ALTERNATIVE CALCIUM SALTS FOR THE FIRMING OF BRINED SWEET CHERRIES

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ABSTRACT

ALTERNATIVE CALCIUM SALTS FOR THE FIRMING OF BRINED SWEET CHERRIES

by

Bruce Leon Vibbert

Napoleon and Windsor varieties of sweet cherries (Prunus avium L.) were bleached in sulfur dioxide brines containing calcium chloride, calcium nitrate, calcium oxide, calcium carbonate, calcium acetate, calcium propionate, calcium lactate, calcium gluconate or alum as firming agents.

Calcium absorption by the cherry fruit was dependent on brine calcium concentration and not on any effect of the anion of the salt. Equilibrium of both calcium and soluble solids was attained before 500 hours after brining. Treatments which required large quantities of citric acid for acidification had a precipitate of calcium citrate which removed much of the calcium from solution.

Texture was evaluated using the Chatillon spring push gauge, the Allo-Kramer Shear Press and the Instron Testing Machine equipped with a standard shear compression cell and

a 1.6 mm single punch. The manual Chatillon was the best instrument for texture evaluation. Firmness of brined cherries was at its maximum at less than 1000 ppm calcium. Levels above that were of no significant benefit. Final calcium concentrations in the dyed cherry were between 570 to 710 ppm calcium. All other calcium was removed by water leaching.

Calcium nitrate was the best substitute firming agent in sulfur dioxide brines. It has excellent solubility and low acid requirements. The potential for orchard fertilization with the sulfur dioxide-calcium nitrate brine is good and could provide a desirable method for brine disposal. Nitrate levels are low enough to avoid toxicity problems.

Other salts were unsuitable for dry mix brines when used at levels above 0.25% calcium because of calcium citrate precipitation. At all levels they were questionable because of low solubility and high citric acid requirements. Alum was not an adequate firming agent when used alone.

ALTERNATIVE CALCIUM SALTS

FOR THE FIMING OF

BRINED SWEET CHERRIES

by

Bruce Leon Vibbert

A THESIS

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To my Mother and Father

may they see to enjoy

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INTRODUCTION

The process of preserving fruits with sulfur dioxide has long been known. Reports using sulfur dioxide with and without firming agents for maraschino cherries were published in the late 1920's and early 1930's (Bullis and Wiegand, 1931; Cruess et al., 1932; Atkinson and Stachan, 1935A; Atkinson and Strachan, 1935B). The basic sulfur dioxide brine has changed very little. Liquid or gaseous sulfur dioxide is bubbled into a tank of water. A calcium salt, for firming and pH adjustment, is added in the form of calcium carbonate or calcium hydroxide and mixed until dissolved. The formula was usually in the proportion of two parts sulfur dioxide to one part calcium carbonate.

In maraschino cherry production, sulfur dioxide is used because of its excellent bleaching properties and preservative qualities. It is also easily removed. Jurd (1964) reports that the bleaching of the anthocyanin pigment is reversible. Reaction of the anthocyanin carbonium ion with a bisulfite ion at pH 3 forms a colorless compound which is reversible at pH 1. Markakis (1974) reports that anthocyanin decoloration may be reversible or irreversible, depending on sulfur dioxide strength. Sulfur dioxide has little effect on the carotene compounds and only slight effect on chlorphyll (Joslyn and

Braverman, 1954) and will not bleach brown spots on bruised fruit, once they have developed.

Whittenberger (1968) reported that hand harvested cherries should be brined within 8 hours and probably within 4 hours. Mechanically harvested cherries should be brined within 4 hours and preferably within 1 hour to maintain good quality. With the advent of mechanical harvesting, it has become more important to brine the cherries as soon after harvest as possible. Traditionally, the cherries were harvested by hand and transported to the briner in 20 quart boxes, where they were dumped into the brine. Delays of 12 hours between harvest and brining were not uncommon, but quality was reasonably good. The physical abuse inherent with mechanical harvesting will not permit such long delays before brining. Most growers today are mechanically harvesting over 90% of their crop. Due to bruising, the quality of the fruit and consequently the price was being reduced. Work done by Tennes et al. (1975) dealt specifically with this problem. A new type of brine mix was developed that allowed the growers to brine their cherries in the orchard, thus eliminating the delay and the bruising. Because the traditional type brine is very corrosive, it is very inconvenient to transport into the orchards. In order to brine in the orchards, it was felt that the brine must be mixed from a dry form which could be added to water when needed. Various workers had reported using sodium bisulfite or sodium metabisulfite as a source of sulfur dioxide (Cruess, 1935; Brekke et al., 1961). This granular form of sulfur dioxide should be transported to the orchard dry and mixed with water on location in waterproof pallet boxes. Calcium chloride was chosen as the calcium salt because of its solubility. Citric acid was used as an acidulant. These three components were weighed into plastic bags in proper quantities for a calibrated metal pallet box. This type of brining has mushroomed in only two years to the point where several briners in Michigan use this type of brine for the majority of their pack.

The brining industry is not without its problems. Rapidly developing environmental awareness by the U.S. population has resulted in strict regulation of both municipalities and industry. Effluent restrictions have been legislated by federal, state and local government agencies to provide effective water pollution control measures. Effluent limits are being place on suspended solids, pH, biological oxygen demand, sulfur compounds and dissolved solids.

Brine from the maraschino cherry process is degraded only with difficulty. The presence of high concentrations of sulfur dioxide prevents normal microbial degradation. Municipal treatment plants equipped only for biological treatment of wastes cannot adequately treat brining wastes.

Traditionally, the normal means of disposal consisted of dilution. Strong sulfur dioxide brine was shipped along with the bleached cherries to a finishing plant. At this point, the sulfur dioxide levels were reduced by dilution with other plant waste water. Once the levels of sulfur dioxide were below several hundred parts per million, municipal treatment plants could treat the waste with some success. The only waste that the briner incurred was a small quanitity of low sulfur dioxide wash water. This has been spray irrigated onto surrounding orchards from a holding lagoon.

With the new effluent restrictions being enforced, the cherry finishers specified that brined cherries be shipped in water, with sodium benzoate used as a preservative. This became a serious matter for the briner as he was not equipped for strong brine disposal.

Work by Brekke et al. (1966) reported that brine can be reused up to three times without sacrificing firmness. Activated carbon has been investigated to remove the anthocyanin pigments before reusing the brine (Soderquist et al., 1971; Beavers et al., 1970A). Using decolorized brine actually resulted in a product of superior quality because the presence of higher soluble soilds prevented cracking that is often prevalent with mature fruits. This procedure has a very promising future but is not being used commercially to date. Brine recycling can be utilized to significantly reduce quantities of waste brine. Sapers et al. (1975) has outlined a procedure for treating strong brine by precipitation of the sulfur dioxide as calcium sulfite. A further step also incorporated the recovery of sugars from the brine which could be used in the manufacture of maraschino cherries. Mauldin et al. (1975) has outlined a method of aerobic biological degradation of low sulfur dioxide wastes using actividED sludge.

Odor is also a problem with brine disposal. Plant waste water is generally stored in lagoons before spray irrigation. The sulfur dioxide levels are low enough to permit microbial growth, usually anaerobic. This anaerobic breakdown of sulfur dioxide yields very pungent compounds including hydrogen sulfide. Gerrish (1975) has used both ozone and hydrogen peroxide as a means of reducing the odor from these lagoons.

One other pollutant from cherry brine is the dissolved salts. Calcium salts are the major ones of concern. As the dry type brine mixes become more widely accepted, the quantities of calcium chloride used will be constantly increasing. Calcium chloride is also used in the traditional brines as an additional firming agent. It is believed that calcium chloride firms better than other calcium salts and that it will inhibit polygalacturonase. Polygalacturonase is an enzyme which attacks the pectin structure of the cherry resulting in softening of the fruit. Various reports in the literature have shown that calcium chloride will not firm any better or inhibit enzyme acitivity (Yang et al., 1960; Watters et al., 1961; Atkinson and Strachan, 1962; Lewis et al., 1963; Atkinson and Strachan, 1964; Brekke et al., 1966).

The chloride ion is a problem because it is one component of the brine which will not be bound up by soil when spray irrigated. Instead, it is leached through the soil into groundwater supplies in the form of salt. This is one substance that health departments are becoming more and more aware of.

Pressure is being placed on cherry briners and finishers to reduce chloride concentrations in their effluents.

Cruess (1933) reported that calcium sulfite could be used in place of calcium carbonate in traditional type brines. Blumenthal (1935) found that calcium sulfate could be used to harden soft cherries in brine. Woodroof and Cecil (1943) reported the experimental use of calcium phosphate in brine formulations. These salts were used in traditional type brines. Since that time very little work has been done in the area of alternative calcium salts. Beavers et al. (1975) reported that alum could be used successfully as a secondary firming agent in brines.

It was the purpose of this study to evaluate various sources of calcium for use in the powdered brine mixes, and whether another salt could be substituted for calcium chloride. As part of this study, calcium chloride was evaluated for any special properties.

Various methods of texture determination were evaluated as a means of examining the performance of various firming agents.

MATERIALS AND METHODS

Raw Product

Napoleon and Windsor varieties of sweet cherry (*Prunus avium* L.) were used in this study. The cherries were obtained from the Old Mission Penninsula near Traverse City, Michigan. Harvests from two years, 1974 and 1975, were used in this study. In 1974, the cherries were hand harvested on July 17, 18, and 25, and brined within 2 hours to insure good quality (Whittenberger et al., 1968). In 1975, Napoleon and Windsor cherries were mechanically harvested on July 15, and 17, respectively. They were transported dry in shallow pallet boxes to a commercial brining plant. Time between harvest and brining was less than two hours. Samples for this study were taken at the brining plant.

Cherry samples brined in 1974, had a high percentage of stems, as they were hand harvested. Those collected in 1975, had a very low percentage of stems. Cherries that were to be mechanically harvested were sprayed with Ethephon. These ethylene treatments result in increased fruit abscission from the stem, causing the fruit to detach from the tree more easily.

The cherries were brined in one gallon plastic containers with snap-on lids. Both 1974 and 1975 brines were made using a quantity of sodium bisulfite to yield a theoretical 1.25% sulfur dioxide. In 1974, calcium ion levels of 0.50% were used with sufficient citric acid added to reduce the pH to 2.8. Three calcium ion levels were used in 1974, (0.25%, 0.50% and 0.75%). The pH was adjusted with citric acid to 3.0. Duplicate samples were used in 1974, triplicate samples in 1975.

Eight calcium salts and alum were selected for use in this study. These salts and their amounts are shown in

Tables 1 and 2. Four pounds of fresh cherries were brined in 1.8 liters of solution.

Table 1. 1974 Brine Formulations[1]

Treatment	Calcium salt g./liter	Citric acid g./liter
Calcium chloride	19.4	1.67
Calcium nitrate	31.1	1.67
Calcium oxide*	7.4	74.4
Calcium acetate*	23.2	76.7
Calcium lactate*	40.6	62.8
Calcium gluconate	56.7	50.0
Alum [$AlK(SO_4)_2 \cdot 12H_2O$]	5.3	1.67

[1] All brines contained 21.0 g. Na HSO_3 per liter.

* Brines with precipitate.

In 1974, several commercial brines that had been used the previous season were included in the study. A light color brine, typical of that from Napoleon cherries, and a dark brine, typical of the Windsor variety, were adjusted with sodium bisulfite and calcium chloride to full strength. These brines were used to compare with fresh brine as to effect on color of the final, bleached cherry.

