

A STUDY OF THE EFFECT OF BREAK-POINT  
CHLORINATION ON THE QUALITY OF  
FROZEN APPLES

by

MAHMOUD ERFAN

A THESIS

submitted to

OREGON STATE COLLEGE

in partial fulfillment of  
the requirements for the  
degree of

MASTER OF SCIENCE

June 1949

APPROVED:

---

Professor of Food Technology

In Charge of Major

---

Head of Department of Food Technology

---

Chairman of School Graduate Committee

---

Dean of Graduate School

## ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. Thomas B. Niven under whose direction and supervision this work was undertaken; to Dr. Oliver J. Worthington for his advice, and to Dr. Earl Litwiller and Professor Thomas Onsdorff for their help.

Acknowledgment is also due Mrs. Betty Sweeny for setting up and supervising the taste-tests.

## TABLE OF CONTENTS

Chapter	Page
I. Introduction.....	1
II. Review of Literature.....	5
Historical.....	5
Efficiency of chlorine action.....	6
Mode of action of chlorine.....	8
Break-point chlorination.....	10
Reactions of break-point chlorination.....	11
Germicidal efficiency of break-point chlorination.....	15
Effect on taste and odor.....	16
Chlorination in the food plants.....	18
III. Experimental.....	23
A. Analytical Methods	
Determination of available chlorine.....	23
Determination of break-point in tap water.....	26
Ascorbic acid determination.....	28
Effect of residual chlorine on ascorbic acid.....	30
B. Preparation of Samples	
Procedure for apple slices.....	33
Without the addition of sugar or ascorbic acid.....	33
Without the addition of ascorbic acid, sugar added.....	35
With the addition of ascorbic acid and sirup.....	39
Procedure for apple-sauce.....	41
Without the addition of sugar or ascorbic acid.....	41
With the addition of ascorbic acid, no sugar.....	44
With the addition of ascorbic acid and dry sugar.....	48

## TABLE OF CONTENTS--Continued

Chapter	Page
IV. Discussion of Results.....	54
V. Summary and Conclusion.....	59
Bibliography.....	61

\*\*\*\*\*

\*\*

## LIST OF TABLES

Table	Page
I. Determination of break-point in tap water	28
II. Effect of residual chlorine on ascorbic acid in aqueous solution.....	32
III. Effect of residual chlorine on ascorbic acid in a 35 degree Brix sirup.....	32
IV. Effect of chlorine on the quality of apple slices. No sugar or ascorbic acid added....	35
V. Effect of chlorine on the quality of apple slices. No ascorbic acid added. Dry sugar added.....	36
VI. Effect of chlorine on the quality of apple slices. No ascorbic acid added. Dry sugar added.....	37
VII. Effect of chlorine on the quality of apple slices. No ascorbic acid added. Dry sugar added.....	37
VIII. Effect of chlorine on the flavor and texture of apple slices. Ascorbic acid and sirup added.....	40
IX. Ascorbic acid determination in apple slices prepared with chlorinated water.....	41
X. Effect of chlorine on the quality of apple-sauce. No sugar or ascorbic acid added....	44
XI. Effect of chlorine on the quality of apple-sauce. Ascorbic acid added. No sugar.....	45
XII. Ascorbic acid determination in apple-sauce prepared with chlorinated water.....	46
XIII. Effect of chlorine on the flavor and color of apple-sauce. Ascorbic acid and dry sugar added.....	49
XIV. Ascorbic acid determination in apple-sauce prepared with chlorinated water.....	51

LIST OF TABLES--Continued

Table		Page
XV.	Effect of chlorine on the flavor and color of apple-sauce. Ascorbic acid and dry sugar added.....	51
XVI.	Ascorbic acid determination in apple-sauce prepared with chlorinated water.....	53

## LIST OF FIGURES

Figure		Page
I.	Ortho-tolidine color development in break-point chlorination of tap water.....	29
II.	Frozen apple slices. Dry sugar added; no ascorbic acid.....	38
III.	Frozen apple slices with ascorbic acid and sirup.....	42
IV.	Frozen apple-sauce with ascorbic acid. No sugar.....	47
V.	Frozen apple-sauce with ascorbic acid and sugar.....	50
VI.	Frozen apple-sauce with ascorbic acid and sugar.....	52

A STUDY OF THE EFFECT OF BREAK-POINT CHLORINATION  
ON THE QUALITY OF FROZEN APPLES

CHAPTER I

INTRODUCTION

Chlorine is becoming indispensable for the protection of public health in water purification and in other sanitation fields. This is largely because it is a powerful germicide, non-poisonous to man when used in concentrations required to destroy pathogenic organisms ordinarily encountered in the control of water.

Other germicides will also satisfactorily destroy microscopic life, but, as Costigan (7)\* reports, "Chlorine's unique combination of availability, ease of handling, dispensing simplicity, freedom from poisonous residuals, and its specific high toxicity for most water-born organisms, makes it today's most important chemical sanitation agent."

The practices of chlorinating the water supply in the food industry to control bacterial growth, and to prevent the accumulation of odor-producing slimes, have recently received much new interest and publicity. The

---

\*Numbers in parentheses refer to bibliography.

reasons for this new interest could be summarized in the following:

1. Increased attention to food-plant sanitation by federal and state control departments.
2. Continuous use of mechanical handling equipment which require more attention and care in order to keep them clean and in a sanitary condition.
3. Urgent need by food packers to achieve and maintain the quality of their products at a high level in order to overcome the competition which exists in the food field.
4. The introduction of break-point chlorination to prevent slime-formation and the development of odors.

In the past years the use of chlorine as a sterilizing agent in the food industry has been restricted to the marginal chlorination of the cooling waters and canals. This was carried out as a measure against can-spoilage due to the entrance of contaminated waters through the double seam. Thus its use was limited to the purpose of obtaining bacteriological cleanliness, while physical cleanliness was still done by the time consuming manual removal of slime and odors through the use of water, steam, and various detergents.

Chlorination techniques however, have changed rapidly in the past few years. And out of the abundance of information and studies which were carried out regarding the application and control of chlorine, there arose gradually a new concept of chlorination known as break-point

chlorination. This process takes advantage of the fact that the production and maintenance of free available chlorine residual will produce superior bacteriological results and can secure far more reliable sanitary safety than has been hitherto attainable. Apart from having twenty to thirty times the germicidal value of combined chlorine, the residual beyond the break-point has also a much greater oxidation potential. Thus when break-point chlorination techniques were carried out on waters containing undesirable odors and flavors, it was noticed that the organic substances which caused the development of such odors were oxidized, and the water rendered palatable.

The theory of break-point chlorination is that when chlorine is added to water, it combines with the organic matter in it forming chloramines, which have odors and flavors of chlorinated water. With further addition of chlorine, until the concentration becomes high enough to oxidize the chloramines, these flavors and odors are eliminated from the water, and after all the chloramines are oxidized, additions of chlorine appear as free residual. This point, after which the free residual starts appearing, is known as the break-point.

With all these facts in mind, break-point chlorination of the entire water supply has been practiced in some canning and freezing plants. Even though the work had its limitations, the results were very encouraging.

However, because of various products and packing conditions, it is essential to have more complete data regarding the effect of chlorine on the processed foods. Each product should be studied separately in order to find out whether or not the quality of the finished product is affected in any manner, through the use of chlorine, which would render it inferior to that of the untreated product.

Because sanitation plays an important role in determining the quality of frozen foods, and the fact that residual chlorine will not be dissipated by heat treatments as they are applied in a minimal quantity, it was decided to undertake this study on frozen foods.

In choosing the product to be treated with chlorine, several factors had to be considered, namely availability, importance, and susceptibility to change in quality. Apples seemed to fit these requirements.

The objective of this study therefore, is to find out whether or not in-plant chlorination beyond the breakpoint, carried out on a laboratory scale, has any deleterious effect on the quality of frozen apple slices and applesauce, as far as the flavor, odor, color, texture, and vitamin C content are concerned.

## CHAPTER II

### REVIEW OF LITERATURE

#### Historical

The first application of chlorine as a water disinfecting agent was at Maidstone, England during the 1887 typhoid fever epidemic (27). The earliest perfected use of the process of water chlorination was at Middlekerke, Belgium in 1902.

In America, George W. Fuller experimented with hypochlorites as sterilizing agents at Louisville, Kentucky, about 1896. The first commercially successful attempt to chlorinate the water supply was made by George A. Johnson in 1908. Bleaching powder of hypochlorite was applied to the Jersey city water supply on a continuous basis at Boonton, New Jersey (13).

The elapsed fifty years are divided by Hedgepeth into five periods of progress (16).

1. 1896 to 1906. Experimental use of chlorine.
2. 1906 to 1916. The acceptance of chlorination as an integral part of water processing.
3. 1916 to 1926. The learning how period and gathering of more information.
4. 1926 to 1936. The action or application period.
5. 1936 to 1946. Period of refinement.

## Efficiency of Chlorine Action

The efficiency of chlorine action in water, particularly disinfection, or the chlorine kill, is influenced by many factors that should be studied thoroughly in order to reach the maximum chlorine kill with the minimum amount of chlorine.

Costigan (7) summarizes these factors in the following:

### Organic matter:

The quantity and type of organic matter in the water to be treated markedly affect the germicidal efficiency of chlorine. This is because of the protective action of the organic matter to the bacterial cell. Also the organic matter may react with the chlorine to form less toxic substances (19).

### Hydrogen ion concentration:

Has the greatest influence on chlorine. Hypochlorites at a low pH are quicker acting than those at high pH. Charlton and Levine (5) described pH as the most important factor in determining the efficiencies of hypochlorites. Rudolph and Levine (23) found that the concentration of undissociated hypochlorous acid at pH 8 was

approximately 20 per cent of that at pH 6, whereas at pH 10 it was but 1 per cent of that at pH 8. This suggested that the concentration of undissociated hypochlorous acid is intimately associated with the rate of disinfection by chlorine solutions.

#### Temperature:

Most organisms are more readily killed at higher temperature than at low. McCulloch and Costigan (20) found that almost twice the concentration of hypochlorite was required to kill *E. typhosa* at 20°C as at 40°C. Rudolph and Levine (23) report that in general the killing time of calcium hypochlorite on *B. metiens* was reduced from 60 to 65 per cent by a rise of 20°C, in a range from 20 to 50°C.

