from standpoint of surface soil up to point of final brush washer; bins and fruit handling equipment remain cleaner and no physical breakdown of fruit occurred. Graders preferred washed fruit but culled more oranges entering bins when they were unwashed. Final graders culled from each process equally.

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## THE TASTE OF CITRUS JUICE

### II. CITRATE SALTS AND pH

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Citrus juice is a buffered solution which contains weak acids, primarily citric (7), and salts of weak acids, predominantly potassium salts (1). The hydrogen ion concentration in a buffered solution is determined

by the nature of the acid and by the concentrations of salt and acid, as given in the following formula:

$$\text{pH} = \text{pK}_a + \log \frac{C_s}{C_a} \quad (2)$$

where  $\text{pK}_a = -\log K_a$ ;  $K_a$  is the ionization constant of the acid;  $C_s$  is the concentration of salt;  $C_a$  is the concentration of acid.

Juice obtained from different lots of citrus fruit exhibit considerable variability in pH.

Since there is a close correlation between pH and tartness (5,3,4) it is of practical value to learn whether variation of acidity or salt concentration is the predominant factor determining the tartness of juice.

The first paper of this series (5) dealt with the relationship between acidity and pH in citrus juice. This paper investigates the relationship between pH and concentration of salts in citrus juice.

Sinclair and Eny (6) estimated the concentration of salts in California citrus juices by measuring the alkalinity of the ash. This method is rather tedious if a large number of samples are to be examined. Because of the long duration of the season, variability in bud wood, root stock, soil, and cultural practice, it was felt desirable to examine a large number of samples to properly evaluate fruit utilized at a Florida processing plant. To facilitate the investigation, a quick method for estimating salt concentration in juice was developed. Salts in the juice are converted into free acid by passing the solution through a column of cation exchange resin in the hydrogen form. The liberated acid is determined by titration.

#### MATERIALS AND METHODS

**Raw Material.** Each day of the 1958-59 season, two samples of grapefruit juice were taken at our canned juice processing plant. Freshly extracted juice samples were obtained from the blend tanks before any sugar was added. The samples were frozen and kept in a frozen state until a convenient number had been accumulated for analysis. The samples were thawed in cold water when required.

**Determination of Free Acidity, Brix and pH.** Five ml. of juice were diluted with 45 ml. of distilled water and titrated to a permanent pink end point of phenolphthalein using 0.1 N sodium hydroxide.

The Brix was determined with a refractometer, correcting for citric acid according to the method of Stevens and Baier (8).

The pH of the juice was determined with a Beckman model G meter, using glass and calomel electrodes.

**Determination of Salt Concentration.** Mix 25 ml. of juice with 25 ml. of isopropyl alcohol to coagulate pectin and precipitate insoluble colloidal material. The juice was centrifuged and the clear supernatant used for the determination.

Ten ml. of the supernatant was passed, at a rate of 2 ml. per minute, through a 10 x 150 mm. column of Rohm & Haas IR120 resin in the hydrogen form. The juice sample was washed through the column with 40 ml. of 50% isopropanol-water solution. The concentration of acid was determined by titration to a permanent pink end point of phenolphthalein with 0.1 N sodium hydroxide. Another 10 ml. of the clear supernatant was diluted with 40 ml. of 50% isopropanol-water mixture and titrated to a permanent pink end point of phenolphthalein with 0.1 N sodium hydroxide.

The difference between the two titration values is a measure of the salt concentration expressed as equivalents of sodium hydroxide. The increase in titratable acidity in the juice when passed through the column, is due to conversion of salts into free acid by ion exchange. The pH of the titration mixture is effected to some extent by the alcohol concentration. Determination of salt by difference between the two titration values avoids error by making the alcohol concentration in both

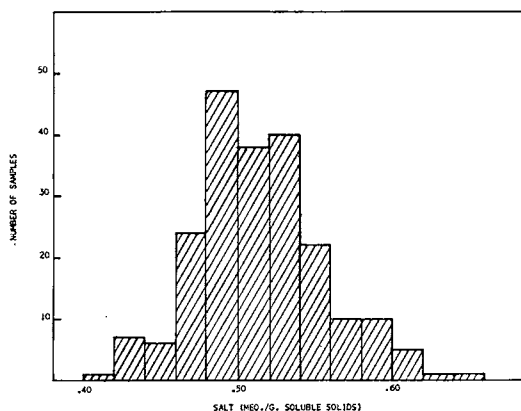


Figure 1. Salt Concentration in Juice, Frequency Distribution.

titration mixtures the same.