In 1975, a fresh commercial brine was included as a

Table 2. 1975 Brine Formulations[1]

Treatment	Calcium %	Calcium salt g./liter	Citric acid g./liter
Calcium chloride	0.25	9.2	2.2
	0.50	18.4	1.37
	0.75	27.6	0.79
Calcium nitrate	0.25	14.7	1.8
	0.50	29.5	0.79
	0.75	44.2	0.26
Calcium carbonate	0.25	6.3	36.8
	0.50	12.5	61.5
	0.75	18.8	81.8
Calcium acetate	0.25	11.0	36.3
	0.50	22.0	63.2
	0.75	33.1	90.7
Calcium lactate	0.25	19.3	27.6
	0.50	38.5	44.6
	0.75	57.8	59.7
Calcium propionate	0.25	12.7	36.5
	0.50	25.5	62.0
	0.75	38.3	85.4

[1] All brines contained 21 g. Na HSO_3 per liter.

* Treatments which had precipitate.

reference for other treatments. It was made up using the traditional liquid sulfur dioxide and calcium carbonate brine with additional calcium chloride added.

After harvest and brining, all samples were transported to the Michigan State University Food Science Building. They were stored at ambient room temperature (70°F). The 1974 samples were stored for five months during which time additional sodium bisulfite solution was added, as needed to maintain the liquid and sulfur dioxide level. The 1975 samples were stored for ten weeks before analysis or processing. No additional sodium bisulfite was added.

An additional study was conducted, in 1975, on Napoleon cherries. Equal brine and cherry samples were taken at various intervals after initial brining to evaluate the rate of calcium uptake by the cherry. All treatments of the main experiment were included, but were not replicated.

Brines were analyzed as soon after sampling as possible to prevent sulfur dioxide losses. With the exception of the calcium uptake experiment, all brine samples were analyzed before any cherries were removed.

Pitting

All samples in this study were pitted using a laboratory model Dunkley cherry pitter (Dunkley Co., Kalamazoo, Michigan).

pH

All pH measurements in this study were taken with a Beckman Zeromatic pH Meter (Beckman Instruments Inc., Fullerton, California).

Soluble Solids

All soluble solids measurements were taken on a Valentine Refractometer, Model 350B (Valentine and Co., Vista, California).

Color

Color was measured only on 1974 samples using a Hunter Lab Model D25 Color and Color Difference Meter. The procedure used was that described by Kraut (1972).

Texture

Texture of the cherries was evaluated using the Chatillon spring push gauge, 0-1000g., with a stainless steel tip, 1.6 mm. in diameter (John Chatillon and Sons, New Gardens, New York), the Instron Universal Testing Machine (Instron Corporation, Canton, Mass.) using the Chatillon tip and the standard shear compression cell, and the Allo Kramer Shear Press with the standard shear compression cell.

The single punch manual type instrument has gained wide acceptance for texture measurement of many food products (Bourne, 1975). Within the cherry industry, the Chatillon spring push gauge is the most prevalent. Yang et al. (1959) reported on the uses of a Chatillon spring push gauge for evaluating firmness of brined cherries. Brekke and Sandomire (1961) studied the effectiveness of the Chatillon type instrument to detect differences in firmness of brined cherries.

The Chatillon instrument was clamped to a ring stand and the fruit was guided and pushed onto the tip. This decreased the human variability that tended to occur when the tip was pushed by hand into the hand held fruit. Two measurements were made on each cherry perpendicular to the steam blossom axis. Twenty unpitted cherries were measured for each sample. The mean value of the 40 observations was calculated and used in statistical calculations.

Using the Instron, two types of measurements were made. With the Chatillon tip attached to the Instron, a 1 to 50 kilogram load cell was used. All measurements were made with a full scale load equal to 1 kilogram and a crosshead speed of 20 cm/min. Twenty pitted cherries were used from each lot. Two measurements were taken on each fruit. Values were recorded as maximum puncture force in grams. With the standard shear compression cell, a 50 to 2500 kilogram load cell was used. The full scale load of 200 kilograms and a crosshead speed of 20 cm/min. were used. Measurements were taken on triplicate 100 g samples of pitted cherries. Data were obtained for peak heights. The area under the curve was determined with an Instron Integrator. Typical curves for both Napoleon and Windsor variety cherries are shown in Figure 1. The first or primary peak was broad and represented most of the force. The second or secondary peak was sharp and occured when the parallel plates of the test cell were just entering the slots at the base of the cell. Maximum peak height equalled either primary of secondary peak height. The work force was calculated by the following formula.

$$\text{WORK} = \frac{S\ C\ A\ V_x}{500} = \text{kg-cm}$$

S = selector setting (10)

C = kilograms per 10 divisions of chart

A = area (divisions per minute)

V_x = crosshead speed (cm/min)

The Allo Kramer Shear Press with a 3000 pound proving ring was used. In 1974, a downward travel speed of 32 cm/min. was used. In 1975, both 32 and 20 cm/min. downward travel speeds were used. Triplicate 100 g. samples of pitted cherries were used. Maximum force corresponding to maximum peak height is reported as kilograms per 100 g.

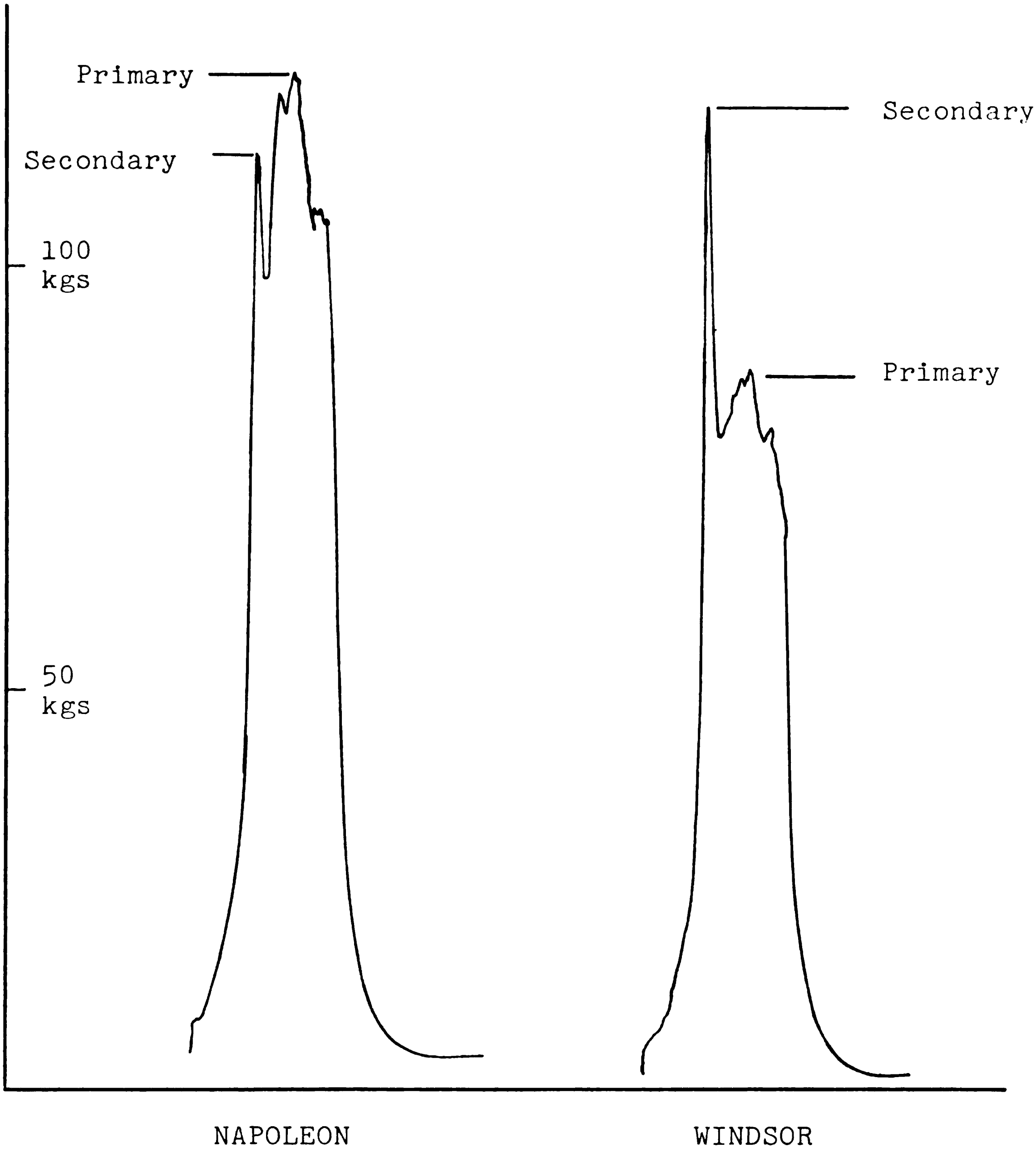

Figure 1. Typical Peak Configurations of Napoleon and Windsor Cherries Evaluated with the Instron and the Standard Shear Compression Cell.

Dyeing

The cherries in this study were dyed according to a general procedure outlined to the author by a cherry finisher in Michigan.

Sulfur dioxide was leached from 3 pounds of pitted cherries over a period of five days by changing the soak water daily with cool, tap water. Then the cherries were soaked in one liter of 40^{o} Brix sirup, adjusted to pH 3.5 with citric acid, and containing 0.3 mg. F D & C Red #4 (Poncean SX). No flavoring was added. Each day for 3 days, the sirup was drained off the cherries, readjusted with sugar to 40^{o} Brix, and heated to dissolve the sugar. The cherries were packed into 16 oz. glass jars and filled with $180^{o}F$ 40^{o} Brix sirup. The jars were passed through an exhaust box, sealed and cooled. They were stored for future testing and visual evaluation.

ANALYTICAL METHODS

Sulfur Dioxide Determination

Sulfur dioxide content of the cherry brines was determined using the method of the Association of Official Agricultural Chemists (AOAC, 1965), as modified by Payne et al. (1969).

Calcium Determinations

Calcium determinations were made on all cherry brine samples and some selected cherry tissue samples.

Calcium determinations were made on brine samples using a modified method of the AOAC method for direct titration of calcium and magnesium with standard EDTA solution as outlined by Payne _et al_. (1969). The end point of this titration requires trace amounts of magnesium disodium EDTA added to the ammonium buffer as directed by the American Public Health Association (1961).

Calcium in cherry tissue was determined by the following procedure. Weigh accurately 50 grams of pitted cherries. Add 50 ml of distilled water and blend at high speed in a small Waring blender for two minutes. Transfer accurately, 50 grams of slurry to a 250 ml beaker. Add 100 ml of 20% v/v hydrochloric acid and mix with a magnetic stirrer for five minutes. Add 40 ml of 20% w/w sodium hydroxide. Mix and transfer, quantitatively, to a 250 ml volumetric flask. Bring to volume. Filter through Whatman #1 filter paper into a 125 ml erlenmeyer flask. Collect at least 75 ml of filtrate. Pipet 20 ml of filtrate into a 500 ml erlenmeyer flask and procede with analysis as described for brine samples (20 ml of filtrate equals 2 grams of original sample).

Nitrate Determination

Nitrate was determined using an Orion nitrate proble Model 92-07 in conjunction with a Beckman Digital pH Meter, Model 4500. Dyed and sugared cherries were analyzed. Nitrate standard solutions were treated with 0.5 g sulfanilamide to eliminate nitrite interference.

RESULTS AND DISCUSSION

Calcium Salts

The primary objective of this study was to determine if the firming agent, calcium chloride, used in powdered brine mixes, could be replaced by another compound. In order to be an adequate substitute, several criteria must be met.