#### Concentration:

Concentration is certainly important, but in view of modern chlorination practice the exact effective concentration more than ever becomes one of individual determination for any given plant. McCulloch (19) states that the reason no one has presented data which show only the influence of different concentrations of chlorine upon microorganisms, is because the hydrogen ion concentrations of the disinfectant solution also are altered by any form of chlorine and even slight changes in the degree of

alkalinity exert much more influence upon the germicidal efficiency of chlorine solutions, than do rather large changes in the concentration of chlorine.

#### Turbidity:

Chlorine is effective only on naked organisms and cannot be expected to penetrate into suspended solid matter with sufficient efficiency to ensure the desired bacterial kill in water.

Rudolph and Levine (23) report the existence of two phases in the killing of bacterial cells using a hypochlorite solution. The first phase is the penetration of the main killing principle into the bacterial cell, which is more rapid with the increase of undissociated hypochlorous acid. The second phase is the chemical union of this principle with the protoplasm of the cell causing the death of the organism.

#### Mode of Action of Chlorine

Although chlorine compounds have been used as germicides for more than half a century, it is still uncertain how chlorine compounds destroy microorganisms.

Many theories have been presented by different

investigators regarding the action of chlorine. Chang (4) summarizes the opinion expressed by different investigators in the following theories: the nascent oxygen theory, the nascent oxygen and direct chlorination theory, and, the formation of toxic substances theory.

However, the most recent theory suggested by Green and Stumpf (10) explains the germicidal action of chlorine in terms of inhibition of some key enzymatic process, in the bacterial cell. According to the theory known as the enzyme-trace substance theory, which postulates that any substance natural or synthetic which in trace amounts has a profound influence on biological process, must either be an enzyme system or inhibit or modify some enzyme reaction. Thus the trace level at which chlorine exerts its bactericidal action suggested an explanation in terms of inhibition of some enzymatic system. Their experimental data are consistent with the position that chlorine is bactericidal by virtue of its ability to paralyze the oxidation of glucose at the point in the fermentation cycle where triosephosphoric acid is oxidized to phosphoglyceric acid. The triosephosphoric dehydrogenase enzyme catalyses an oxidation reaction which is essential to the entire process. The oxidation of glucose will stop as soon as the triosephosphoric dehydrogenase is prevented from functioning. This enzyme is widely distributed in animal and plant

tissues and in bacteria.

Further work done by Knox, Stumpf, Green, and Auerbach (17) has shown that chlorine in bactericidal amounts or less inhibits various sulphhydryl enzymes and other enzymes sensitive to oxidation. Inhibition of essential enzymes in this way causes death of the bacterial cell; inhibition of glucose oxidation is paralleled by the percentage of bacteria killed. The aldose of *Escherichia Coli* has been shown to be one of the essential enzymes of glucose oxidation sufficiently sensitive to chlorine to explain its bactericidal effect.

#### Break-Point Chlorination

Sir Alexander Houston reported in 1919 that chlorine will destroy tastes and odors in water. In a later report to the Metropolitan Water Board of London, he presented data confirming his former statement, accompanied by the added information that as the chlorine dose increased the more certain would be the absence of tastes following de-chlorination (11).

In 1939, Faber (8) and Griffin (11) presented data showing that some waters exhibit a break in the chlorine residual curve, providing a sufficient amount of chlorine is applied to the water and the contact time is adequate. They also showed that tastes were intensified with slight

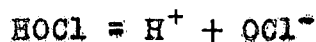
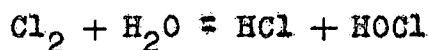
increases in the chlorine dose, but that above certain amounts of added chlorine the tastes disappear leaving only a chlorinous taste and odor.

Careful investigations of Clement and Chamberlin (6), have shown that when ammonia or some of its substituted derivatives are found in water, increasing application of chlorine to that water will produce the break-point curve. No other compound than ammonia, or its substituted derivatives will produce such a characteristic residual.

### Reactions of Break-Point Chlorination

The phenomenon of break-point chlorination gave rise to discussions as to exactly what takes place in the treated water.

Hedgepeth (16) in his explanation states that chlorine reacts with water to form hydrochloric acid and hypochlorous acid. The hypochlorous acid ionizes or dissociates into hydrogen ions and hypochlorite ions. Both reactions are dependent upon the pH value of the water, the first reaction predominating at low pH values and the second at high pH values:



When chlorine is added to water, therefore, a portion of it may be present as molecular chlorine ( $\text{Cl}_2$ ) or

as hypochlorous acid ( $\text{HOCl}$ ), or as hypochlorite ion ( $\text{OCl}^-$ ), and may be designated as free available chlorine.

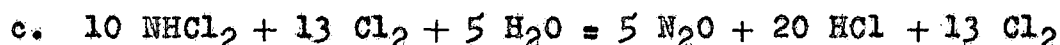
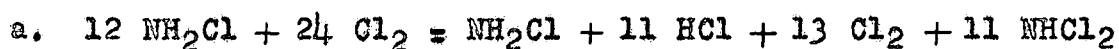
The intensity with which any oxidizing agent enters into chemical reaction is measured by its oxidation potential. Chemical reactions which occur when chlorine is added to water, and the rate at which they proceed, are dependent upon the oxidation potential of the free available chlorine.

When chlorine combines with other substances its oxidation potential is reduced or may be completely neutralized. Chlorine reacts with ammonia to form chloramines and with other organic nitrogen compounds to form chloro-derivatives. With many forms of organic matter, particularly the hydrocarbons, chlorine addition products are formed. Those chlorine compounds, lower in oxidation potential than free available chlorine, may be designated as combined available chlorine.

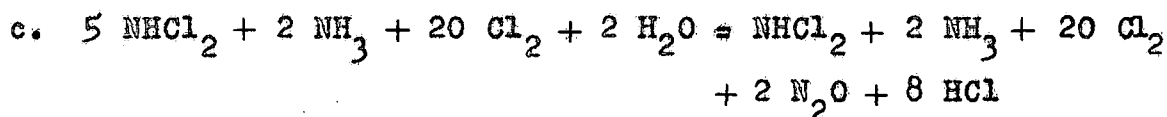
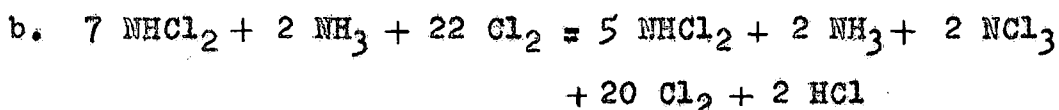
After free residual chlorination of a water, the residual which remains must consist almost wholly of free available chlorine and must contain little combined available chlorine. Apparently the true chloramines are first formed when water containing free ammonia is chlorinated by this process but, because chlorine is present in excess, they form intermediate compounds and are destroyed as the reaction goes to completion.

Thus the reactions of the process are explained by the chemistry of chloramines, that is, the reaction of chloramines in excess of chlorine. The chloramines first formed may exist as long as ammonia is in excess but are decomposed when chlorine is in excess. The final reactions that may occur are as follows:

1. At pH 9.0 when an excess of chlorine reacts with monochloramine. ( $\text{NH}_2\text{Cl}$ )



2. At pH 4.5 to 5.0 when an excess of chlorine reacts with dichloramine. ( $\text{NHCl}_2$ )



3. At pH values in the range between 4.5 and 9.0 when an excess of chlorine reacts with a mixture of monochloramine and dichloramine, combinations of the reactions given under 2 and 1 will occur.

The above reactions serve to explain the composition of the residuals which result in the application of the break-point process. When the pH value of water is relatively high, the final residual is shown, on the right of equation 1 c, to consist entirely of free available chlorine (represented in this equation as  $\text{Cl}_2$  rather than  $\text{HOCl}$ ). When the pH value of the water is relatively low the final residual is shown, on the right of equation 2 c, to consist almost entirely, but not wholly, of free available chlorine. These reactions illustrate that ammonia may not be completely removed at low pH values.

In waters having pH below 4.4 nitrogen trichloride is formed according to the equation:



Thus this phenomenon of break-point is explainable in that as additional chlorine is added it combines with other substances to form chloramines and other organic nitrogen compounds to form chloro-derivatives. Those chlorine compounds are lower in oxidation potential than free available chlorine. When an excess of chlorine is added beyond this point the chloramines formed are destroyed and chlorine appears once again as free available chlorine.

A characteristic of the chlorine reaction curve is that after the break-point is passed, and in the area where the free chlorine predominates, the curve will rise at an

angle approaching 45 degrees from the zero residual (9).

Freidrichs (9) reports that at least 0.05 parts per million ammonia must be present in the water before any break-point will take place.

Clement and Chamberlin (6) say it is extremely hard to find the "hump and dip," except by microanalysis, when the water has a low level of ammonia. It was found that the amount of ammonia sufficient to give the induced break-point in these waters was 0.25 parts per million in order to obtain good results.

The break-point will usually be after the addition of 10 times as much chlorine as the ammonia-nitrogen present (6). For practical purposes, however, the ratio is usually 12:1 because of the presence of other organic material in the water.

#### Germicidal Efficiency of Break-Point Chlorination

Freidrichs (9) says that the value of break-point chlorination lies in the higher germicidal value and the greater oxidation potential of the free chlorine, as compared with partially combined chlorine.

Laux (18) reports that laboratory tests on water treated with chlorine beyond the break-point was practically free from bacteria-forming gas in lactose broth.

Results of experiments carried out by Streeter (25)

brought out very strikingly the marked difference existing between the bactericidal power of free chlorine and that of chloramines. With free chlorine, concentrations of 0.05 to 0.10 parts per million killed all of the coliform bacteria within two or three minutes, whereas with the same concentrations of chloramine periods of 40 to 90 minutes were required.

To kill all of the bacteria within periods of two to three minutes, concentrations of chloramine ranging between two to three parts per million were needed. From these results it was indicated that free chlorine is twenty to thirty times more powerful as a bactericidal agent than chloramine.

#### Effect on Taste and Odor

The literature is abundant with the fact that chlorine beyond the break-point is being used quite successfully in municipal water purification for the destruction and control of the development of off odors and undesirable tastes.

It has been noted that most of the odoriphore groups are easily oxidized and decomposed by fairly strong oxidizing agents. The liberation of nascent oxygen from water when chlorine is added and the combination of this oxygen with the taste and odor compounds is believed to be

responsible for the action of chlorine in removing these compounds (8). There is the further possibility that chlorine may unite with certain organic compounds to form substitution products which do not produce objectionable tastes and odors.