After approximately ten determinations, the exchange column was back washed with water and regenerated with a 9% solution of hydrochloric acid in 50% isopropanol-water. The column was washed with 50% isopropanol-water until free of acid.

#### RESULTS AND DISCUSSION

**Range of Variation in Salt Concentration.** The salt concentration in 212 samples of grapefruit juice is summarized in the frequency distribution graph shown in Figure 1.

These samples exhibit greater uniformity in salt concentration than in the other characteristics measured. Variation in concentration of total solids, free acid, hydrogen ion, and ascorbic acid is encountered in citrus juice used

for commercial processing. This is understandable in view of the variation in root stock, bud wood, maturity, soil, rainfall, and cultural practice in the wide spread area in which commercial fruit is grown.

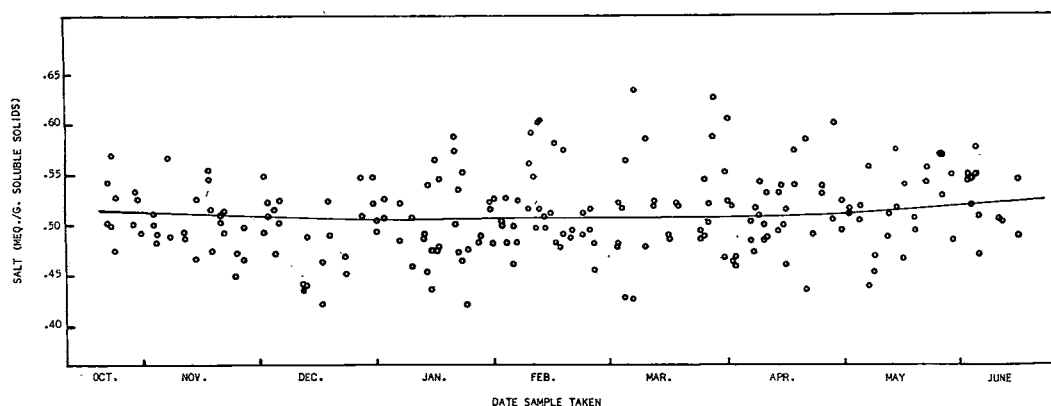


Figure 2. Trend in Salt Concentration in Juice During Season.

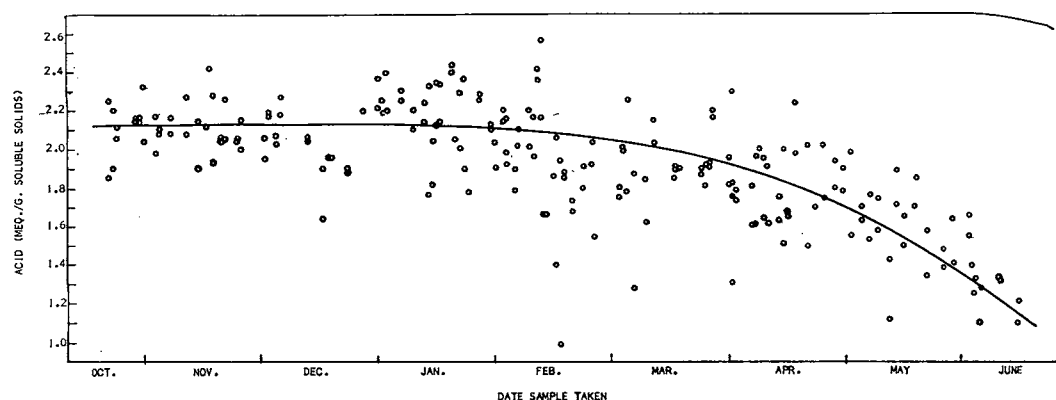


Figure 3. Trend in Juice Acidity During Season.