For practical application, the salt should be very soluble. Calcium salts, as a rule, are relatively insoluble. This factor eliminated many calcium salts. Several salts that were selected for study are insoluble in water but are soluble under acidic conditions. These are calcium carbonate, and calcium oxide.

A suitable firming agent must be non-toxic in order to be used in a food product. Availability of the compound will determine practical application, but this was not a factor in the selection of salts for this study. Cost is also a factor, and is directly related to availability.

In this study eight calcium salts were selected for evaluation. In addition, alum, which is also used as a firming agent, was used plus various samples of commercial brine mixes. These salts and their formulations used in 1974, and 1975, are listed in Tables 1 and 2, respectively.

Dry type brine mixes consist of three basic components. Sodium bisulfite is the source of sulfur dioxide when dissolved in water. Calcium chloride is used as the firming agent. Citric acid has been used primarily as an acidulant. It also provides additional benefits as a chelator of the calcium. Recently, fumaric acid has been substituted for citric acid, in some cases, because of lower cost. However, its chelating ability is less than that of citric acid (Beavers, 1975).

Quantities of sodium bisulfite and calcium salts to be used were determined by calculation based on available sulfur dioxide and calcium respectively. Sufficient citric acid was added to reduce the brine to pH 3.0. It should be noted from Tables 1 and 2 that large amounts of the organic calcium salts were required to yield equal quantities of calcium. This fact has implications in terms of cost per pound of calcium and in the physical bulk of material handled. It can also be seen that for most of the formulations large quantities of citric acid were required to reduce the pH. The exceptions are calcium chloride, calcium nitrate and alum. These required relatively small amounts of citric acid to acidulate the brine. Citric acid is the single most costly item involved in using dry brine mix.

After the 1974 cherries had been brined, several treatments contained a white precipitate (Tables 1 and 2). Precipitation was observed in treatments using calcium oxide, calcium acetate, calcium lactate, calcium propionate and calcium carbonate. After consultation with knowledgeable people in industry and of the university and after reviewing the literature, it was concluded that the precipitate was calcium sulfite. Payne et al. (1969) reported that there is some calcium sulfite formed in all brines. It exists in an unstable supersaturated condition and will precipitate if upset by temperature changes, seeding or vibration. If brine ingredients are added in the incorrect order, it is possible to form an excess of calcium sulfite which will precipitate more rapidly. In 1974, the citric acid and calcium salt were added first and dissolved, then the sodium bisulfite. The correct procedure is to add the calcium salt last. This assures that the pH has been reduced before the calcium salt is added. On the basis of improper ingredient addition, it was concluded that calcium sulfite could have been formed instead of the normal calcium bisulfite.

In 1975, the brines were made up by dissolving the calcium salt in the citric acid-sodium bisulfite solution to prevent, if possible, any precipitation. However, precipitation occured in the brines containing 0.50% and 0.75% levels of calcium carbonate, acetate, lactate and propionate.

Although calcium gluconate did not precipitate in the 1974 study, it was excluded from the 1975 study because excessive time and effort were required to dissolve the salt.

Several qualitative tests were made on the precipitate in an attempt to determine its composition. The white precipitate was collected, washed thoroughly and dried. It was found to be insoluble in dilute hydrochloric acid indicating that it was not calcium sulfite, sulfate, carbonate or oxide. It was not oxidized to sulfate by iodine and there was no decrease in the sulfur dioxide levels in the brines. Therefore, it was concluded not to be sulfite. Microscopic examination of the crystals showed a crystalline structure similar to that of calcium citrate. Since the precipitate occured only when high levels of citric acid were used, it was believed to be calcium citrate. It is interesting to note that no precipitate occured when calcium gluconate was used (Table 1). Apparently the citric acid level was below that required to cause precipitation.

Tables 3 and 4 are ascending listings of mean calcium concentrations for each treatment and Duncan's mean separation test for Napoleon and Windsor varieties, respectively. It can be seen that there are three natural groupings. The first group is composed of all treatments that precipitated, except calcium lactate. Both the 0.50% and 0.75% calcium treatments are included in this group. It appears that once precipitation has begun it will continue to a certain level regardless of initial calcium concentration.

The second group contains all of the 0.25% calcium treatments plus the higher levels of calcium lactate. Calcium

Table 3. Ascending Grouping of Brine Calcium Concentrations for Napoleon Cherries, 1975.

Treatment	Calcium %	Calcium concentration (ppm)	
Calcium carbonate	0.75*	1044	a+
Calcium propionate	0.75*	1113	a
Calcium carbonate	0.50*	1130	a
Calcium acetate	0.75*	1146	a
Calcium propionate	0.50*	1148	a
Calcium acetate	0.50*	1153	a
Calcium nitrate	0.25	1627	b
Calcium carbonate	0.25	1644	b
Calcium lactate	0.25	1692	bc
Calcium lactate	0.75*	1703	bc
Calcium acetate	0.25	1708	bc
Calcium propionate	0.25	1724	bc
Calcium chloride	0.25	1792	cd
Calcium lactate	0.50*	1868	d
Calcium nitrate	0.50	2932	e
Calcium chloride	0.50	3026	e
Calcium nitrate	0.75	4045	f
Commercial	-	4284	g
Calcium chloride	0.75	4359	g

* Denotes treatments which had precipitate.

+ Equal letters denote no significant difference at the 5% level.

Table 4. Ascending Grouping of Brine Calcium Concentrations for Windsor Cherries, 1975.

Treatment	Calcium %	Calcium concentration (ppm)	
Calcium carbonate	0.75*	881	a+
Calcium acetate	0.50*	938	a
Calcium acetate	0.75*	945	a
Calcium propionate	0.75*	966	a
Calcium propionate	0.50*	1008	a
Calcium carbonate	0.50*	1024	a
Calcium carbonate	0.25	1557	b
Calcium nitrate	0.25	1588	b
Calcium acetate	0.25	1598	b
Calcium lactate	0.25	1620	b
Calcium lactate	0.75*	1636	b
Calcium chloride	0.25	1640	b
Calcium propionate	0.25	1644	b
Calcium lactate	0.50*	1862	c
Calcium nitrate	0.50	2627	d
Calcium chloride	0.50	2928	e
Calcium nitrate	0.75	3631	f
Commercial	-	4071	g
Calcium chloride	0.75	4314	h

* Denotes treatments which had precipitate.

+ Equal letters denote no significant difference at the 5% level.

lactate is apparently just on the borderline of precipitation and maintains more calcium in solution.

The third group is not as distinct as it contains the higher concentrations of the unprecipitated treatments, calcium chloride and calcium nitrate.

Based on solubility, several salts can be eliminated from consideration as a possible alternative to calcium chloride. Calcium acetate, propionate, carbonate and lactate at the 0.50% and 0.75% calcium levels precipitated. All levels of calcium chloride and nitrate are acceptable. Only the 0.25% calcium levels of the salts that precipitated are acceptable, but the citric acid requirements are high.

Calcium Uptake by Cherry Fruit

In addition to its ease of handling calcium chloride is said to have certain other advantages. People within the industry believe that calcium chloride is absorbed faster by the cherry, resulting in more rapid firming than other salts. It has also been said to have some inhibitory effect on polygalacturonase. Yang *et al*. (1960) reported that calcium chloride does not appear to have any inhibitory effect on polygalacturonase. Steele and Yang (1960) reported that softening of cucumber tissue was the result of the breakdown of insoluble protopectin and not the calcium pectate structure. Therefore, calcium chloride might not inhibit the enzyme but may firm the fruit enough to prevent severe softening if the enzyme is present.

Calcium uptake and the final calcium concentration in Napoleon cherries are shown in Figures 2, 3 and 4, respectively, for 0.25%, 0.50% and 0.75% initial calcium levels in the brine. Calcium depletion of the brines during bleaching are shown in Figures 5, 6 and 7, respectively, for 0.25%, 0.50% and 0.75% calcium treatments.

The cherries brined in the 0.25% calcium brine showed similar rates of uptake during bleaching. Figure 5 shows the average brine calcium depletion of all 0.25% calcium treatments. The calcium concentrations of both the brine and the fruit were about equal after 500 hours of bleaching. None of the calcium treatments demonstrated any advantages in calcium absorption.

In the 0.50% calcium brines the calcium uptake was similar for calcium carbonate, propionate, lactate and acetate. After 200 hours the absorption leveled off. Calcium chloride and nitrate showed somewhat faster absorption and higher final calcium concentrations in the fruit. Figure 6 shows similar trends for brine calcium depletion. Calcium propionate, carbonate and acetate decreased in calcium more than chloride and nitrate. Calcium lactate depletion was similar to that of chloride and nitrate up to 200 hours. After that point the depletion increased. There was less precipitate in the calcium lactate brine than in those of calcium acetate, carbonate or propionate. This could explain why the calcium depletion for calcium lactate was less than the others.

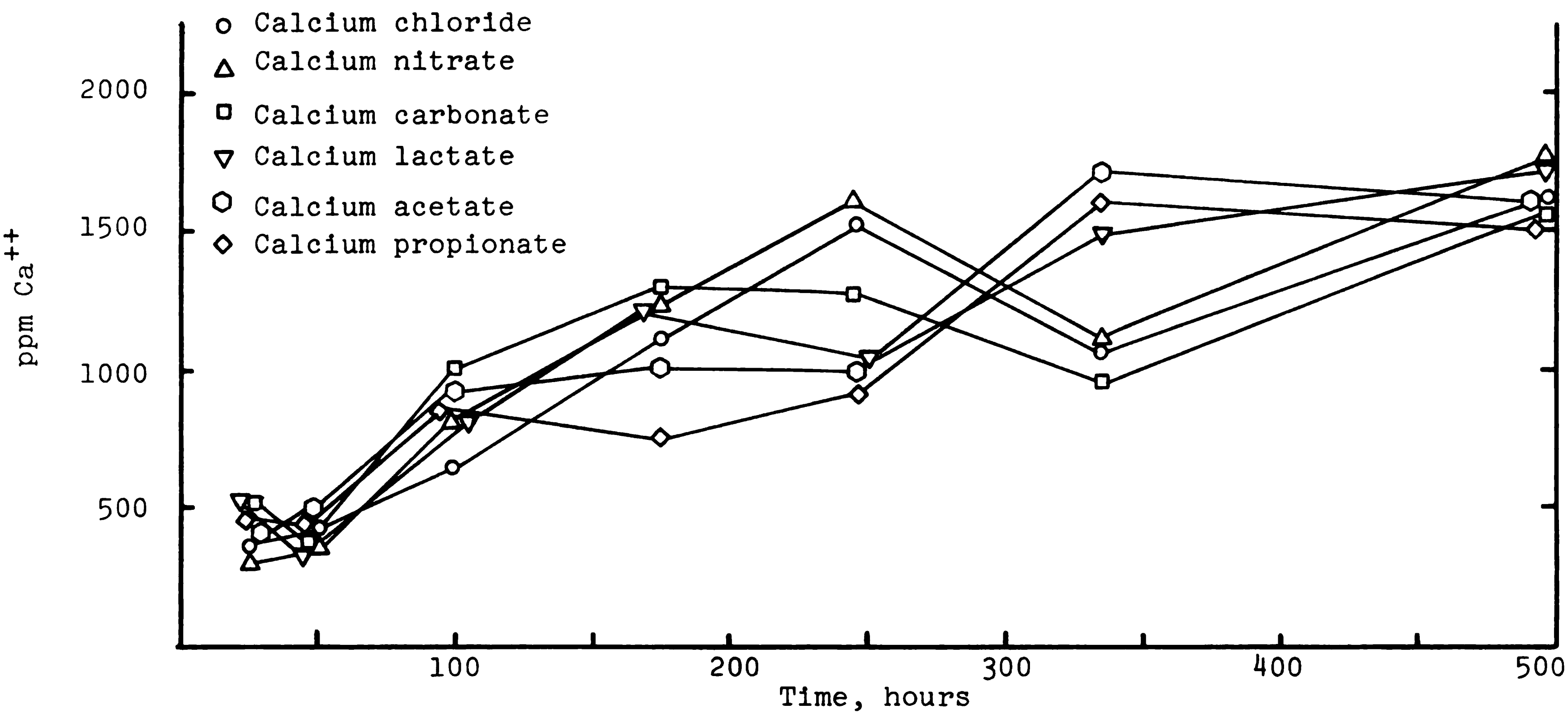

Figure 2. Change in Cherry Fiber Calcium During Brine Curing (2500 ppm initial calcium).