Watzel (28) stated that oxybenzenes, naphthols, and anthracene derivatives--tar, creosote oil, and the like--after high chlorination give higher substituted aromatic derivatives which, as a rule, have either no smell or only a slight smell. High chlorination, and therefore the production of hypochlorous acid, has the property of breaking up the benzene nucleus of many isocyclic compounds which have one or more hydroxyl groups in their nuclei. He points out that it is difficult to analyze precisely the action of chlorine on the taste and odor substances in water because their chemical composition is for the most part not yet determined. Investigations were cited which show that high chlorination can completely decompose urea from human and animal wastes into nitrogen and carbon dioxide, that the albuminoid-nitrogen can be reduced to minute traces, and that other substances are almost completely oxidized.

A number of typical tastes and odors are listed by Baylis (2) as being susceptible to elimination or reduction by over doses of chlorine: chloro, fishy, algae,

grassy, decaying vegetation, chlorophenol, aldenol, and hydrogen sulfide.

### Chlorination in the Food Plants

The effect of chlorination as a germicide in the food plants is readily shown by experiments carried out by Merrill et al in 1938 (21). Experiments were carried out during the corn pack in two plants. Chlorine was introduced as a gas and the level used was one part per million in the cooling tanks.

Original counts in one plant were about 9000 organisms per ml and 100,000 organisms per ml in the other. In both cases the count was reduced to 25 organisms per ml. The data shows that on the first day that number ten cans were packed, about 1800 cans were put up without chlorination. Twenty-one swells developed in this lot; 11 per 1000. Approximately 29,000 cans were packed subsequently and all were cooled with chlorinated water. Only nine swells developed in this large lot.

The introduction into canning and frozen food plant water supplies of sufficient quantities of chlorine to achieve break-point chlorination was reported by Hall and Blundell (14) in 1946. Experimental projects were set up for three plants, a corn cannery, a pea cannery, and a freezing plant. The maximum free chlorine residual which

could be carried without objectionable odors and flavors was in excess of ten parts per million and was not determined. During the first five days of the survey, sterilized water was used in the plant and then the chlorinator was turned off for the next five days. At the end of the tenth day the chlorinator was turned on again and the survey continued for another five days. The line remained in good sanitary condition for the period of time sterilized water was used in the plant. General plant observations were made on slime growths and it was noted that whenever water was in regular or intermittent contact with the equipment no slime growth occurred. The bacterial count increased, when the chlorinator was shut off, from 56 to 67 times the average count obtained during the period in which sterilized water was used.

Similar results were also obtained in the corn plant.

The freezing plant, packing a general line of vegetables and a few fruits, used sterilized water practically all of the season. In no case at any of these plants using sterilized water has any product affect, favorable or unfavorable, been found which could be attributed to the use of sterilized water.

Zuch and Somers (29) carried out tests to find out the type of contact between the product and the chlorine

which is most apt to produce off flavors in the final product. Their work was however, done only on a canned variety of fruits and vegetables. Standard commercial canning practice was employed, with variations in chlorine concentration over a broad range of 2 to 50 parts per million. Observations made on canned samples included flavor, color, ascorbic acid, pH, vacuum, and drained weight. Of these factors, only flavor was found to be significant. Chlorine contacts were assumed to be of three types provided:

1. By the wash water
2. By the brine or sirup filling medium
3. By heated water or solution as in blanching, scalding, or lye peeling where such was required in the process.

Three types of test packs were made involving the use of chlorinated water in all contacts, in wash water and heated water or solution only, and in wash water only. Of the products tested, peaches were found to be most susceptible to off flavors, these resulting from the use of sirup preparation of water which was chlorinated to five parts per million. This finding corresponds with that of one canner in commercial packing according to Ritchell (22).

Stephens (24) reported that the application of in-plant chlorination should be carried out with caution when

processing fruits, especially pears and freestone peaches.

Brownlee, Guse and Murduck of the Continental Can Company (3) carried out studies during the pea and corn packs in 1946, with the cooperation of the Baker Canning Company, Wisconsin, to arrive to a measure of understanding of the function of break-point chlorination in the plant. The experimental work during the pea and corn packs consisted of five days of chlorination using powdered calcium hypochlorite, containing 70 per cent available chlorine. This was followed by five days of no chlorination, then five days of chlorination using chlorine gas. In general the dosage used ranged from 1.5 to 2 parts per million. Results of their studies show that there was a reduction of bacterial contamination throughout the plant.

Reduction in peas ranged from 43 to 99 per cent, and in corn from 34 to 87 per cent. Tap water and brine were negative for the most part. It was noticed that slime build-up was practically prevented during the chlorination periods. Such slime that did develop, however, was much easier to remove due to the fact that it did not have the tenacious character normal to slime. Thus the plant operator is aided by being able to provide better and faster clean-up periods.

The only drawback found in the use of hypochlorites was its operational high cost, and they are also limited to

a 2 per cent solution and could not be used where higher concentrations are required during the clean-up periods.

Haynes and Mundt (15b) reported that constant low-pressure sprays of chlorinated water beyond the break-point resulted in a reduction of bacterial content in frozen beans. Slime was also eliminated from operating and maintaining surfaces, floors and runways; odors, characteristic of vegetable processing plants, were quickly eliminated.

Harris (15a) reports that investigations on in-plant chlorination have been very encouraging. Much information, however, must be assembled before break-point chlorination can be recommended for the food industry, either generally or specifically. The break-point may occur at a different chlorine concentration for each water tested, and in some cases is hardly recognizable, according to Harris.

Ritchell (22) says that slime and odors may be prevented or greatly reduced on all surfaces which are continuously sprayed with chlorinated water. Frequent application of chlorinated water during the packing period to equipment and surfaces not constantly bathed with chlorinated water will assist in control.

No corrosion in equipment was reported which was attributed to chlorinated water.

## CHAPTER III

### EXPERIMENTAL

#### A. Analytical Methods

##### 1. Determination of Available Chlorine

###### a. The Laux Flash Method

The method which was used to determine the amount of both free and combined available chlorine is based on the Laux test (18). In this test special emphasis is given to the speed of color development when ortho-tolidine is added to the sample.

Free available chlorine, from a practical viewpoint, reacts instantly with ortho-tolidine at all temperatures. The reaction between ortho-tolidine and chloramines on the other hand, is relatively slow, especially at temperatures less than 60° F. It thus follows that the reading obtained immediately following the addition of ortho-tolodine will approximate the amount of free available chlorine present, and that any color developing thereafter will approximate the amount of combined chlorine or chloramine present.

Accurate results are obtained when the first reading is made exactly five seconds, and the second reading made exactly five minutes, after the addition of the ortho-tolidine.

## The Test

### A. Reagent

1. Ortho-tolidine reagent. Standard ortho-tolidine.

### B. Procedure

1. 0.5 ml of ortho-tolidine was added to 15 ml cell of the Wallace and Tiernan Color Comparator.
2. The cell was filled to the mark with the sample to be tested.
3. The residual was read exactly 5 seconds after addition of sample to cell containing ortho-tolidine.
4. The residual was read again after 5 minutes.

### C. Interpretation

The 5-second reading will approximate the amount of free available chlorine residual present. The 5-minute reading will be a measure of the total residual present. The difference between the two readings will be representative of the amount of chloramine present.

#### b. The Drop Dilution Method

The drop dilution method of residual chlorine determination consists of the addition of one or more drops of the water under test to a cell containing a known volume of ortho-tolidine and distilled water. This method has the

advantage of simplicity and speed, coupled with a good degree of accuracy. It is particularly useful for all residuals greater than 10.0 parts per million (12).

### The Test

#### A. Reagents and Equipment

1. Distilled water.
2. Standard ortho-tolidine.
3. Dropper furnished with Wallace and Tiernan Chlorine Comparator set. The dropper delivers between 19 to 21 drops per ml equivalent to 1/20 of a milliliter, also expressed as 0.05 ml.
4. Wallace and Tiernan Comparator, complete with chlorine color disc and 15 ml sample cells.

#### B. Procedure

1. Sample was collected in a small glass container.
2. 0.5 ml of ortho-tolidine was added to center tube and filled to the mark with distilled water. (Wallace and Tiernan sample cells contain 15 ml when filled to mark. Wallace and Tiernan droppers contain 0.5 ml when filled to mark.)
3. The other tube was filled with distilled water.
4. One drop of water under test was added to center tube, mixed and the residual read immediately. When no color appeared, additional drops were

added one at a time until a reading within the range of the color disc appeared.

### C. Computation of Residual

$$\frac{\text{Capacity of cell}}{\text{ml Cl water added}} \times \text{Comparator reading} = \text{ppm Cl present}$$

## 2. Determination of Break-Point in Tap Water

In order to determine the different doses of chlorine which are to be applied to the water used for processing the apples, a preliminary test had to be carried out on the water used to find out where the break-point will occur when treated with increasing amounts of chlorine.

The water used was the regular city water, which had already been marginally chlorinated with a dose of five parts per million chlorine and one part per million ammonia. However, when tested with the regular orthotolidine method no free, or combined, residual was detected.

### Procedure

#### a. Chlorine water

Chlorine water was used for this work. A suitable solution was obtained by bubbling chlorine gas through water obtained from the laboratory tap. Prior to the start of the test the chlorine was diluted to 100 parts

per million, thus the volume of the treated samples did not increase by more than one per cent when the chlorine water was added.

b. Samples

A series of ten aliquot portions of the water under test were set up each 500 ml.

c. Chlorine application

As is known that the break-point is a function of ammonia content of the water, and because most of the ammonia in the water has already combined with the first application of chlorine, the amount of chlorine used was in proportion with the amount of  $\text{NH}_3\text{-N}$  assumed to be still in the water. The following amounts of chlorine water were added to the samples: 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 ml. The samples were allowed to stand for thirty minutes away from any excessive light or heat sources.

d. Residual chlorine

At the end of the contact period the free residual chlorine and the total residual were determined according to the Laux test, using ortho-tolidine and the Wallace and

Tiernan Chlorine Color Comparator.

Results of these tests are shown in Table I and Figure I.