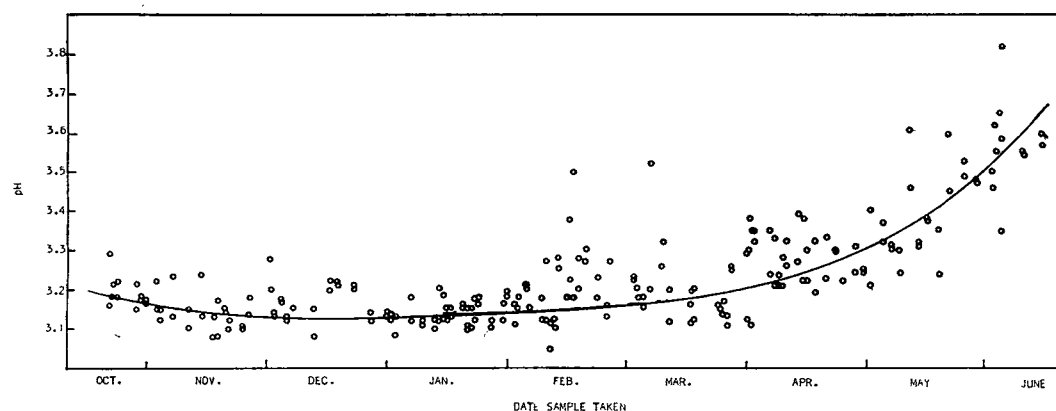


Figure 4. Trend in pH of Juice During Season.

Much of the difference in composition between individual fruit samples is due to variation in the water content of the fruit. The salt concentration (in Figure 1) is expressed as milliequivalents of salt per gram of soluble solids. The value is derived from the titration data by calculating the milliequivalents of salt in 100 grams of juice and dividing by the Brix. This mode of expression corrects for variation in water content similar to the commonly used term "Brix/acid ratio." Correcting for differences in water content allows a more understandable comparison of the various other components in juice.

*Change in Salt Concentration During the Normal Harvest Season.* The concentration of salt in the juice samples were plotted against the date on which the sample was taken to determine whether a consistent trend occurs

during the season as the fruit continues to hang on the tree for a greater length of time. The trend line (shown in Figure 2) indicates that the concentration of salt in the juice remained relatively constant throughout the entire season.

*Change in Free Acidity During the Normal Harvest Season.* Figure 3 shows the trend in concentration of free acidity, expressed as milliequivalents per gram of soluble solids, throughout the harvest season. The concentration of free acid, in contrast to the uniform concentration of salt, showed uniformity only for the first four and one half months of the season then a definite decline in the average value occurred as the season continued. This trend in the free acid concentration is well documented in previous work which reports the value as Brix/acid ratio (9).