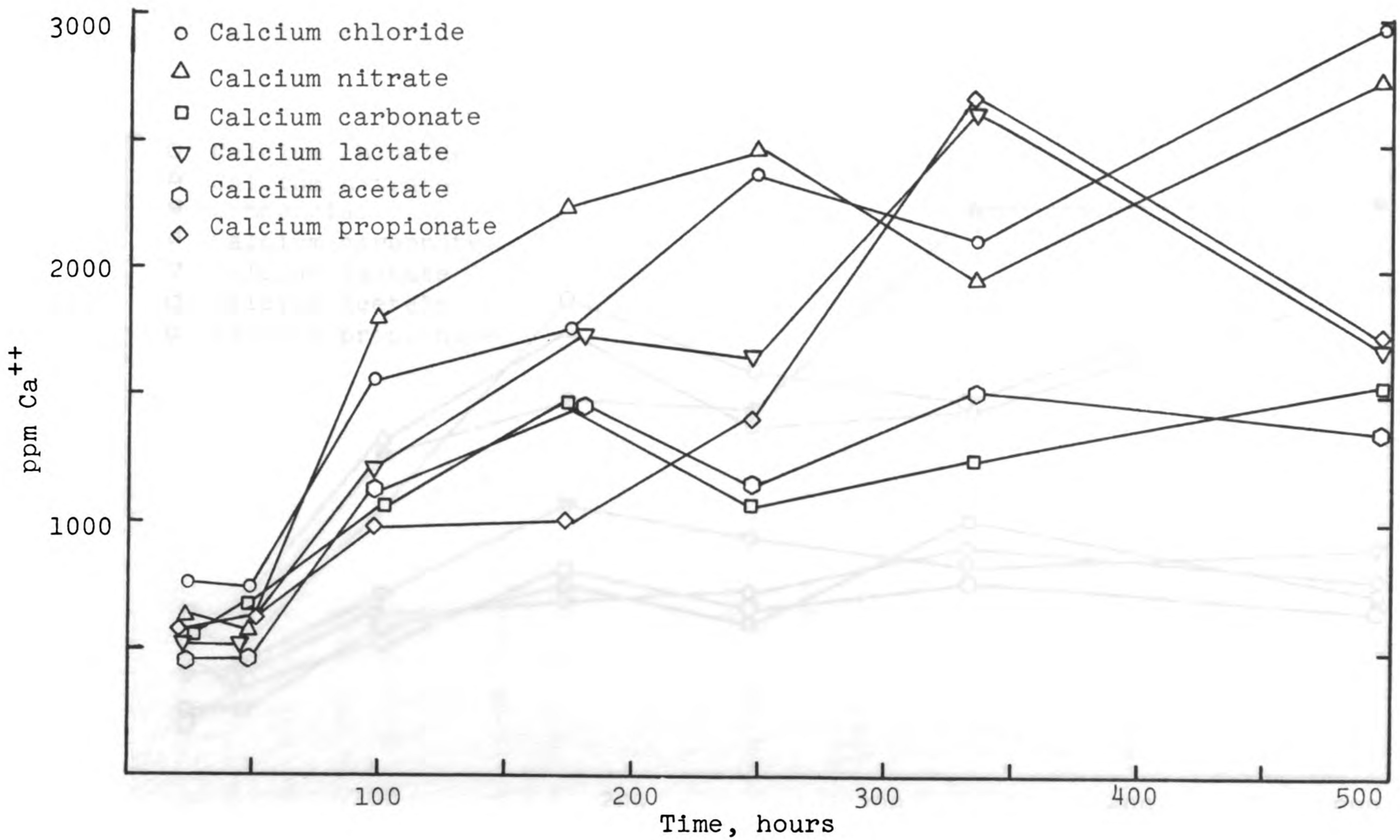

Figure 3. Change in Cherry Fiber Calcium During Brine Curing (5000 ppm initial calcium).

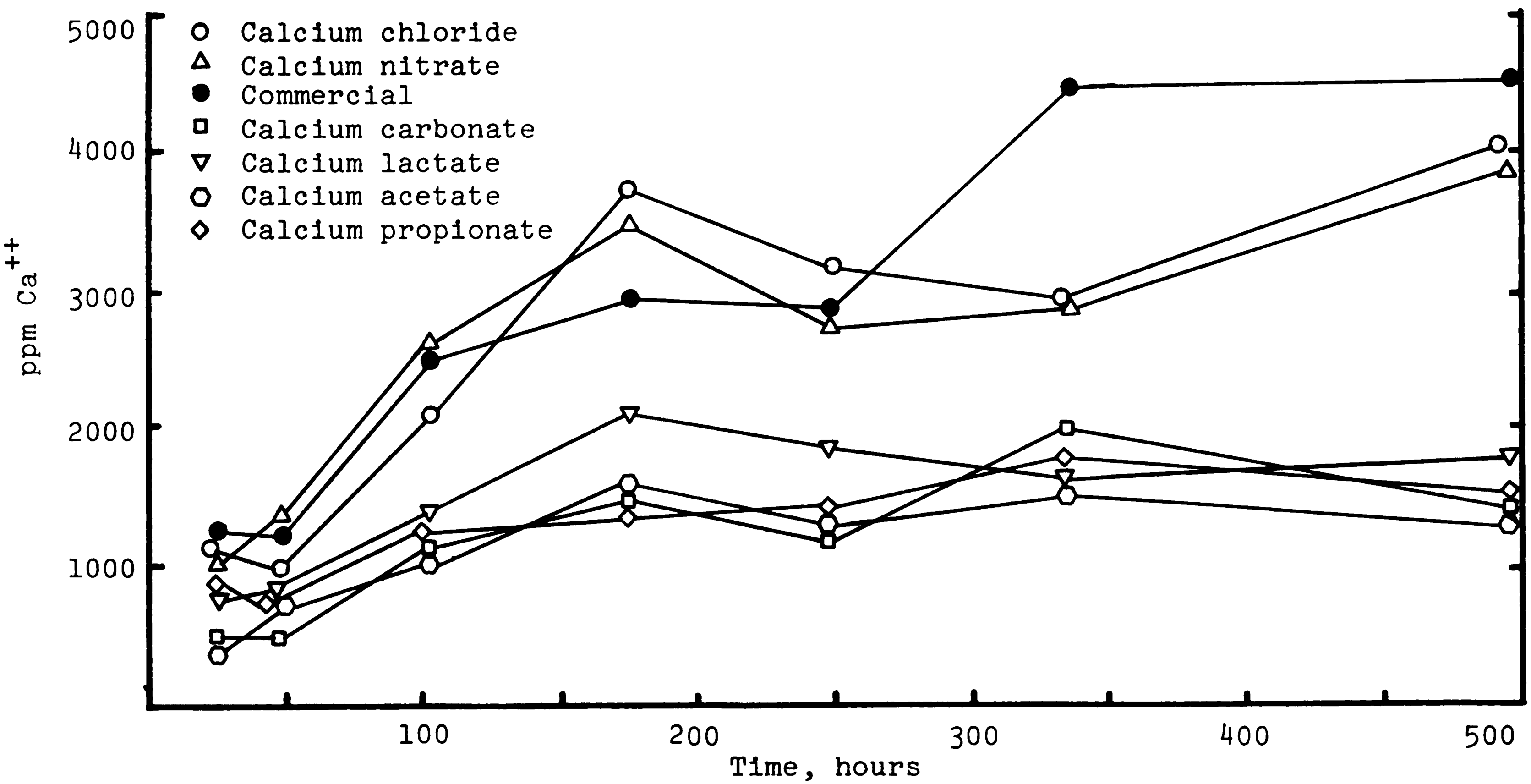

Figure 4. Change in Cherry Fiber Calcium During Brine Curing (7500 ppm initial calcium).

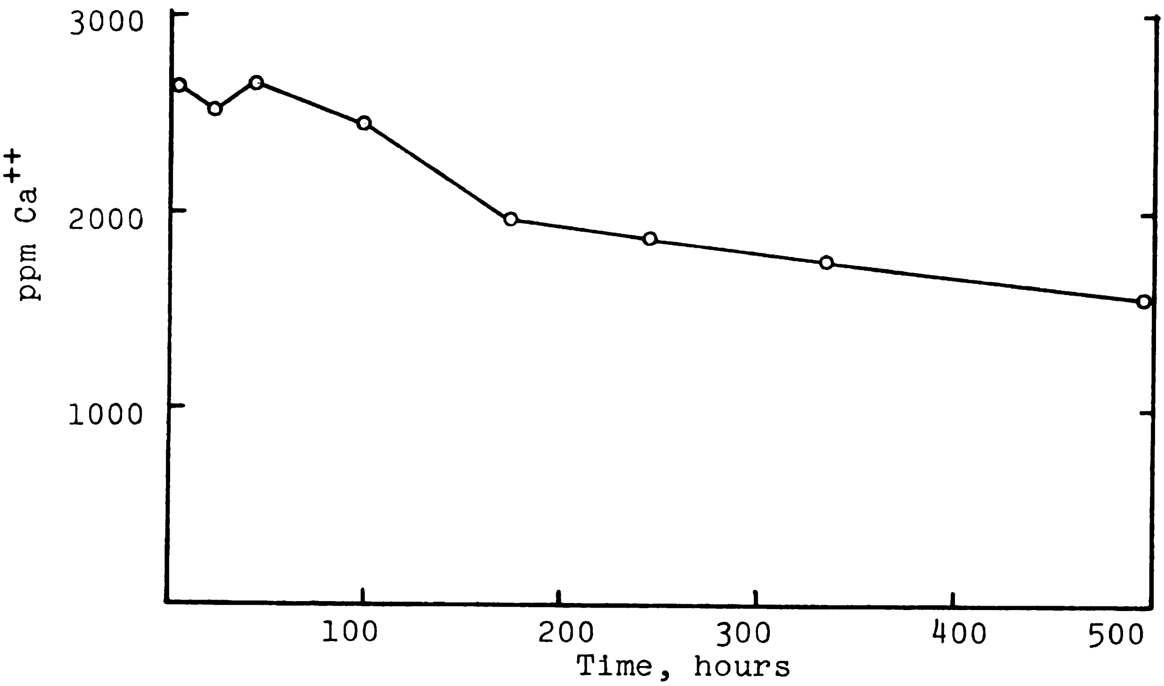

Figure 5. Average Change in Brine Calcium During Brine Curing (2500 ppm initial calcium).

Figures 3 and 6 together show that calcium uptake by the fruit was dependent on the calcium concentration in the brine.