TABLE I  
DETERMINATION OF BREAK-POINT IN TAP WATER

No. of Sample	Chlorine water added in ml	Chlorine dose in ppm	Residual Reading	
			5 Seconds	5 Minutes
1	0.5	0.1	0.0	0.05
2	1.0	0.2	0.0	0.15
3	1.5	0.3	0.05	0.17
4	2.0	0.4	0.05	0.25
5	2.5	0.5	0.07	0.25
6	3.0	0.6	0.05	0.15
7	3.5	0.7	0.17	0.25
8	4.0	0.8	0.30	0.40
9	4.5	0.9	0.40	0.50
10	5.0	1.0	0.50	0.60

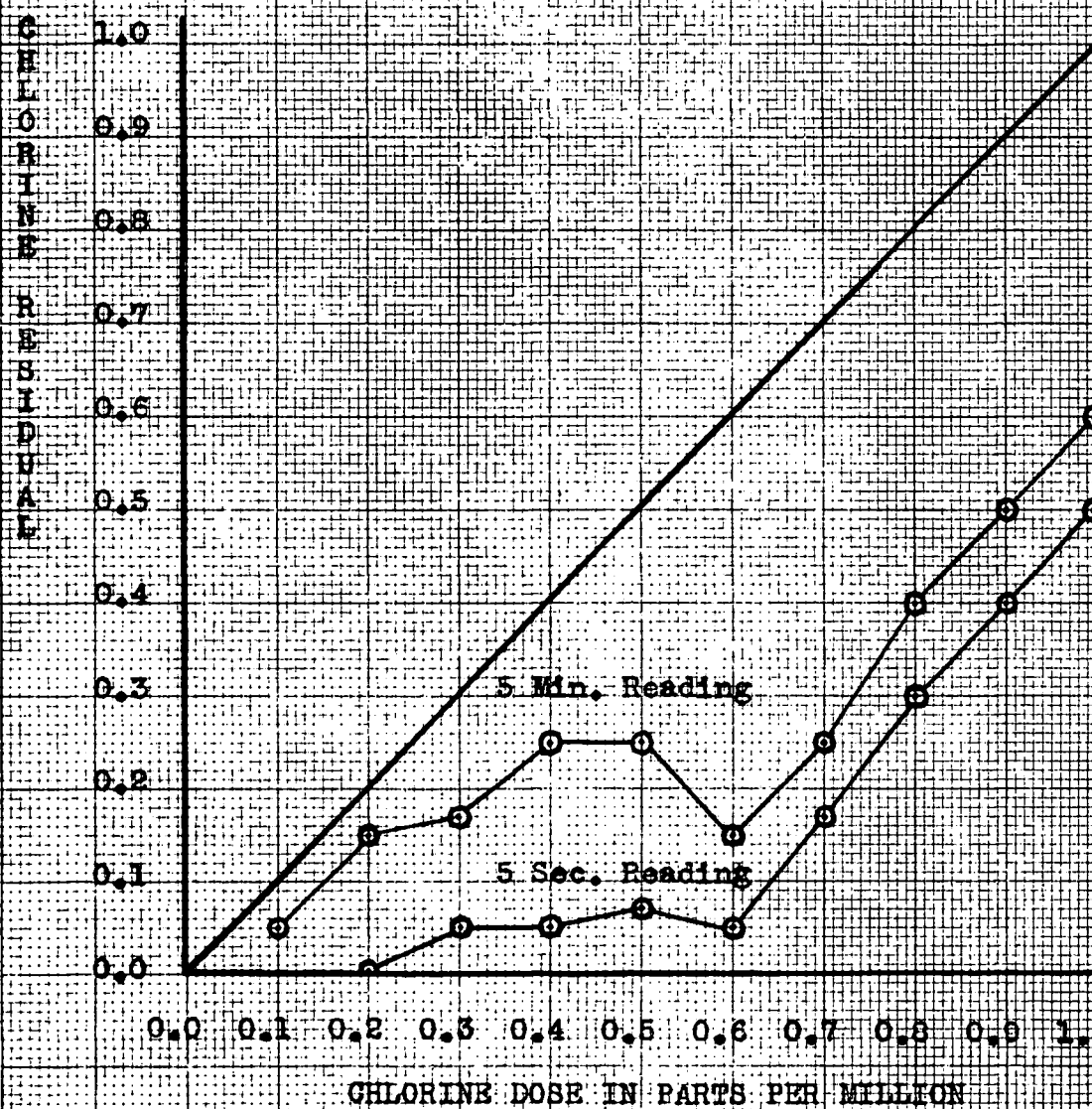
### 3. Ascorbic Acid (vitamin C) Determination

The Oregon State College modification of the colorimetric method was the procedure used for this determination. A sample of 30 grams was weighed and blended in a Waring blender for two minutes with 170 ml of 3 per cent metaphosphoric acid, then filtered through dry fluted filter paper, and the first 10 ml of the filtrate was discarded.

The Fischer electrophotometer was set at zero using a tube of distilled water as the reference liquid. Then 1 ml aliquote of the filtrate was pipetted into another dry

FIGURE 1.

ORTHO-TOLIDINE COLOR DEVELOPMENT  
IN BREAK-POINT CHLORINATION  
OF TAP WATER



clean photometer tube, and 9 ml, of sodium-citrate-meta-phosphoric acid buffer (pH 3.6) was added, making a total volume of 10 ml of liquid in the tube. The tube was placed in the photometer and 10 ml of dye added to it with a rapid delivery pipette; the reading was taken and designated as  $X_1$ . A crystal of ascorbic acid was added to the tube to decolorize the dye completely; the reading was taken and designated as  $X_2$ . This reading was taken in order to correct the extraneous color turbidities introduced by the extract.

Into another matched tube, 10 ml of buffer solution was added, 10 ml of dye solution mixed therewith, and the reading taken and called  $D_1$ . This was decolorized with a crystal of ascorbic acid, and the reading  $D_2$  was recorded. The reading  $D_2$  subtracted from the reading  $D_1$  gave the dye factor. This dye factor was determined only once for the days use. The amount of ascorbic acid present was calculated from the following equation:

$$\text{Milligrams ascorbic acid in aliquot} = 0.00258 (D_1 - D_2) - (X_1 - X_2)$$

The above ascorbic acid factor for this instrument, using a B525 m/u filter, was 0.00258 mg.

#### 4. Effect of Residual Chlorine on Ascorbic Acid

Due to the fact that residual chlorine beyond the

break-point has a high oxidation potential, and due to the fact that ascorbic acid is readily oxidized, it was believed that chlorine might have some effect on the stability of ascorbic acid which is added to the apples in order to prevent browning.

To find out the extent of chlorine oxidation power in the doses used in the preparation of the apples, ten aliquot portions of 500 ml of water were set up in Erlenmeyer flasks. To the first five flasks chlorine water was added to produce concentrations of 0, 2, 5, 10, and 50 parts per million residuals respectively. The same doses were applied to the other five samples, then sugar was added to make a sirup of 35 degrees Brix.

Then to all the samples 200 mg of ascorbic acid was added, making the original ascorbic acid content in all the samples 40 mg per 100 g.

The ten samples were held for thirty minutes away from any strong light sources, after which vitamin C assays were carried out on them using the Fischer electrophotometer.

Results of this test are shown in Tables II and III.

TABLE II  
EFFECT OF RESIDUAL CHLORINE ON ASCORBIC ACID  
IN AQUEOUS SOLUTION

Cl dose	Ascorbic acid content mg/100 g	Ascorbic acid lost mg/100 g	Per cent lost
0 ppm	37.10	2.90	7.25
2 ppm	36.12	3.88	9.70
5 ppm	36.08	3.92	9.80
10 ppm	28.89	11.11	27.77
50 ppm	23.33	16.67	41.67

TABLE III  
EFFECT OF RESIDUAL CHLORINE ON ASCORBIC ACID  
IN A 35° BRIX SIRUP

Cl dose	Ascorbic acid content mg/100 g	Ascorbic acid lost mg/100 g	Per cent lost
0 ppm	38.28	1.72	4.30
2 ppm	38.28	1.72	4.30
5 ppm	38.28	1.72	4.30
10 ppm	38.28	1.72	4.30
50 ppm	38.28	1.72	4.30

## B. Preparation of Samples

### Objective

This work was undertaken to find out whether or not in-plant chlorination of the water supply, beyond the break-point has any detrimental effect on the final quality of frozen apples.

The study was carried out under a laboratory scale, adhering as closely as possible to the commercial practices for the preparation and freezing of apples.

The factors studied for both apple slices and apple-sauce were: flavor, color, texture, aroma, and effect on ascorbic acid.

The source of chlorine used was sodium hypochlorite and chlorine water.

### PROCEDURE FOR APPLE SLICES

#### 1. Without the Addition of Sugar or Ascorbic Acid

As the source of chlorine, sodium hypochlorite ( $\text{NaOCl}$ ) was used for this and the following experiments on apple slices. It was obtained from the men's gymnasium at Oregon State College, and was prepared by the reaction of gaseous chlorine in a solution of caustic soda.

The chemical equation is as follows:



The Baldwin variety of apples was used for this and the following experiments of apple slices. The apples were picked from a Camp Adair orchard.

The apples were first washed thoroughly to remove all spray residues, dirt, or other organic matter that would interfere with the flavor of the final product. The fruit was then peeled by means of a mechanical peeler manipulated by power. The peeled and cored fruit was trimmed by hand, then immersed immediately in a dilute brine solution (3 per cent sodium chloride) to retard browning. Salt retards browning by breaking down the organic peroxides, thus retarding the action of the enzyme peroxidase (26). The fruit was then sliced uniformly by hand into eight even slices. A short blanch (ninety seconds) at 212° F was given to the slices, after which they were cooled by dunking in a tank of cold water for three minutes. The slices were drained, then packed in 14-ounce cellophane-lined cartons. After heat-sealing, the cartons were frozen at -10° F for 14 hours, then stored at 0° F.

The cartons were opened after one week and organoleptic tests made on them to determine the effect of chlorine on the quality. The results are shown in Table IV.

TABLE IV  
EFFECT OF CHLORINE ON THE QUALITY OF APPLE SLICES

Cl dose	Flavor	Color	Aroma	Texture
Control	fair	repulsive	good	good
2 ppm	fairly good	repulsive	fair	acceptable
5 ppm	acceptable	repulsive	fair	fair
10 ppm	fair	repulsive	fair	fair
50 ppm	fair	repulsive	fair	poor

Treatment: Without the addition of sugar or ascorbic acid.

Storage time: One week

Thawing time: 14 hours

Taste-Tester Comments:

All the samples browned badly due to oxidation. Thus changes in color could not be determined. All the chlorinated samples lost some of their crispness, which was still retained in the control samples. Tests were run in triplicates.

## 2. Without the Addition of Ascorbic Acid. Dry Sugar Added

The same procedure of preparing the apple slices was used. Dry sugar was added to the slices at the ratio of 4 fruit to 1 sugar. Thus each carton contained 12 ounces of apple slices and three ounces of sugar. The cartons were

frozen and stored at the same temperature of the previous experiment.