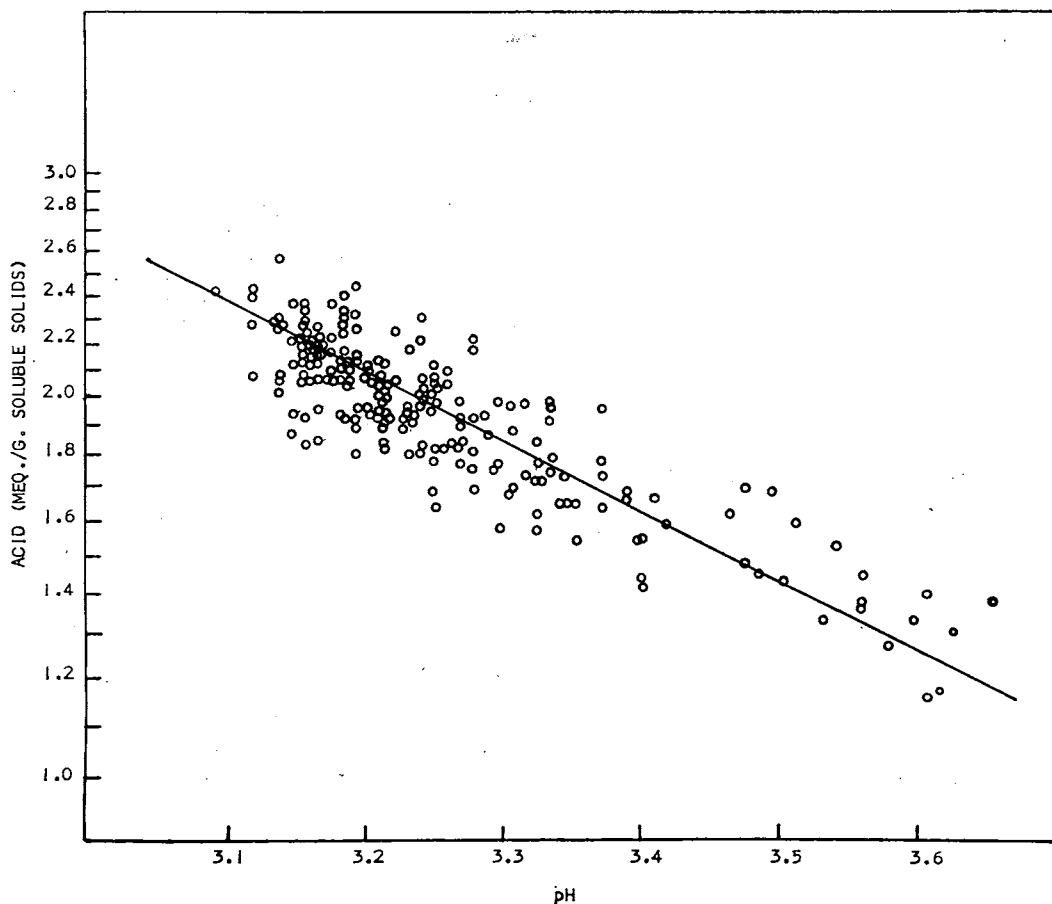


Figure 5. Relationship Between Acid Concentration and pH in Grapefruit Juice.

*Change in pH During the Normal Harvest Season.* Figure 4 shows the trend in pH to be the inverse of that demonstrated by the free acid concentration. The average pH showed little change during the first four and one half months after which there was an upward trend for remainder of the season.

*Relationship Between Acidity and pH.* Relationship between pH and free acidity for the present series of samples is shown in Figure 5. Figure 5 shows that the pH of juice is a function of the log of the free acid concentration, expressed as milliequivalents per gram of soluble solids.

*Relationship Between Salt Concentration and pH.* Figure 6 shows the relationship between the pH of juice and the experimentally determined salt concentration. The values obtained for the concentration of salt in juice exhibited some variability but the variation appears to be random. The average value of

the salt concentration was the same at all levels of pH.

#### SUMMARY

1. The average value of the concentration of salts in grapefruit juice (expressed as milliequivalents per gram of soluble solids) is the same throughout the entire season.

2. Variation in the pH of grapefruit juice is due primarily to differences in free acidity.

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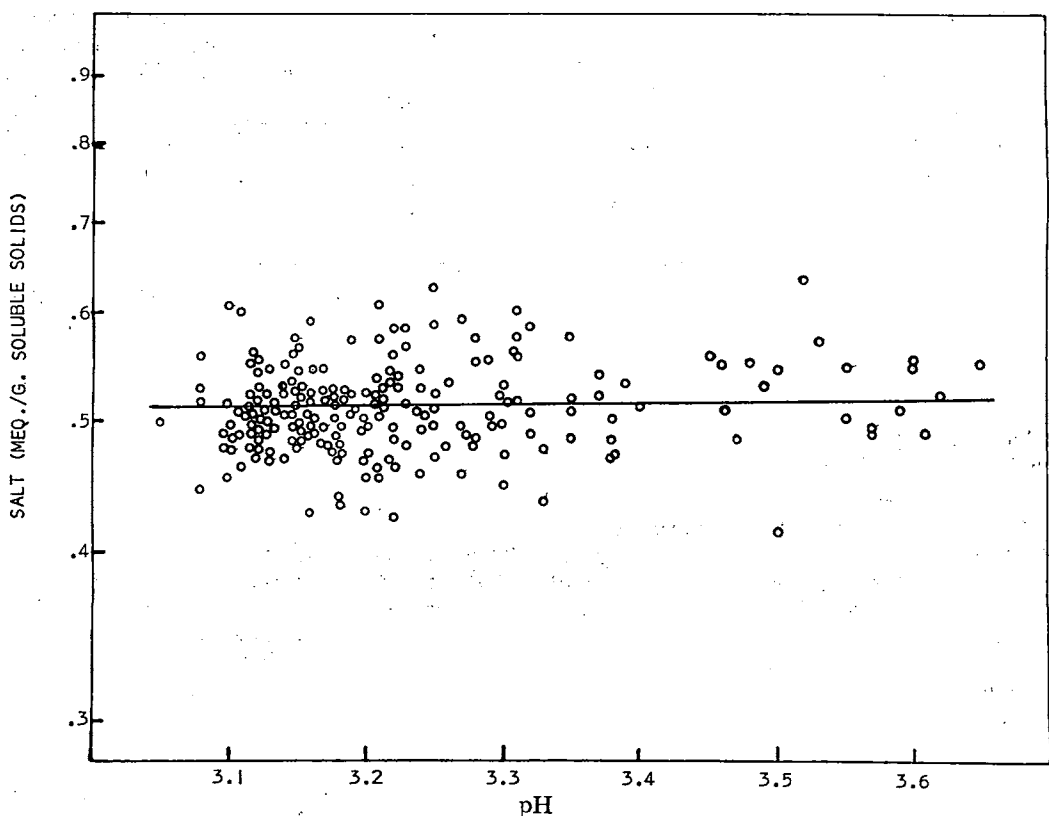