In the 0.75% calcium treatments the calcium uptake was more rapid in the nitrate, chloride and commercial brines. The calcium absorption by calcium carbonate and the organic calcium salts was similar to the absorption at the lower levels. After 200 hours no further increases were seen. These similar absorptions were due to equal brine calcium concentration. Table 3 shows that both 0.50% and 0.75% treatments, which precipitated, were not significantly different

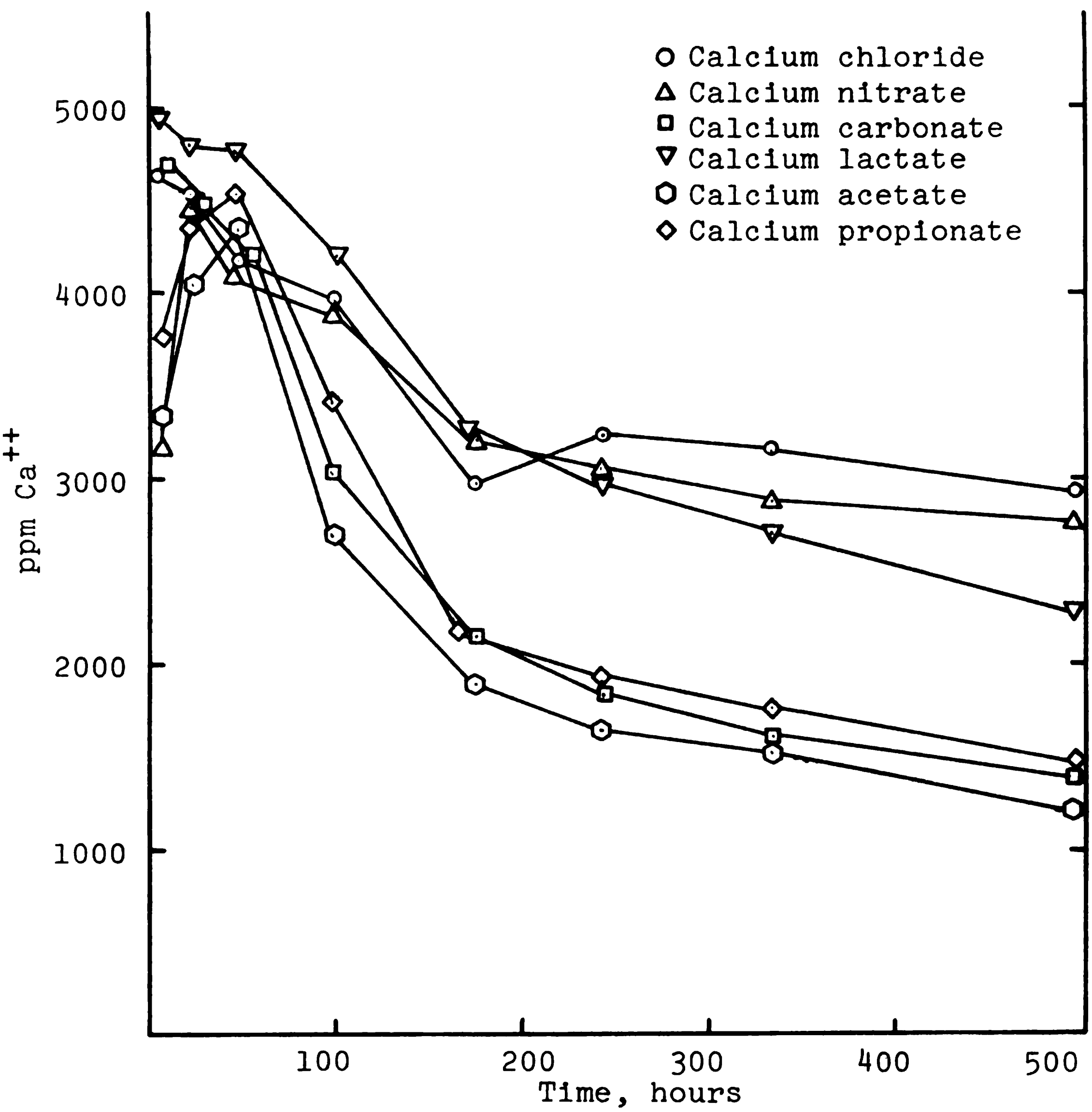

Figure 6. Change in Brine Calcium Concentration During Brine Curing (5000 ppm initial calcium).

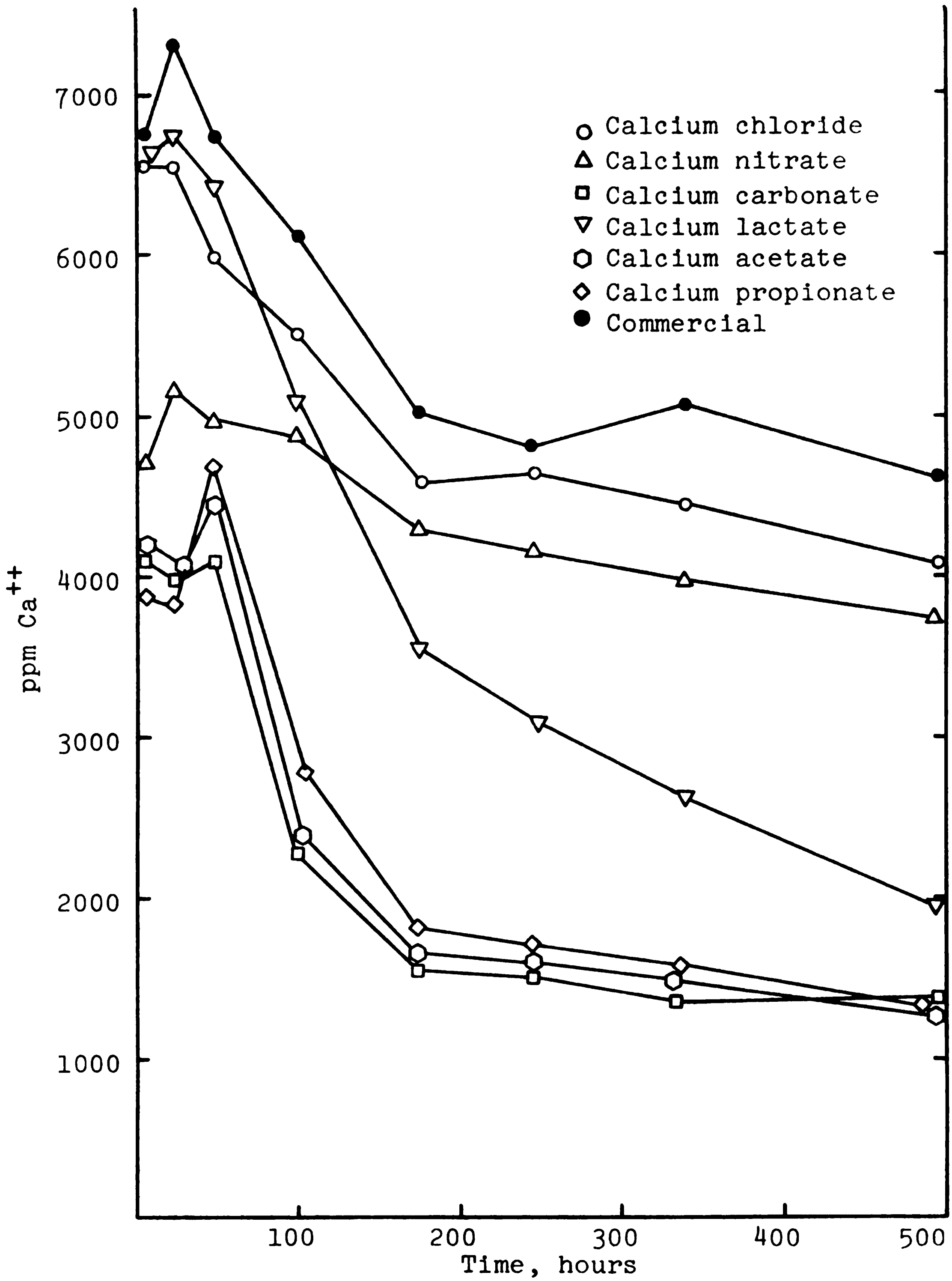

Figure 7. Change in Brine Calcium Concentration During Brine Curing (7500 ppm initial calcium).

in calcium concentration after bleaching, except for calcium lactate. Figure 7 shows the brine calcium depletion during bleaching. Calcium carbonate, propionate and acetate had almost identical curves. Calcium lactate depletion was less probably because the precipitation of calcium citrate was slower. Calcium nitrate, chloride and the commercial sample showed similar calcium depletion.

Based on these figures it can be concluded that the calcium absorption by the cherry fruit is dependent on a concentration gradient between the brine and the fruit. Treatments which precipitated and showed reduced brine calcium concentrations demonstrated a corresponding reduction in cherry calcium concentration. There was no difference in the behavior of calcium chloride as compared with the rest of the treatments studied.

Texture Evaluation

The primary function of calcium in the brine solution is to firm the fruit. The most logical means of evaluation of calcium effectiveness is the measurement of fruit firmness.

A comparison between the data obtained using the Chatillon and Instron instruments with the 1.6 mm tip is shown in Table 5. The values obtained with the Instron were higher than those obtained with the Chatillon. The standard deviation of the manual Chatillon test was less than that obtained for the Instron. The higher standard deviation for the Instron data

Table 5. Manual versus Mechanical Means of Texture Evaluation

Variety	Puncture Force (grams)	Standard Deviation*
	CHATILLON (manual)	
Napoleon	233.41	27.48
Winsdor	189.12	23.28
	INSTRON (mechanical)	
Napoleon	253.45	38.31
Windsor	222.18	32.18

* Average of 55 samples containing observations per sample.

was probably related to the greater sensitivity of the Instron and to the use of pitted cherries instead of unpitted fruit. The Instron detected one gram differences while the Chatillon recorded only ten gram differences. Szczesniak et al. (1972) reported a similar behavior when testing cucumbers on both the manual Magness Taylor pressure tester and the Instron. The standard deviation for both methods was higher for Napoleon cherries than for the Windsor variety.

The data obtained using the Allo-Kramer Shear Press with the standard shear compression cell at 32 cm/min. and the Chatillon instrument generally gave higher F statistics for the shear press data indicating higher significant differences for all data than obtained by the Chatillon method (Table 6).

The shear press data obtained using the Instron at 20 cm/min. and the Allo-Kramer Shear Press at 20 cm/min. and

Table 6. Analysis of Variance of Chatillon Puncture Force and Shear Press Force. 1974 data.

Source	d.f.	F-Statistic Chatillon	F-Statistic Shear Press
Napoleon			
Calcium salt	8	8.42 ***	13.56 ***
Harvest date	2	7.83 **	68.89 ***
Windsor			
Calcium salt	8	27.38 ***	34.10 ***
Harvest date	2	123.96 ***	48.48 ***

** Significant at the 0.01 level.
*** Significant at the 0.001 level.

32 cm/min. are presented in Table 7. The rate of downward travel had little effect on the force measured by the Allo-Kramer Shear Press. The values obtained with the Instron were about 6% higher than those obtained for the Allo-Kramer.

The curves obtained for Napoleon and Windsor varieties showed differences in configuration (Figure 1). The higher peak for Napoleon samples was typically the broad peak associated with compression whereas for the Windsor samples the highest peak was the secondary sharp peak associated with the shearing.

Szczesiak et al. (1974) reported that products with a distinct skin typically exhibit two individual peaks when tested in a similar type shear compression cell, due to the

Table 7. Effect of the Sensing Instrument on the Firmness Values of Cherries Using the Standard Shear Compression Cell. Instron Testing Machine vs. Allo-Kramer Shear Press.