They were then opened after one, three, and 12 weeks. The results are shown in Tables V, VI, and VII and in Figure II.

TABLE V  
EFFECT OF CHLORINE ON THE QUALITY OF APPLE SLICES

Cl dose	Flavor	Color	Aroma	Texture
Control	good	good	fair	good
2 ppm	good	very good	fairly good	fairly good
5 ppm	good	good	fairly good	fair
10 ppm	good	fairly good	fair	fair
50 ppm	fair	fairly good	poorly fair	fair

Treatment: No ascorbic acid added, dry sugar added 4:1.

Storage time: One week

Thawing time: 14 hours

Taste-Tester Comments:

All the chlorinated samples lost some of the apple crispness which was retained in the control. Chlorine aroma could be detected by some of the testers in the 50 ppm samples. The tests were run in triplicate.

TABLE VI  
EFFECT OF CHLORINE ON THE QUALITY OF APPLE SLICES

Cl dose	Flavor	Color	Aroma	Texture
Control	good	fair	fair	good
2 ppm	good	fairly good	fair	fairly good
5 ppm	good	fair	fairly good	fair
10 ppm	good	fair	fair	fair
50 ppm	fair	fair	fair	fair

Treatment: No ascorbic acid added, dry sugar added 4:1.

Storage time: Three weeks

Thawing time: 14 hours

Taste-Tester Comments:

No chlorine odor or flavor could be detected in the 50 ppm or any other samples. Tests were run in triplicate.

TABLE VII  
EFFECT OF CHLORINE ON THE QUALITY OF APPLE SLICES

Cl dose	Flavor	Odor	Texture
Control	fairly good	acceptable	acceptable
2 ppm	good	fairly good	fairly good
2 ppm	good	fairly good	fairly good
50 ppm	fair	fairly good	acceptable

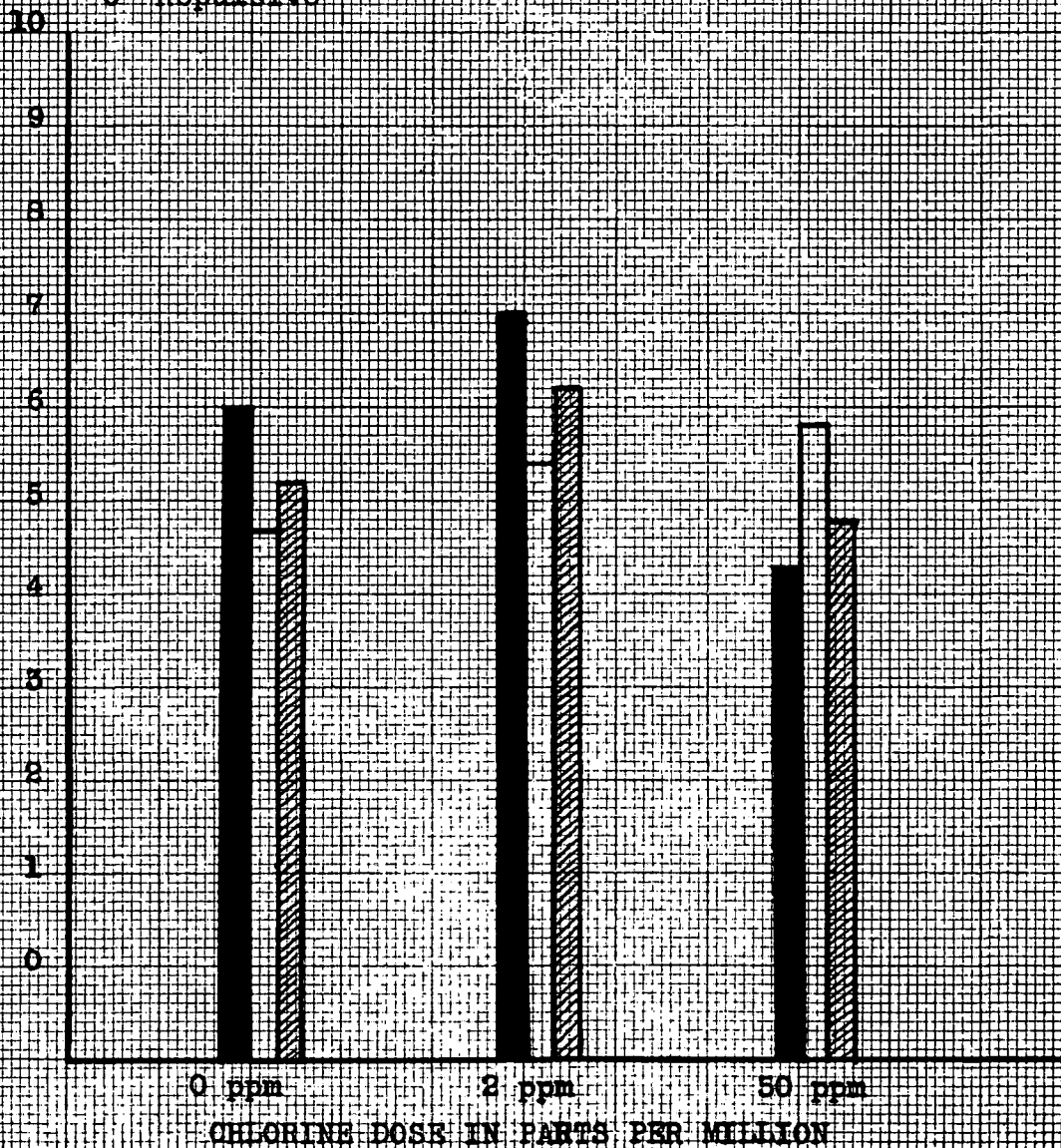
FIGURE II.

## SCORE

- 10- Ideal
- 9- Excellent
- 8- Very good
- 7- Good
- 6- Fairly good
- 5- Acceptable
- 4- Fair
- 3- Poorly fair
- 2- Poor
- 1- Very poor
- 0- Repulsive

## FROZEN APPLE SLICES

DRY SUGAR ADDED  
NO ASCORBIC ACID

Flavor Odor Texture 

Treatment: No ascorbic acid added, dry sugar added 4:1.

Storage time: Three months

Thawing time: 14 hours

Taste-Tester Comments:

The control was sweet but hard and had a light off odor. The 2 ppm samples had a soft texture but were generally good. The 50 ppm samples were too hard in texture and had a metallic odor. Tests were supervised by the experiment station.

3. Ascorbic Acid and Sirup Added

The apples were first washed thoroughly in order to remove all spray residues, dirt, or other organic material that would interfere with the flavor of the finished product. The fruit was then mechanically peeled and cored, then immersed immediately in a dilute brine (3 per cent sodium chloride) to retard browning. The fruit was then sliced evenly by hand, given a short blanch for ninety seconds at 212° F, and cooled by dunking in a tank of cold water for three minutes. After draining, 12 ounces of slices were packed in 16-ounce cellophane-lined cartons. Four ounces of a 35° Brix sirup containing the ascorbic acid was added to the slices, after which they were heat-sealed. The cartons were frozen at -10° F for 14 hours,

then stored at 0° F.

#### Preparation of the Sirup:

According to Bauernfeind and Siemers (1), one gallon of a 35° Brix sirup containing ascorbic acid to obtain 200 mg per pound of finished pack will require the following ingredients:

3.36 pounds of sugar

6.24 pounds of water

0.27 ounces of ascorbic acid.

To prepare two pounds of this sirup we used the following amounts:

317.5 grams of sugar

591 ml of water

1.6 grams of l- ascorbic acid.

Results are shown in Table VIII and Figure III.

Results of the effect of chlorine on the ascorbic acid are in Table IX.

TABLE VIII  
EFFECT OF CHLORINE ON THE FLAVOR AND TEXTURE OF APPLE SLICES

Cl dose	Flavor	Texture
0 ppm	fairly good	fairly good
2 ppm	fairly good	acceptable
2 ppm	fairly good	acceptable
50 ppm	acceptable	fairly good

Treatment: Ascorbic acid and 35° sirup added.

Storage time: One week

Thawing time: 14 hours

Taste-Tester Comments:

The control samples were lacking in flavor but were firm. The 2 ppm samples were a little mushy but were sweet and had a good flavor. The 50 ppm samples were good in texture but chlorine odor was detected by some of the testers. Tests were supervised by the experiment station.

TABLE IX

ASCORBIC ACID DETERMINATION IN APPLE SLICES  
PREPARED WITH CHLORINATED WATER

Cl dose	Ascorbic acid content mg/100 g	Ascorbic acid lost mg/100 g	Per cent lost
0 ppm	42.15	3.85	8.34
2 ppm	42.08	3.92	8.56
50 ppm	41.89	4.11	8.81