Figure 6. Relationship Between Salt Concentration and pH in Grapefruit Juice.

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## MEASUREMENT OF COLOR CHANGES IN GREEN BEANS

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Variations in the color of green beans may arise as a result of differences in variety, maturity, storage, and processing. Since the chlorophyll in green beans is relatively sensitive to heat, even mild blanching may cause significant color change by converting some of the chlorophyll to pheophytin.

Conversion of chlorophyll to pheophytin is complete in most canned green beans. As a result the canned product has an olive or olive-brown color. Color of the product may vary substantially in both shade and uniformity from a muddy gray-brown to a clear bright olive-green.

The olive-brown color is often present in frozen green beans to a lesser extent than in the canned product. Color of the frozen product may vary substantially also.

This study was conducted to gather more information about the basic color differences that occur in green beans and to develop simple and reliable methods of evaluating these differences.

### *Literature Review*

Smith and Benitez (3) reviewed methods used to estimate chlorophyll and its derivatives in plant materials.

Mackinney and Weast (2) measured the chlorophyll breakdown in blanched green beans by determining the optical density of extracts at 535 and 560 mu. Dietrich et al (1) estimated chlorophyll retention in frozen beans by blending a sample with acetone, then filtering and washing the residue with acetone. Optical density readings of the filtrate were made at 534 and 556 mu. Chlorophyll was completely converted to pheophytin by adding an oxalic acid solution to the filtrate and

allowing to stand overnight. Sweeney and Martin (4) studied the effect of heat treatment on chlorophyll degradation in broccoli and suggested that changes in absorbance at 665 mu could be used as an index of chlorophyll *a* retention.

The ratio of Gardner *a* to *b* color difference readings for beans was used as an index of color (1) and Gardner *a* readings and subjective color ratings were found to be correlated with chlorophyll retention (4).

### MATERIALS AND METHODS

#### *Absorption spectra of acetone extracts*

Duplicate 50-gram samples of deseeded fresh, frozen, and canned green beans were blended with 250 ml. of undiluted acetone for 3 minutes and filtered through Whatman No. 1 filter paper. Optical density readings of the clear filtrate were recorded for the wavelength range of 400 to 700 mu. Absorption curves were compared with those of pure chlorophyll *a*, chlorophyll *b*, pheophytin *a*, and pheophytin *b* (3).

#### *Measurement of chlorophyll *a* retention*

The measurement of chlorophyll *a* retention was based on the degree of reduction in absorbance at a wavelength of 665 mu in relation to the absorbance at a wavelength of 556 mu. The latter wavelength represented the crossover point of the chlorophyll *a* and pheophytin *a* curves.

A 50 gram sample of fresh deseeded beans was blended with 250 ml. of undiluted acetone for 3 minutes and filtered. The optical density of the filtrate was measured with a Beckman DU spectrophotometer at wavelengths of 556 and 665 mu. The ratio of optical density readings at 665 and 556 mu was used as an index of 100% chlorophyll *a* retention. A 100 ml. aliquot of the extract was treated with 1 ml. of 1% oxalic acid in 90% acetone and allowed to stand overnight. The ratio of the optical density readings at 665 and 556 mu was used as an index of 0% chlorophyll *a* retention. A straight line relationship between 100% retention and 0% retention was used to

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