Treatment[a]	Instron (20 cm/min)	Shear Press (20 cm/min)	Shear Press (31.9 cm/min)
1	125.3	109.3	121.8
2	137.4	126.1	126.3
3	131.7	119.7	118.6
4	113.7	114.3	117.0
5	123.7	111.6	112.7
6	118.3	113.4	114.3
7	98.0	92.5	92.2
8	119.3	107.0	113.6
9	120.3	117.0	115.9
10	120.7	109.8	110.6
11	120.0	112.9	108.4
12	113.0	112.0	111.1
13	115.3	111.4	107.3
Mean	119.7	112.1	113.1

[a] Selected samples of Napoleon variety from 1975.

nature of the skin and the pulp of a product. Typically, the skin is tougher than the pulp and will shear upon force but not compress. The shearing action typified by a very sharp peak indicated great force, but for only a short time. The pump of a product such as cherries is usually firm but compressible with little resistance to shear. This results in a broad, flat, peaked curve. Apparently brined cherries exhibit this phenomenon. Windsor cherries showed a sharp peak about equal to that of Napoleon cherries, but the broad peak was much lower in magnitude. This indicated that the pulp of Windsor cherries was softer than Napoleons while the skin was equal.

Table 8 includes the analyzis of variance for the primary, secondary and maximum peak force data. Although the theory is sound, none of the measurements are very sensitive to changes in firmness and do not support the theory of pulp and skin effect on peak configuration.

Table 8 also includes the analysis of variance for total work force exerted on the sample. The work required to masticate a sample would indicate which samples demonstrated the greatest resistance to physical degradation. Samples that were generally more firm would tend to give higher values. Although this is generally true this type of measurement is not very sensitive to true changes in firmness.

Table 8. Analysis of Variance of all Textural Parameters in 1975.

NAPOLEON

Source	d.f.	F STATISTIC I[1]	II	III	IV	V	VI
Calcium level	2	5.37 ***	.798 ns	.193 ns	.246 ns	1.87 ns	.512 ns
Calcium treatment	5	28.74 ***	12.13 ***	2.65 *	5.79 ***	.861 ns	4.57 ***
Interaction	10	2.24 *	2.02 ns	1.08 ns	1.23 ns	1.52 ns	1.20 ns

WINDSOR

Source	d.f.	F STATISTIC I	II	III	IV	V	VI
Calcium level	2	3.65 *	1.72 ns	1.43 ns	.943 ns	3.59 *	3.59 *
Calcium treatment	5	47.23 ***	29.54 ***	5.07 ***	5.32 ***	9.04 ***	9.04 ***
Interaction	10	1.22 ns	1.72 ns	.368 ns	.261 ns	1.23 ns	1.23 ns

[1] I: Chatillon puncture force; II: Instron puncture force; III: Instron work; IV: Instron primary peak force; V: Instron secondary peak force; VI: Instron maximum peak force.

* Significant at 5% level.
** Significant at 1% level.
*** Significant at 0.1% level.

Effect of Calcium on Texture

The firming of the fruit is related to the reaction between calcium and pectin. Maximum fruit firmness will occur when the pectin has been saturated with calcium. Additional calcium will not increase firmness. The calcium levels used in this study were within the ranges used in the industry.

In 1974, texture of brined cherries was evaluated using a Chatillon push gauge and an Allo-Kramer Shear Press. 1974 data are shown in Tables 9 and 10 for Napoleon and Windsor varieties, respectively. Duncan's Multiple Range Test was used to calculate significant differences between means at the 5% level. Several of the calcium concentrations in Table 9 were significantly different. However, the control and alum treatments, which had no calcium added, except that present in water, differed significantly in firmness from all other treatments when evaluated by the Chatillon. The Shear Press was able to detect significant differences showing that as calcium concentration increased so did firmness. Table 10 shows a similar trend for Windsor cherries. Because of precipitation in calcium oxide and calcium acetate the calcium concentrations were lower, with firmness also lower, though not always significant.

Correlation analysis is a better way to evaluate the relationship of different parameters. Correlation analysis will statistically evaluate the effect of one parameter on another. In this case the calcium concentration is the

Table 9. Effect of Calcium on Firmness of Napoleon Cherries in 1974.

Treatment	Calcium Concentration (ppm)		Chatillon Punch Force (grams)		Shear Press Force (kg/100g)	
Control	260	a+	151.5	a	95.8	a
Alum	260	a	173.4	a	113.8	b
Calcium acetate*	1045	b	221.1	b	131.8	c
Calcium Oxide*	1048	b	225.8	b	136.3	cd
Light brine	2411	c	223.6	b	143.9	cd
Calcium gluconate	2523	c	238.0	b	150.0	d
Dark brine	2739	d	245.9	b	148.6	d
Calcium chloride	2755	d	248.6	b	148.3	d
Calcium nitrate	2839	d	231.6	b	145.6	cd

+ Equal letters denote no significant difference at the 5% level.

* Samples with precipitate.

Table 10. Effect of Calcium on Firmness of Windsor Cherries in 1974.

Treatment	Calcium Concentration (ppm)		Chatillon Punch Force (grams)		Shear Press Force (kgs/100g)	
Control	260	a+	134.7	a	79.5	a
Alum	260	a	145.5	a	86.5	a
Calcium acetate*	1040	b	193.1	b	111.7	b
Calcium oxide*	1611	c	187.0	bc	114.7	bc
Light brine	2402	d	215.0	d	129.5	d
Calcium gluconate	2757	e	201.6	d	121.7	d
Dark brine	2861	e	220.4	d	128.6	d
Calcium chloride	2881	e	214.6	d	129.4	d
Calcium nitrate	2927	e	206.8	cd	127.0	d

+ Equal letters denote no significant difference at the 5% level.

* Treatments which formed precipitate.

independent variable and textural parameters are the dependent variables. A high correlation coefficient indicates a strong dependence of firmness on calcium concentration. Table 11 is a listing of important simple correlation coefficients for the 1974 study. Chatillon puncture force and shear press are correlated best to calcium concentrations. As a rule of thumb, a correlation should be above 0.75 to be significant. Those in Table 11 are below that but do indicate a trend of increased firmness with increased calcium.

In 1975, three levels of calcium were studied to obtain more information about effect of calcium concentration on cherry firmness. Tables 12 and 13 are listings of such data for Napoleon and Windsor varieties, respectively. Due to precipitation of some treatments the final calcium concentration in the brine was lower than others. However, the firmness of cherries corresponding to those precipitated treatments was not lower. In several cases high concentration of calcium resulted in greater firmness but these variations were within experimental error. The firmness of all treatments, regardless of concentration, was almost equal. This would indicate that even at the 0.25% brine calcium level maximum calcium pectate has been formed and that additional calcium did not yield additional firming. Table 14 is a tabulation of the change in firmness of Napoleon cherries during brine curing. Table 15 shows the change in cherry fiber calcium during brine curing. Comparison of these two tables showed that maximum firmness of the fruit was reached

Table 11. Simple Correlation, 1974.

Parameter	Calcium	Chatillon	Shear Press
	NAPOLEON		
Calcium	1.0		
Chatillon	.613	1.0	
Shear Press	.569	.713	1.0
Sulfur dioxide	.019	.021	.179
pH	-.350	-.293	-.355
Soluble solids	.480	.320	.317
	WINDSOR		
Calcium	1.0		
Chatillon	.594	1.0	
Shear Press	.756	.852	1.0
Sulfur dioxide	-.124	-.029	-.080
pH	-.096	-.005	-.121
Soluble solids	.654	.446	.515

Table 12. Brine Calcium Concentration vs. Firmness of Napoleon Cherries, 1975.

Treatment	Calcium %	Initial Calcium Conc. (ppm)	Final Calcium Conc. (ppm)	Chatillon Punch Force (grams)	Std. Dev.	Instron Punch Force (grams)	Std. Dev.	Instron Shear Force (kgs/100g)
Calcium chloride	0.25	2345	1792	255	29.4	268	35.8	125.9
	0.50	4085	3025	284	30.0	295	38.8	131.4
	0.75	6781	4359	267	33.2	289	43.3	133.6
Calcium nitrate	0.25	1386	1623	238	25.3	280	49.5	124.0
	0.50	3326	2931	263	31.2	272	39.9	122.6
	0.75	4955	4045	246	30.5	267	33.0	119.9
Calcium carbonate	0.25	2597	1643	220	29.0	229	39.6	111.5
	0.50*	4772	1129	248	27.5	259	34.4	119.3
	0.75*	4413	1044	220	27.3	236	39.5	116.4
Calcium acetate	0.25	2690	1707	218	18.5	251	45.8	121.6
	0.50*	4786	1153	210	24.0	228	42.6	117.3
	0.75*	4448	1145	190	31.3	200	40.0	102.5
Calcium lactate	0.25	2711	1692	231	23.0	242	42.0	119.0
	0.50*	5009	1867	225	28.0	248	37.4	119.2
	0.75*	7079	1703	228	29.6	255	42.8	123.1
Calcium propionate	0.25	2758	1723	223	26.1	252	35.8	120.3
	0.50*	4839	1148	215	24.9	240	27.8	120.8
	0.75*	4523	1112	217	23.6	248	36.2	118.9
Commercial	-	6750	4284	251	27.1	275	31.8	128.1

* Denotes treatments which had precipitate.

Table 13. Brine Calcium Concentration vs. Firmness of Windsor Cherries, 1975.

Treatment	Calcium %	Initial Calcium Conc. (ppm)	Final Calcium Conc. (ppm)	Chatillon Punch Force (grams)	Std. Dev.	Instron Punch Force (grams)	Std. Dev.	Instron Shear Force (kgs/100g)
Calcium chloride	0.25	2479	1640	225	24.6	246	36.2	112.5
	0.50	4152	2927	239	27.6	246	36.6	110.7
	0.75	6788	4313	221	21.2	253	33.1	107.0
Calcium nitrate	0.25	1239	1588	212	26.2	245	36.8	105.0
	0.50	3804	2637	215	31.7	230	30.3	106.0
	0.75	5483	3630	216	24.5	243	32.1	102.4
Calcium carbonate	0.25	2583	1557	192	24.4	220	33.0	98.6
	0.50	4744	1024	189	22.1	223	32.6	111.5
	0.75	4104	881	168	15.6	212	30.5	105.6
Calcium acetate	0.25	2683	1598	166	26.8	220	28.7	102.2
	0.50	4965	938	172	21.2	210	28.4	103.4
	0.75	4020	945	167	21.2	206	25.6	101.3
Calcium lactate	0.25	2674	1620	171	21.4	214	31.0	104.0
	0.50	4960	1861	175	26.5	212	34.2	104.4
	0.75	7024	1636	172	22.6	214	28.2	102.4
Calcium propionate	0.25	2719	1644	180	20.5	205	35.2	95.5
	0.50	4752	1808	168	17.8	210	24.6	99.1
	0.75	4231	966	157	22.0	186	33.0	87.9
Commercial	-	6750	4071	196	24.5	227	30.5	104.6

* Denotes treatments which had precipitate.