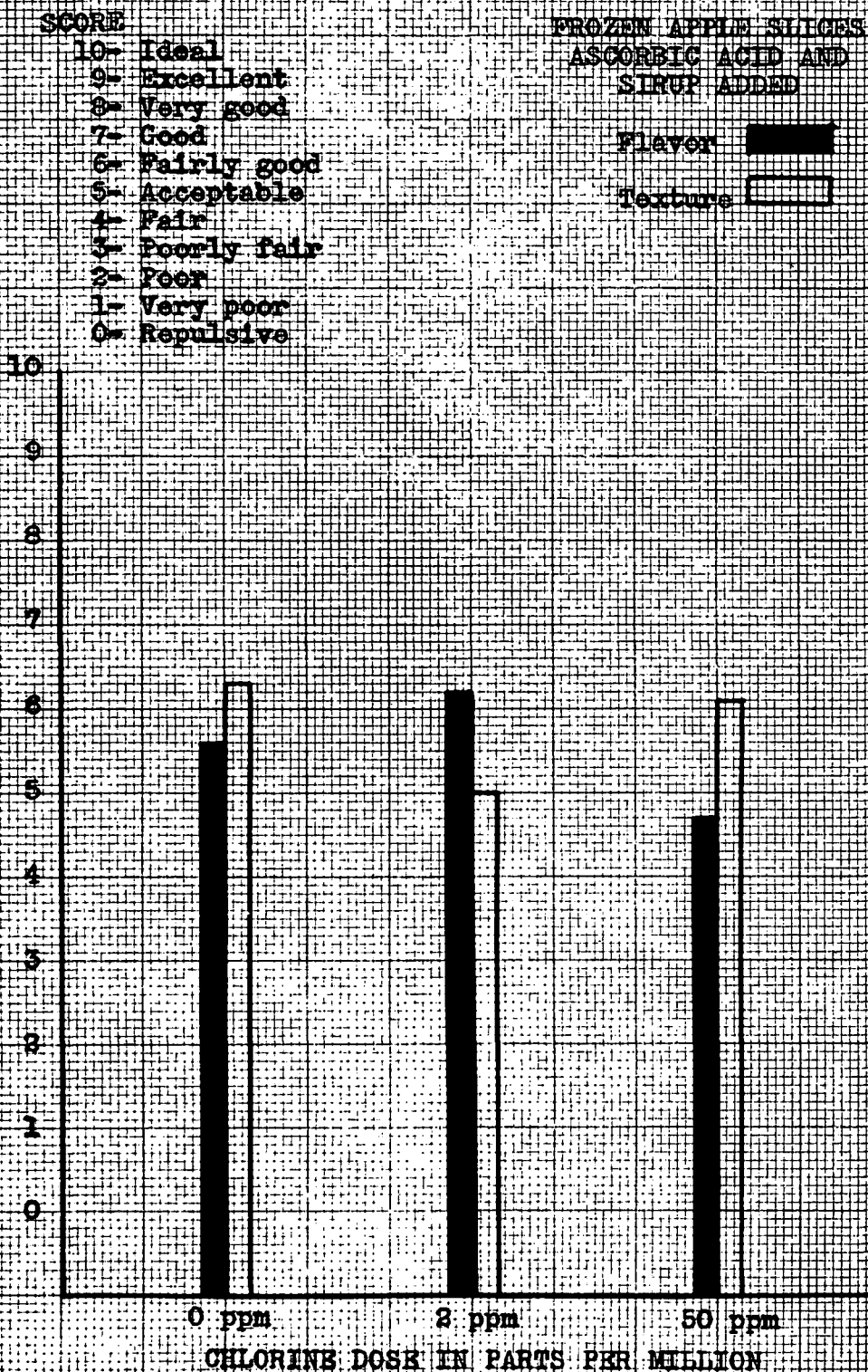
Treatment: 35° Brix sirup added.

PROCEDURE FOR APPLE-SAUCE

1. Without the Addition of Sugar or Ascorbic Acid

The source of chlorine used for this experiment was the same as in the apple slices, i.e., sodium hypochlorite.

FIGURE III.



The Baldwin variety of apple was also used.

Procedure:

The apples were first washed thoroughly to remove all spray residues, dirt, or other organic matter that would interfere with the flavor of the final product. The fruit was then peeled by means of a mechanical peeler manipulated by power. The peeled and cored fruit was trimmed by hand, then immersed immediately in a dilute brine (3 per cent sodium chloride) to retard browning. The fruit was then sliced by hand and the slices cooked for five minutes in order to soften them and to inactivate the oxidative enzymes. Immediately after blanching they were cooled by dunking in a tank of cold water for three minutes. The slices were then run through a hammer mill in order to pulp them, and the apple-sauce was collected in a pan. Fourteen ounces of sauce was then packed in 16-ounce cellophane-lined paper cartons, heat-sealed, and frozen at  $-10^{\circ}$  F for 14 hours. Storage was at  $0^{\circ}$  F.

Taste-test results are shown in Table X.

TABLE X  
EFFECT OF CHLORINE ON THE QUALITY OF APPLE-SAUCE

Cl dose	Flavor	Color	Aroma	Texture
Control	fair	fair	fairly good	fair
2 ppm	fairly good	fair	fair	fair
5 ppm	fair	fair	acceptable	fair
10 ppm	acceptable	fair	acceptable	fair
50 ppm	fair	fair	fair	fair

Treatment: No sugar or ascorbic acid added.

Storage time: Three months

Thawing time: 1½ hours

Taste-Tester Comments:

There was no noticeable change in color in the treated and untreated samples. All the samples were flat in flavor except the 2 ppm samples. A chlorine aroma could be detected in the 50 ppm samples. The texture was soft in all the samples. Tests were run in triplicate.

## 2. With the Addition of Ascorbic Acid. No Sugar Added

The source of chlorine used for this and the following experiments was liquid chlorine. The solution was obtained by bubbling chlorine gas into a bottle containing tap water.

The variety of apples used for this experiment was the Jonathan variety. It was obtained from the Albany Cold Storage, and had been in cold storage for 15 days.

### Procedure:

The same procedure was used for preparing this lot. However, after the apple-sauce was obtained, it was weighed carefully and ascorbic acid was added to produce 200 mg per pound of finished pack. The sauce was mixed thoroughly to distribute the ascorbic acid evenly throughout the lot. Fourteen ounces of apple-sauce were then packed in 16-ounce cellophane-lined paper cartons, heat-sealed, and frozen at  $-10^{\circ}$  F. Storage was at  $0^{\circ}$  F.

Taste-test results are shown in Table XI and Figure IV. Results of the ascorbic acid determination are shown in Table XII.

TABLE XI

EFFECT OF CHLORINE ON THE FLAVOR AND COLOR OF APPLE-SAUCE

Cl dose	Flavor	Color
Control	fair	fairly good
2 ppm	fairly good	very good
2 ppm	fairly good	very good
50 ppm	poorly fair	acceptable

Treatment: With the addition of ascorbic acid. No sugar added.

Storage time: One week

Thawing time: 1½ hours

Taste-Tester Comments:

The best samples were the 2 ppm. The control had a metallic flavor. The 50 ppm samples had an off flavor and were slightly gray and dark in color; chlorine flavor could be detected. The lack of sugar was objectionable according to some of the testers. Tests were supervised by the experiment station.

TABLE XII

ASCORBIC ACID DETERMINATION IN APPLE-SAUCE  
PREPARED WITH CHLORINATED WATER

Cl dose	Ascorbic acid content mg/100 g	Ascorbic acid lost mg/100 g	Per cent lost
0 ppm	39.53	6.47	14.06
2 ppm	39.18	6.82	14.82
50 ppm	36.24	9.76	21.21


Treatment: No sugar added.

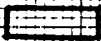
FIGURE IV.

SCORE

- 10- Ideal
- 9- Excellent
- 8- Very good
- 7- Good
- 6- Fairly good
- 5- Acceptable
- 4- Fair
- 3- Poorly fair
- 2- Poor
- 1- Very poor
- 0- Repulsive

FROZEN APPLE SAUCE  
ASCORBIC ACID ADDED  
NO SUGAR

Flavor 

Color 

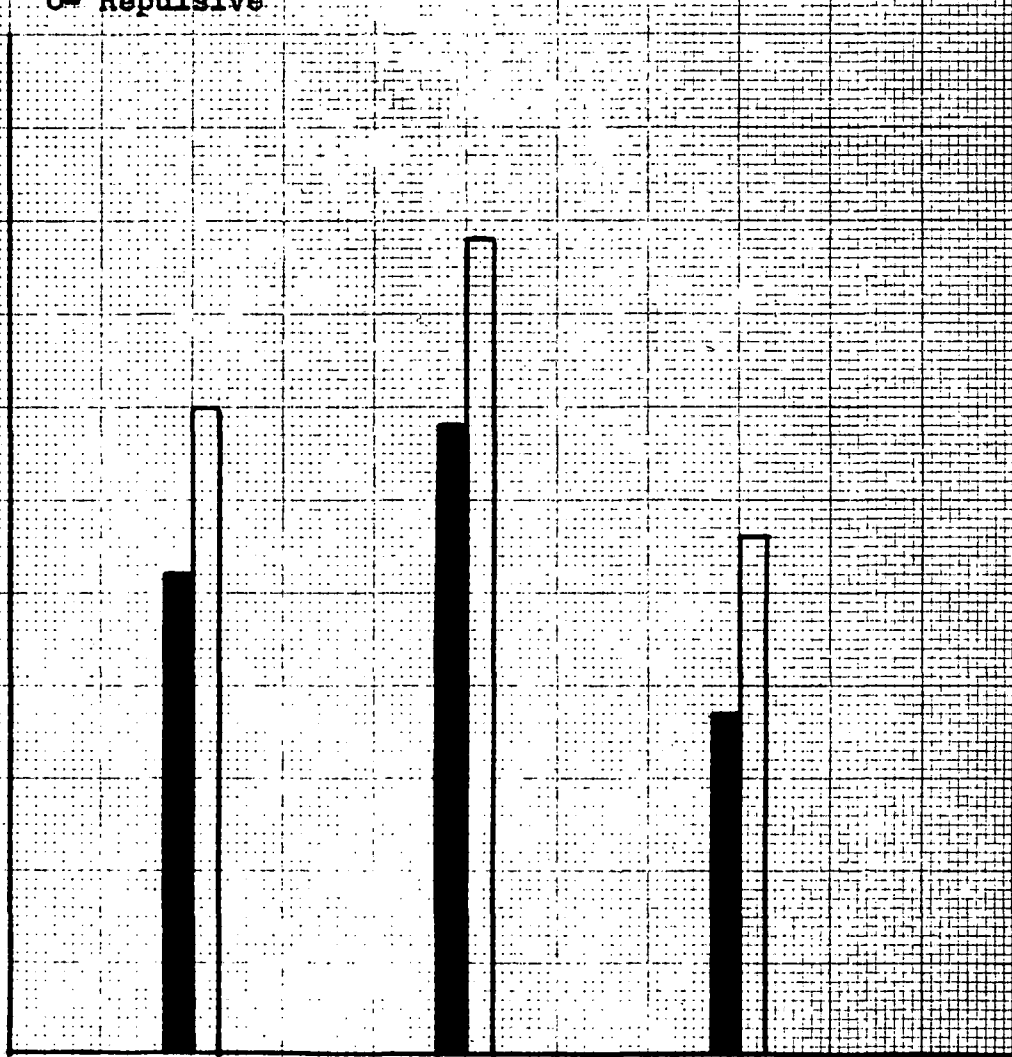
10  
9  
8  
7  
6  
5  
4  
3  
2  
1  
0

0 ppm

2 ppm

50 ppm

CHLORINE DOSE IN PARTS PER MILLION



### 3. With the Addition of Ascorbic Acid and Dry Sugar

This treatment was applied to two different apple varieties. The first was the Red Delicious, and the second was the Spitzenburg. They were both obtained from the Albany Cold Storage, and had been in storage for the period of one month.