Table 14. Change in Napoleon Cherry Firmness During Brine Curing

Treatment	Calcium %	Chatillon Punch Force, grams — Time, hours						
		24	48	102	176	244	334	506
Calcium chloride	0.25	187	177	215	219	233	222	241
	0.50	165	184	212	195	217	259	229
	0.75	181	202	215	229	219	227	225
Calcium nitrate	0.25	178	171	188	208	208	225	225
	0.50	187	184	204	215	209	212	239
	0.75	158	168	209	205	209	234	235
Calcium carbonate	0.25	169	173	188	186	201	188	203
	0.50*	157	170	203	185	215	206	218
	0.75*	146	173	194	195	211	227	219
Calcium acetate	0.25	165	178	182	209	224	200	218
	0.50*	181	190	192	210	222	216	252
	0.75*	197	189	204	198	205	205	209
Calcium lactate	0.25	139	198	169	188	204	204	199
	0.50*	155	180	211	204	207	209	227
	0.75*	163	192	204	234	234	198	244
Calcium propionate	0.25	168	184	173	208	221	201	230
	0.50*	170	187	187	207	241	214	248
	0.75*	168	221	233	204	196	201	230
Commercial	-	161	216	224	209	265	232	262

* Denotes treatments which had precipitate.

Table 15. Change in Cherry Fiber Calcium Concentration During Brine Curing of Napoleon Cherries, 1975.

Treatment	Calcium %	Calcium Concentration, ppm						
		Time, hours						
		24	48	102	176	244	334	506
Calcium chloride	0.25	370	427	646	1120	1542	1094	1620
	0.50	792	722	1556	1750	2360	2094	2979
	0.75	1120	990	2108	3710	3177	2858	4010
Calcium nitrate	0.25	328	396	783	1279	1609	1120	1752
	0.50	641	567	1185	2245	2438	1958	2766
	0.75	1010	1391	2628	3464	2771	2870	3583
Calcium carbonate	0.25	510	388	1005	1281	1292	946	1568
	0.50*	589	667	1052	1458	1078	1245	1531
	0.75*	495	479	1250	1594	1156	1943	1391
Calcium acetate	0.25	396	420	911	1000	982	1672	1573
	0.50*	474	443	1089	1474	1141	1523	1443
	0.75*	377	738	1029	1609	1284	1536	1349
Calcium lactate	0.25	521	365	792	1222	1010	1479	1740
	0.50*	505	479	1234	1818	1677	2375	1703
	0.75*	750	708	1425	2130	1849	1510	1781
Calcium propionate	0.25	474	391	856	786	911	1635	1542
	0.50*	589	641	995	1021	1401	2406	1698
	0.75*	891	698	1292	1578	1276	1740	1451
Commercial	-	1260	1208	2469	2875	2839	4427	4536

* Denotes treatments which had precipitate.

approximately at the same time that the calcium level in the fruit reached 1000 ppm. There was considerable variation between treatments and individual periods but the trend was apparent. Maximum firmness of the fruit was reached when the calcium concentration was relatively low.

Calcium analysis of the final dyed and sugared maraschino cherry indicated that the concentration was much greater than would be expected if leaching were the only factor (Table 16). Removal of sulfur dioxide during freshening in preparation was approximately 97%. If calcium followed the same pattern, the concentration in the final product would range from about 50 to 120 ppm, depending on initial calcium concentration. Determined values were significantly greater indicating calcium

Table 16. Calcium Concentration in Finished Maraschino Cherries.

Treatment	Calcium %	Final Cherry Concentration (ppm)	Finished Cherry Concentration (ppm)	Predicted Cherry Concentration (ppm)
Calcium chloride	0.25	1536	569	46.0
	0.50	2938	627	88.0
	0.75	4078	662	122.0
Calcium nitrate	0.25	1609	572	48.2
	0.50	2734	669	82.0
	0.75	3724	707	112.0

binding by the pectin compounds. If both bound and free calcium were combined together, the increase in total calcium in the final product, as initial concentration was increased, can be explained by the higher concentration of free calcium due to higher initial levels of calcium. It can be concluded that the quantity of calcium bound by pectin was equal at all three calcium levels and that even at the lowest calcium level the pectin was saturated with calcium. From the data the saturation level of pectin would be approximately 500 ppm calcium.

Tables 17 and 18 show correlation coefficients for various parameters measured in 1975. The Chatillon and Instron punch test correlated best with calcium concentration but not enough to make positive conclusions. However, several points can be made from this information. The manual Chatillon instrument showed the best correlation to calcium. Chatillon and Instron punch correlated very well to each other indicating that the methods are related to each other statistically. This has practical application in determining the method of firmness measurement. Not only does the Chatillon instrument yield the most significant data; it is the least costly of all the instruments used.

Nitrate Determination

Calcium nitrate was found to be a very desirable firming agent. It has excellent solubility and required small quantities of citric acid to acidify. However, the levels of

Table 17. Correlation Coefficients for Napoleon Samples in 1975.

	Calcium	Chatillon	INSTRON			
			Punch	Work	Primary	Secondary
Calcium	1.0					
Chatillon	.651	1.0				
Instron punch	.568	.851	1.0			
Instron work	.358	.637	.804	1.0		
Instron primary	.477	.762	.868	.934	1.0	
Instron secondary	.169	.468	.638	.844	.716	1.0
Instron maximum	.423	.727	.821	.918	.954	.825
pH	.317	.463	.430	.224	.358	.011
Soluble solids	-.464	-.666	-.561	-.250	-.386	-.084
Sulfur dioxide	.018	.101	.011	.087	.162	.009

Table 18. Correlation Coefficients for Windsor Cherries in 1975.

	Calcium	Chatillon	INSTRON			
			Punch	Work	Primary	Secondary
Calcium	1.0					
Chatillon	.679	1.0				
Instron punch	.662	.858	1.0			
Instron work	.211	.408	.520	1.0		
Instron primary	.360	.577	.660	.840	1.0	
Instron secondary	.234	.500	.585	.740	.683	1.0
Instron maximum	.234	.500	.585	.740	.683	.200
pH	.295	.443	.440	.181	.251	-.539
Soluble solids	-.524	-.789	-.789	-.428	-.502	.160
Sulfur dioxide	.184	.289	.276	.246	.382	-.122

nitrate must be monitored to avoid nitrate toxicity. It is not clear at this time what nitrate levels must be met in the final product. Current drinking water standards are 45 parts per million (ppm) nitrate. Cured meat products are allowed up to 150 ppm nitrate. A diet of 5 mg/kg body weight of nitrate and up to 300 mg/day nitrate was found to be non-toxic to infants (Committee on Food Protection). The average intake of nitrates by adults is predicted to be 86 mg/day from vegetable sources.

During freshening of the brined cherries in preparation for dyeing, samples were collected for sulfur dioxide analysis. It was felt that sulfur dioxide would be removed from the fruit at the same rate as nitrate. Because sulfur dioxide is much easier to measure it was monitored closely. A removal of an average of 97% of sulfur dioxide was accomplished in 5 days of water freshening. Nitrate concentration in the final dyed product could be calculated theoretically based on the following: nitrate concentration in the strong brine, a 97% removal, and 50% dilution by sirup addition during finishing. Theoretical nitrate concentrations were calculated for the 0.25%, 0.50% and 0.75% treatments. They were determined to be 75 ppm, 135 ppm, and 185 ppm nitrate in the finished product, respectively.

To confirm these calculations, several selected samples were analyzed for nitrate using an Orion nitrate probe. Interference was found due to nitrite produced by reduction of nitrate by sulfur dioxide. Interference was prevented by the addition of 0.5 g. of sulfanilamide. Levels in the 0.25% and 0.50% treatments were determined to be approximately 85 ppm and 122 ppm, respectively. These values are relatively close to theoretical calculations. Tests were also performed on samples with no nitrate additions. Residual levels from the water used were 25 ppm.

Levels of nitrate in cherries firmed with calcium nitrate were low enough to cause no problems with toxicity. At the present there are no standards established for nitrates in fruits and vegetables.

Sulfur Dioxide

In this study the effect of sulfur dioxide reported by Van Buren (1967) has not been significant because the levels of sulfur dioxide used were not varied. Correlation analysis indicated that sulfur dioxide concentrations had little effect on any other parameter (Tables 17 & 18). Table 19 shows that sulfur dioxide levels in the final brines were lower for Windsor cherries than Napoleon. This could be due to the greater concentration of anthocyanin in the Windsor fruit and more binding of the sulfur dioxide as the bleaching process progressed.

Table 19. Soluble Solids, pH and Sulfur Dioxide Composition of Cured Brines, 1975.

			NAPOLEON			WINDSOR		
Treatment	Calcium %	Initial Soluble Solids	Final Soluble Solids %	pH	Sulfur Dioxide ppm	Final Soluble Solids %	pH	Sulfur Dioxide ppm
Calcium chloride	0.25	2.4	9.53	3.49	5120	9.10	3.47	4690
	0.50	3.0	9.93	3.42	4823	9.67	3.46	4550
	0.75	3.8	10.53	3.37	4883	10.20	3.44	4443
Calcium nitrate	0.25	2.8	9.70	3.44	4815	9.27	3.51	4397
	0.50	2.8	10.03	3.32	4502	9.40	3.39	4062
	0.75	3.3	10.40	3.33	3865	9.53	3.23	3627
Calcium carbonate	0.25	5.0	10.70	3.49	4547	10.33	3.55	4353
	0.50	5.7	10.80	3.33	4115	10.53	3.29	4030
	0.75	6.3	11.27	3.20	4067	10.90	3.22	3532
Calcium acetate	0.25	5.5	11.20	3.40	4878	10.47	3.46	4623
	0.50	6.5	11.33	3.13	4898	10.73	3.25	3890
	0.75	7.9	11.73	3.08	4357	11.60	3.11	3610
Calcium lactate	0.25	5.3	10.83	3.41	5377	10.37	3.43	4492
	0.50	6.3	10.37	3.29	4918	10.87	3.34	4100
	0.75	7.3	10.67	3.21	4760	11.27	3.20	4182
Calcium propionate	0.25	5.7	11.70	3.47	4437	10.93	3.51	3983
	0.50	6.8	11.10	3.26	4137	11.60	3.23	3985
	0.75	8.4	11.77	3.08	4502	12.50	3.10	4075
Commercial	-	2.2	10.10	3.20	5020	10.23	3.17	4623

Soluble Solids and pH

Soluble solids and pH data tended to have little bearing on the objective of this study (Table 19). Higher soluble solids were generally found with treatments requiring large quantities of calcium salt or citric acid. Large negative correlations were found between calcium concentration and soluble solids.

The equilbrium of soluble solids between the fruit and the brine is shown in Figure 8. The rate of equilibrium was similar to that of calcium. This would be expected if both calcium and soluble solids migration was due primarily to concentration gradients.

pH data were available but within ranges commonly used commercially. Low correlations showed that changes in pH have little effect on texture of brined cherries within certain limits.