#### Procedure:

After the apple-sauce had been obtained as previously described, it was weighed to determine the amount of ascorbic acid to be added. The ascorbic acid was dissolved in a little water (200 mg dissolved in 20 ml per pound of apple-sauce) and mixed thoroughly with the apple-sauce. Twelve ounces of apple-sauce were then packed in 16-ounce cellophane-lined paper cartons, then one ounce of dry sugar was added. The cartons were heat-sealed, frozen for 14 hours at  $-10^{\circ}$  F, then stored at  $0^{\circ}$  F.

The taste-test results made on the Delicious apples are shown in Table XIII and Figure V. The ascorbic acid determinations are in Table XIV.

Results for the Spitzenburgs are shown in Table XV and Figure VI. Results for the ascorbic acid determinations are in Table XVI.

TABLE XIII

## EFFECT OF CHLORINE ON THE FLAVOR AND COLOR OF APPLE-SAUCE

Cl dose	Flavor	Color
Control	acceptable	good
2 ppm	fairly good	very good
2 ppm	fairly good	very good
50 ppm	fair	good

Variety: Delicious

Treatment: Ascorbic acid and dry sugar added.

Storage time: Ten days

Thawing time: 1½ hours

Taste-Tester Comments:

The 2 ppm samples were the best samples and had a good flavor compared to the control. The control was slightly off color and slightly flat, and was not as sweet as the rest of the samples. The 50 ppm had a slight off flavor (organic). Tests were supervised by the experiment station.

FIGURE V.

SCORE

- 10- Ideal
- 9- Excellent
- 8- Very good
- 7- Good
- 6- Fairly good
- 5- Acceptable
- 4- Fair
- 3- Poorly fair
- 2- Poor
- 1- Very poor
- 0- Repulsive

FROZEN APPLE SAUCE  
ASCORBIC ACID AND  
SUGAR ADDED

Flavor

Color

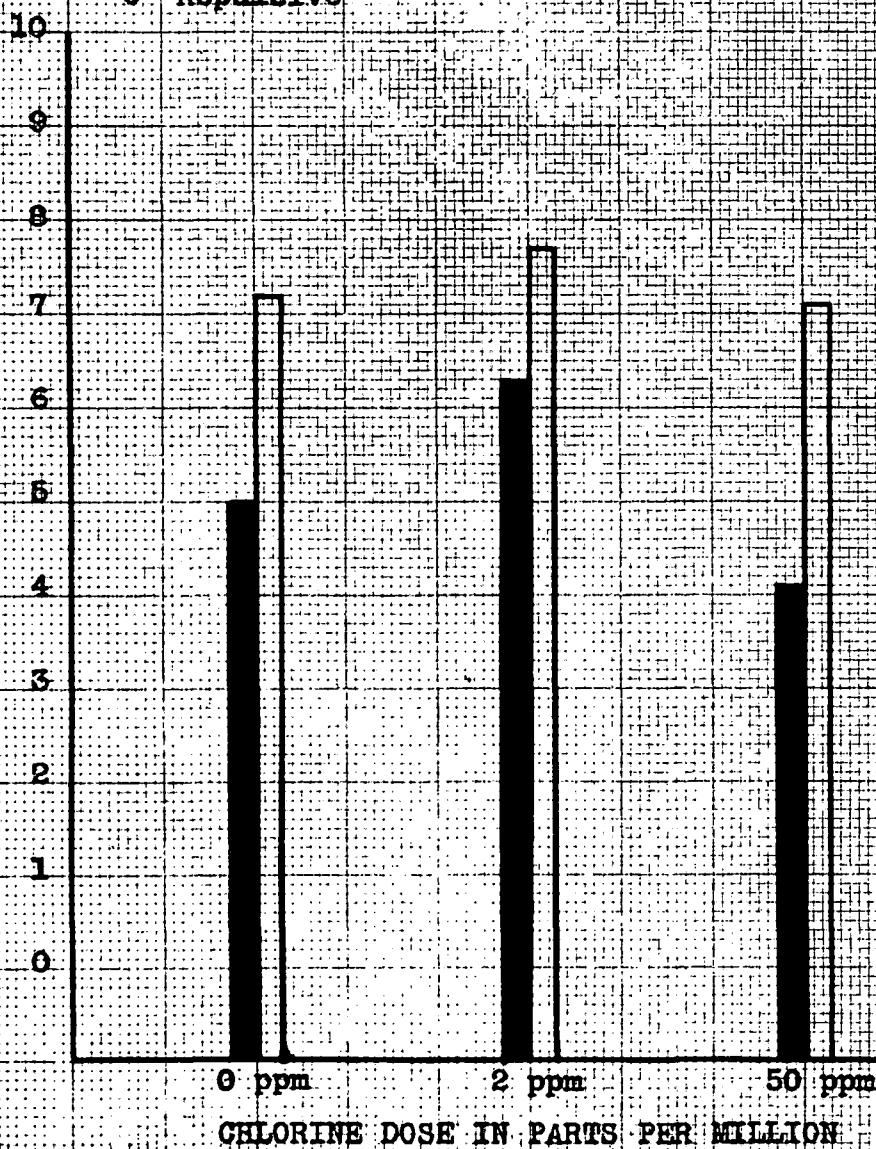


TABLE XIV

ASCORBIC ACID DETERMINATION IN APPLE-SAUCE  
PREPARED WITH CHLORINATED WATER

Cl dose	Ascorbic acid content mg/100 g	Ascorbic acid lost mg/100 g	Per cent lost
0 ppm	40.82	5.18	11.26
2 ppm	40.16	5.94	12.91
50 ppm	39.44	6.56	14.26

Variety: Delicious

Treatment: Dry sugar added 12:1.

TABLE XV

EFFECT OF CHLORINE ON THE FLAVOR AND COLOR OF APPLE-SAUCE

Cl dose	Flavor	Color
Control	good	very good
2 ppm	fairly good	good
2 ppm	fairly good	good
50 ppm	good	good

Variety: Spitzenburg

Treatment: Ascorbic acid and dry sugar added.

Storage time: One week

Thawing time: 14 hours

Taste-Tester Comments:

The samples were all generally good. The differences

FIGURE VI.

## SCORE

- 10- Ideal
- 9- Excellent
- 8- Very good
- 7- Good
- 6- Fairly good
- 5- Acceptable
- 4- Fair
- 3- Poorly fair
- 2- Poor
- 1- Very poor
- 0- Repulsive

FROZEN APPLE SAUCE  
ASCORBIC ACID AND  
SUGAR ADDED

Flavor

Color

10

9

8

7

6

5

4

3

2

1

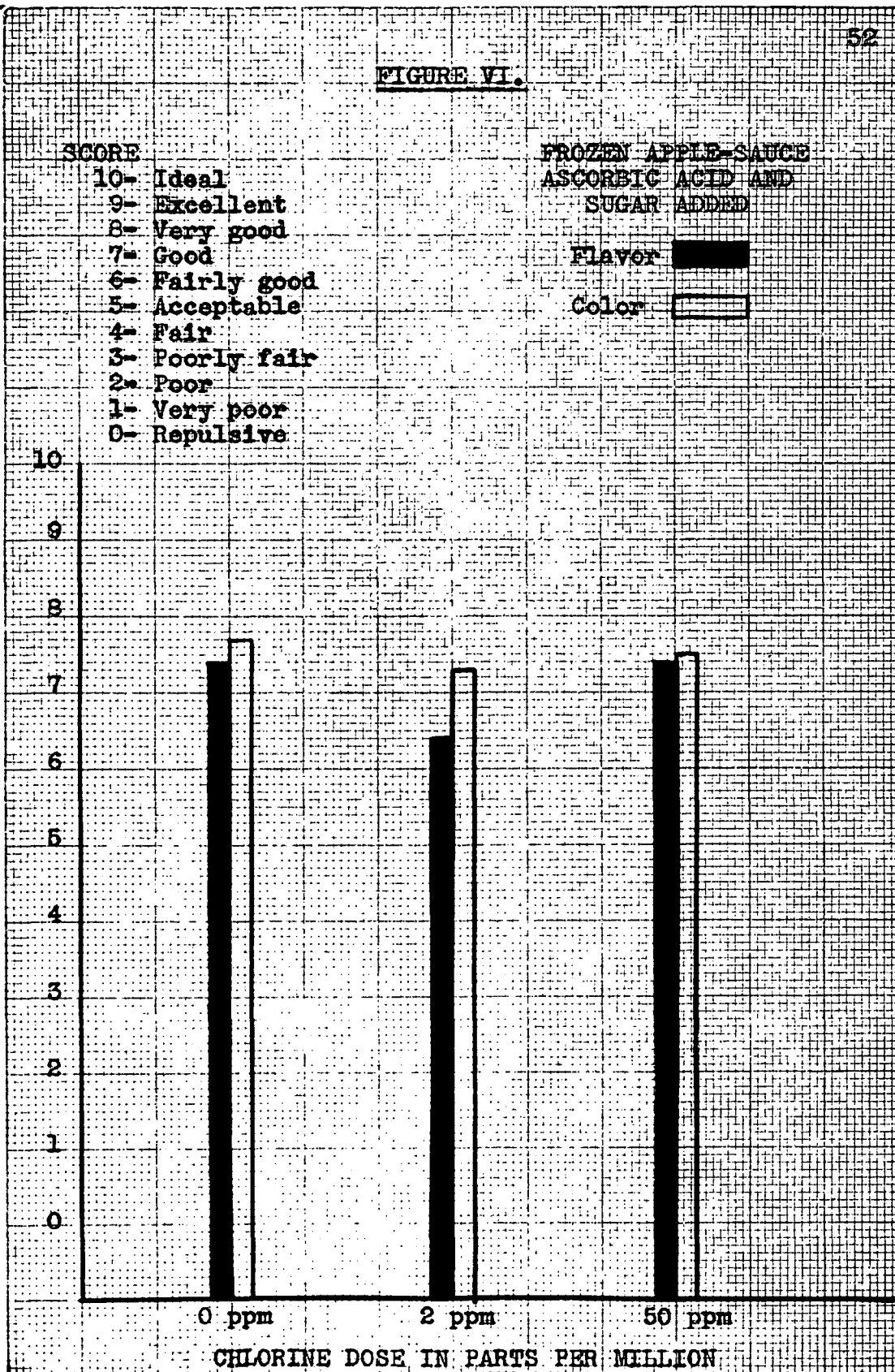
0

0 ppm

2 ppm

50 ppm

CHLORINE DOSE IN PARTS PER MILLION



in color were not very pronounced. The 2 ppm samples had a good apple flavor. Some tester stated that the control was flat and had no apple flavor. The 50 ppm samples had a slight off flavor. Tests were supervised by the experiment station.

TABLE XVI

ASCORBIC ACID DETERMINATION IN APPLE-SAUCE  
PREPARED WITH CHLORINATED WATER

Cl dose	Ascorbic acid content mg/100 g	Ascorbic acid lost mg/100 g	Per cent lost
0 ppm	41.02	4.98	10.39
2 ppm	40.78	5.22	11.13
50 ppm	40.10	5.90	12.82

Variety: Spitzenburg

Treatment: Dry sugar added 12:1.

## CHAPTER IV

### DISCUSSION OF RESULTS

Results of the study made on the laboratory tap water show that the break-point lies somewhere between 0.5 to 0.7 parts per million chlorine applied. According to Figure I the break-point occurs when 0.6 parts of chlorine is applied, whereafter the residual chlorine starts rising again.

It must be born in mind however, that the water under test was already chlorinated with a dose of five parts per million chlorine, and one part per million ammonia. But due to the fact that the chlorinator used for the city water does not control this dose according to the amount of organic matter in the water, it is believed this figure (0.6 ppm) will not be persistent. It will undoubtedly change from time to time, according to the amount of organic matter found in the raw and untreated water.

The work done on the ascorbic acid shows clearly the protective action which the sugar has on the ascorbic acid. In the case where no sugar was added to the chlorinated water containing the ascorbic acid, the loss in the samples treated with 50 parts per million chlorine mounted up to 41.67 per cent, while the control samples with no chlorine lost only 7.25 per cent as shown in Tables II and III.

However when sugar was added there was no apparent change in the ascorbic acid content between the control sample and the chlorinated samples.

Thus the sugar shields the ascorbic acid from the oxidative action of the free residual chlorine. This preservative action could be attributed to the fact that the sugar combines with the chlorine and dissipates it, or forms other substances which have no oxidizing power. Supporting this is the fact that the sirup and the aqueous solution containing the ascorbic acid showed no free or combined residual chlorine immediately after the application of chlorine.

As for the results on the effect of chlorine on the quality of frozen apple slices, and apple-sauce, the data are persistent with the fact that with the application of normal chlorine doses used for sterilizing the water, there was no effect whatsoever that could be noticed by the average consumer.

The organoleptic tests for comparing the quality of the treated and untreated samples were done by having the samples tasted by a panel of tasters, for two or more factors, and having the testers record their rating and comments.

In the case of apple slices, the results expressed in Table IV where no sugar or ascorbic acid was added, show

that oxidation and consequently browning of all the samples took place. When dry sugar was added, no browning occurred. However, in both cases some testers reported that a slight, but not undesirable, chlorine aroma could be detected in the sample treated with 50 parts per million chlorine. But after storing the samples for three and twelve weeks no chlorine aroma could be detected as is shown in Tables VI and VII, but rather a metallic flavor appeared.

When the dry sugar was replaced with a 35 degree Brix sirup containing ascorbic acid, there was no great change between the treated and the untreated samples. And although the samples treated with two parts per million chlorine had a soft texture, yet it had a better flavor than the control samples with no chlorine.

The difference of loss in ascorbic acid shown in Table IX between the control and the samples treated with 50 parts per million chlorine was 0.47 per cent, which is not significant.

As for the apple-sauce, Table X shows the results of the taste-test on the apple-sauce prepared without the addition of either sugar or ascorbic acid. The color remained the same in all the samples, but the apples treated with two parts per million chlorine had a better flavor than the control. A slight chlorine aroma was detected in the samples treated with 50 parts per million chlorine.

When ascorbic acid was added to the apple-sauce made from the Jonathan variety, there was a general improvement in the color, and the apples treated with two parts per million chlorine had by far the best flavor as is shown in Table XI and Figure IV. The lack of sugar however, was unfavored by most of the testers.

The results on the ascorbic acid determination showed that the control lost 14.06 per cent and the samples treated with 50 parts per million chlorine lost 21.21 per cent. This loss is attributed to the fact that the ascorbic acid was dissolved in chlorinated water before being added to the apple-sauce.

Tables XIII and XV show the result of the organoleptic tests on the Delicious and Spitzenburg varieties of apples prepared with the addition of ascorbic acid and dry sugar. The Spitzenburg made a better tasting apple-sauce, and the samples treated with 50 parts per million chlorine had a good flavor.

In general the Spitzenburg processed with 200 mg of ascorbic acid per pound of finished pack, and with the addition of dry sugar at the rate of 12:1, made the best apple-sauce even when treated with 50 parts per million chlorine. However, it should be noted that some of the testers preferred the samples treated with two parts per million chlorine.

There was no significant difference in the ascorbic acid content, as it was dissolved in distilled water before addition to the sauce.

## CHAPTER V

### SUMMARY AND CONCLUSION

1. Work was carried out to find out whether the use of chlorinated water beyond the break-point, in processing frozen apple slices and apple-sauce, had any effect on the quality of the finished product.

2. The break-point was determined in the tap-water, and was found to occur when 0.6 parts per million chlorine was added. This figure however, is not stable and will vary from season to season depending on the organic matter in the raw water.

3. Determination of the loss of ascorbic acid in both aqueous and a 35 degree Brix solution showed that the sugar protects ascorbic acid from oxidation by the residual chlorine.

4. No detrimental effect, which could be attributed to the presence of chlorine was found when frozen apple slices and apple-sauce were tested.

5. The use of 2 parts per million chlorine gave a general improvement of the quality of apple slices and apple-sauce with and without the addition of sugar and ascorbic acid.

6. The use of 50 parts per million chlorine gave a good product of apple-sauce, provided sugar and ascorbic

acid are added.

7. There was no loss in ascorbic acid due to residual chlorine, when added with sugar. However, a loss occurred when ascorbic acid was dissolved in chlorinated water without sugar.

It could thus be concluded from this study that in-plant chlorination of the entire water supply, with doses beyond the break-point, for the processing and freezing of apple slices and apple-sauce has no deliterious effect on the quality of the finished product, but rather improves it.

BIBLIOGRAPHY

1. Bauernfeind, J. C. and Siemers, G. F. Adding ascorbic acid to peaches before freezing. Food ind., vol. 17, No. 7, p. 79, 1945.
2. Baylis, J. R. Elimination of taste and odor in water. McGraw Hill book co., 1935.
3. Brownlee, D. S., Guse, V. C., and Murdock, D. I. In-plant chlorination of cannery water supply. Food packer, vol. 28, No. 1, p. 52, 1947.
4. Chang, S. L. Destruction of micro-organisms. Journal of American water works association. Vol. 36, p. 1192, 1944.
5. Charlton, D. B. and Levine, M. Some observations on the germicidal efficiency of chloramine-T and calcium hypochlorite. Journal of bacteriology, vol. 30, p. 163, 1935.
6. Clement, R. C. and Chamberlin, N. S. Application and control of break-point chlorination in a small water plant. West Virginia university technical bulletin, No. 23, Eng. Expt. Sta., August 1943.
7. Costigan, S. M. A bacteriologist looks at chlorine. Journal of American water works association. Vol. 34, p. 353, 1942.
8. Faber, A. H. Super chlorination practice in North America. Journal of American water works association. Vol 31, p. 1539, 1939.
9. Freidrichs, K. C. Break-point chlorination. Proc. 7th Ann. short course, Louisiana State Univ. Eng. Expt. Sta. bulletin series No. 6, p. 45, 1944.
10. Green, D. E. and Stumpf, P. K. The mode of action of chlorine. Journal of American water works assoc. Vol. 38, p. 1301, 1946.
11. Griffin, A. E. Relation of heavy doses of chlorine in various waters. Journal of American water works association. Vol. 31, p. 2121, 1939.
12. Griffin, A. E. Break-point chlorination. Wallace and Tiernan co. Tech. Pub. No. 213

13. Griffin, A. E. and Chamberlin N. S. Bacteriological improvements by the practice of break-point chlorination. American journal of public health, vol. 35, p. 199, March 1945.
14. Hall, J. E. and Blundell, C. C. The use of break-point chlorination and sterilized water in canning and freezing plants. Supplement to information letter, National canners assoc., Wallace and Tiernan Pub., Feb. 1946.
- 15.a Harris, J. J. Chlorination in the food plant. Continental can co., bulletin No. 13, 1947.
- 15.b Haynes, R. and Mundt, J. O. These chlorine sprays improve processed green beans. Food industries, Vol. 20, No. 7, p. 71, July 1948.
16. Hedgepeth, L. L. Modern water purification. Paper trade, vol. 124, No. 23, p. 51, June 1947.
17. Knox, W. E., Stumpf, P. K., Green, D. E. and Auerbach, V. H. The inhibition of sulphydryl enzymes as the basis of the bactericidal action of chlorine. Journal of bacteriology, vol. 55, No. 5, p. 451, April 1948.
18. Laux, P. C. Break-point chlorination at Anderson. Journal of American water works association. Vol. 32, p. 1027, 1940.
19. McCulloch, E. C. Disinfection and sterilization. Lea and Febiger, 1946.
20. McCulloch, E. C. and Costigan, S. A comparison of the efficiency of phenol, liquor cresoles, formaldehyde, sodium hydroxide against eberthella typhi at various temperatures. Journal of inf. dis. Vol. 59, p. 281, 1936.
21. Merril, C. M., Cameron, E. T., and Williams, C. C. Chlorination studies. The canner, convention number, part 2, vol. 86, p. 61, Feb. 26, 1938.
22. Ritchell, E. C. Chlorination of cannery water supply. Supplement to information letter. National canners assoc., Wallace and Tiernan Pub., Jan. 1947.

23. Rudolphe, A. S. and Levine, M. Factors affecting the germicidal efficiency of hypochlorite solutions. Iowa engr. expt. sta. bull. No. 150, 1941.
24. Stephens, L. T. Sanitation and its maintenance. 27th annual cannery and frozen food packers short course, Oregon State College, Feb. 2-14, 1948.
25. Streeter, H. W. Progress report on studies of water chlorination. Journal of American water works association, vol. 35, p. 421, 1943.
26. Tressler, D. K. and Evers, C. F. The freezing preservation of foods. The Avi publishing co., 1947.
27. Water Quality and Treatment Manual. American water works association, 1941.
28. Watzel, E. Super-chlorination and subsequent de-chlorination. Journal of Ind. eng. chem. Vol. 21, p. 156, 1929.
29. Zuch, T. L. and Somers, I. I. National canners association. Chlorination, research laboratory report. No. 12354B, March 8, 1948.