Maturity

In the 1974 study, cherries were harvested on different dates in order to obtain cherries at different stages of maturity. One means of determining maturity is by the firmness of the cherry. As the cherry matures the protopectin structure is broken down and the pectinic acid and pectic acid concentration is increased (Van Buren, 1967). This series of reactions result in the softening of the cherry. Another means of evaluating maturity is by the sugar

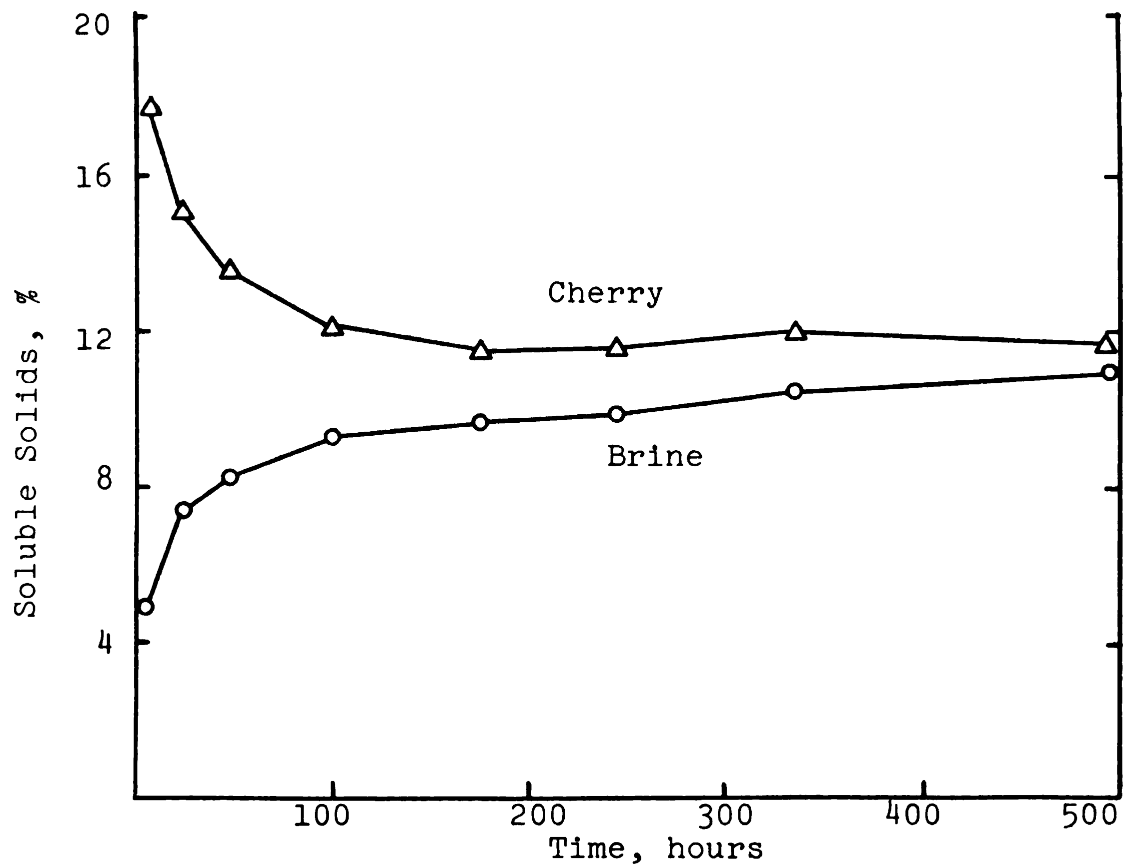

Figure 8. Change in Soluble Solids During Brine Curing of Napoleon Cherries.

concentration of the fruit. As fruit matures the typical reaction is the hydrolysis of insoluble starch compounds to soluble sugar. In the cherry it is typical for the organic acid content to decrease with maturity (Hulme and Wooltoton, 1967). These three indices of maturity are listed in Table 20.

Table 20. Maturity of Fresh Cherries

Harvest dates	Napoleon			Windsor		
	7/17	7/18	7/25	7/17	7/18	7/25
pH	3.4	3.5	3.7	3.55	3.6	3.7
Soluble solids, %	15.65	12.8	13.4	12.45	11.8	14.7
Chatillon force, g.	473.0	371.0	418.5	540.0	293.5	236.75

Chatillon puncture measurements generally decreased as the season progressed. pH increased slightly but soluble solids data were inconclusive.

Firmness of brined cherries was consistently lower for those of later harvest dates as measured by both Chatillon and Shear Press (Table 21).

Color of cherries is also an excellent means of maturity evaluation. Napoleon cherries are typically a light yellow. As they mature, the cheeks of the cherry turn pink and then the entire cherry will turn a light red. Windsor cherries progress from a red, to a deep red, to almost black.

Table 21. Effect of Maturity on Firmness of Brined Cherries, 1974.

Harvest date	Napoleon		Windsor	
	Chatillon Force	Shear Press Force	Chatillon Force	Shear Press Force
	g	kgs/100g	g	kgs/100g
7/17	236.8	152.1	230.9	121.3
7/18	216.4	145.4	186.5	122.3
7/25	200.0	107.2	155.5	99.2

Effect of Brining Solutions on Bleached Cherry Color

The tristimulus color values of the bleached cherries are represented in Table 22. L values represent lightness of color, the higher the value the better. Positive a values represent redness, negative a values indicate greenness. Positive b values represent yellowness, negative b values represent blueness. The data indicated that the reuse of dark brine without decolorization was questionable. The light brine could be used at least once without decolorization.

Table 22. Effect of Brine on Color of Cherries, 1974.

Treatment	L-value		A-value	B-value	
	NAPOLEON				
Dark brine	52.81	a*	.195	30.2	ab*
Calcium nitrate	53.6	b	-.03	30.05	a
Calcium chloride	53.8	bc	-.386	30.68	bcd
Calcium gluconate	54.3	bcd	-.54	30.63	abcd
Control	54.26	bcd	-.308	30.86	cd
Light brine	54.27	bcd	-.16	31.0	cd
Calcium acetate	54.78	bcd	-.54	30.14	ab
Alum	54.96	cd	-.468	31.23	d
	WINDSOR				
Dark brine	46.32	a	3.577	26.49	a
Light brine	48.04	ab	3.86	27.31	b
Calcium chloride	49.12	b	3.317	27.31	bc
Control	49.17	b	3.023	27.77	bc
Alum	49.39	bc	3.975	28.04	c
Calcium gluconate	49.48	bc	3.010	27.27	b
Calcium nitrate	49.8	bc	3.408	27.74	bc
Calcium oxide	50.59	cd	3.072	27.48	bc

* Equal letters denote no significant difference at the 5% level.

SUMMARY

Calcium chloride has been the only salt used in dry mix brines since its development for orchard use. There is no evidence to indicate that calcium chloride has any special properties associated with firming. Its solubility, availability, low cost, ease of handling and low requirement of citric acid for acidification has made it the accepted salt for orchard brining. However, it increases the brine disposal problem because of the chloride ion.

Since calcium is the active ion in the firming reaction, other calcium compounds such as calcium acetate, gluconate, lactate, propionate, carbonate, oxide and nitrate and alum were used to determine their effectiveness in firming brined cherries.

Although calcium carbonate, oxide and the organic salts could be used in the dry mixes as suitable sources of calcium for firming, they all had disadvantages of requiring large amounts of salt to obtain desired levels of calcium, and citric acid for acidification. The large citric acid requirements for carbonate, oxide, acetate, lactate and propionate resulted in the precipitation of calcium as calcium citrate at the higher levels of calcium.

It has been shown that calcium concentrations above 1000 ppm do not yield a significant increase in firmness.

Even at the lowest calcium levels used in this study, maximum firmness was obtained. Because of this even the salts which precipitated at the higher levels could still be considered as a possible alternative if used at concentrations below 0.25%.

Alum was used unsuccessfully. Used alone it does not firm cherries well. It has been used successfully by other workers in conjuction with a calcium salt.

Calcium nitrate was the best substitute for calcium chloride. It does not precipitate, and acid requirements are equal to those of calcium chloride. In addition, the nitrate present could be an asset as a nutrient if the brine were irrigated onto orchards. Nitrate levels in the final product are much below toxic levels.

A single punch type instrument was found to be most suitable for texture evaluation. Both the Instron and Chatillon are suitable for research purposes. The Chatillon could be used in field work because of its low cost and portability.

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A P P E N D I X

Table 23. Change in Brine Calcium Concentration During Brine Curing of Napoleon Cherries.

Treatment	Calcium %	Calcium Concentration, ppm — Time, hours: 0	24	48	102	176	244	334	506
Calcium chloride	0.25	2708	2547	2469	2291	1833	1833	1771	1536
	0.50	4633	4531	4173	3969	2943	3229	3156	2938
	0.75	6562	6552	5973	5523	4593	4656	4438	4078
Calcium nitrate	0.25	1354	2486	2486	2404	1856	1833	1771	1609
	0.50	3146	4460	4134	3938	3229	3063	2875	2734
	0.75	4688	5155	4971	4859	4292	4142	3948	3724
Calcium carbonate	0.25	2569	2557	2508	2240	1962	1833	1802	1552
	0.50*	4646	4419	4224	3048	2146	1885	1615	1375
	0.75*	4094	3989	4091	2280	1552	1521	1354	1281
Calcium acetate	0.25	2688	2578	2936	2598	1979	1885	1740	1547
	0.50*	3385	4040	4345	2711	1896	1667	1510	1219
	0.75*	4146	3977	4439	2332	1625	1521	1490	1245
Calcium lactate	0.25	2646	2531	2659	2547	1983	1846	1771	1573
	0.50*	4965	4803	4726	4214	3271	2996	2708	2292
	0.75*	6535	6741	6403	5073	3542	3083	2625	1953
Calcium propionate	0.25	2729	2663	2823	2690	2121	1958	1781	1583
	0.50*	3804	4365	4531	3416	2156	1896	1750	1370
	0.75*	3896	3825	4695	2772	1808	1698	1583	1229
Commercial	-	6750	7303	6730	6113	5004	4813	5083	4625

* Denotes treatments which had precipitate.

Table 24. Instron Texture Evaluation Using the Standard Shear Compression Cell, 1975.

	Calcium	Napoleon			Windsor		
	%	Primary (kgs)	Secondary (kgs)	Work	Primary (kgs)	Secondary (kgs)	Work
Calcium chloride	0.25	125.9	113.2	274.9	92.0	112.5	220.6
	0.50	131.4	118.8	277.2	90.5	110.7	215.4
	0.75	133.6	120.1	289.1	90.1	107.0	209.6
Calcium nitrate	0.25	123.4	115.9	270.2	90.3	105.0	211.9
	0.50	122.6	115.5	271.8	87.4	106.0	217.3
	0.75	119.9	116.1	270.7	84.4	102.4	200.0
Calcium carbonate	0.25	108.5	109.4	244.4	83.5	98.7	197.2
	0.50*	117.6	118.8	271.4	83.4	111.5	206.7
	0.75*	111.7	116.2	254.5	82.9	106.5	203.0
Calcium acetate	0.25	121.6	117.2	269.7	85.4	102.2	209.4
	0.50*	109.2	117.3	254.2	84.4	103.4	206.0
	0.75*	100.9	100.4	230.2	83.0	101.3	203.9
Calcium lactate	0.25	119.0	111.2	264.9	86.4	104.0	216.7
	0.50*	115.9	119.2	272.5	88.2	104.4	214.6
	0.75*	123.1	119.1	278.2	87.2	102.4	212.7
Calcium propionate	0.25	120.1	115.3	275.0	80.0	95.5	191.1
	0.50*	116.4	119.1	264.9	82.7	99.1	194.9
	0.75*	116.9	118.0	264.9	77.9	87.9	186.8
Commercial	-	128.1	128.2	299.3	87.0	104.6	220.6

* Denotes treatments which had precipitate.

Table 25. Pitting Loss, 1975.

Treatment	Calcium %	Napoleon Pit Loss %	Windsor Pit Loss %
Calcium chloride	0.25	12.63	13.01
	0.50	11.65	12.23
	0.75	11.70	13.70
Calcium nitrate	0.25	11.43	13.05
	0.50	11.45	12.65
	0.75	11.21	13.21
Calcium carbonate	0.25	10.95	12.98
	0.50	11.44	11.70
	0.75	11.15	12.26
Calcium acetate	0.25	10.77	12.52
	0.50	10.69	11.85
	0.75	11.59	12.70
Calcium lactate	0.25	11.45	12.45
	0.50	10.98	12.01
	0.75	12.08	12.32
Calcium propionate	0.25	11.27	12.48
	0.50	12.31	12.46
	0.75	11.14	12.32
Commercial	-	10.12	11.97