AN ABSTRACT OF THE THESIS OF

Akkinapally Venketeshwer Rao for the Ph.D. in Food Science
(Name) (Degree) (Major)

Date thesis is presented June 30, 1966

Title THE EFFECT OF FREEZING AND FREEZE-DRYING ON THE PHYSICO-CHEMICAL CHANGES IN NORTHWEST STRAWBERRIES

Abstract approved
/(Major professor)

Preservation of food by freezing is a common method of processing. Of relatively recent origin is the freeze-drying method. This method has several advantages over other methods of preservation, but is not free of problems, one of which is the maintenance of appearance and texture.

In the present study, the effects of freezing, thawing, freeze-drying, and reconstitution on the physico-chemical properties of Northwest variety strawberries with particular reference to textural characteristics were investigated. Very little prior work is reported with regards to the effect of these factors on fruits.

Strawberries were frozen at two different rates of freezing - slow frozen at 0°F and quick frozen in a blast freezer at -20°F. Frozen berries were examined by physical and chemical methods to evaluate the changes. In a separate study, berries were thawed under standard conditions of relative humidity and temperature and the

drip collected for analysis. Thawed berries were examined by both physical and chemical methods. To study the reconstitution behaviour of the berries, they were freeze-dried and reconstituted under standard conditions of berry to water ratio, temperature of water and time of reconstitution. Reconstituted berries and the remaining solutions were then examined. Measurements of the texture, color, total solids, alcohol insoluble solids, pectins, cellulose, ash, and constituents of ash were made on raw, frozen, thawed, and reconstituted berries. The results indicated the following conclusions:

1. An increase in percent soluble solids, pH, and titratable acids and a decrease in total solids and AIS of the berries were observed upon freezing. Slow frozen berries showed more pronounced effects. Smaller berries were observed to change the least. No significant differences were found in the other constituents.

2. Strawberries lose weight upon thawing depending on the chemical composition of the berries. An inverse relationship was observed between weight loss and total solids, AIS, pectic substances, cellulose, ash and mineral content of the berries. With gradual increase in the weight loss upon thawing, there was a progressive softening of the berries. A direct relationship was found between weight loss and the amount of pectic substances, sugars, titratable acids, ash, and minerals found in the

drip. Slow freezing resulted in higher weight loss and smaller berries lost the least.

3. A linear relationship exists between weight loss of the berries upon thawing and the area of the drip. This method offers a convenient and quick procedure for evaluation of the quality of frozen strawberries, with the added advantage of collecting the drip and storing it for further analysis at a convenient time.

4. Ability to reconstitute was found to be related to rate of freezing and size of berry. Quick freezing and smaller berries gave the best results.

5. Direct relationship was found between the degree of reconstitution and total solids, AIS, pectic substances, cellulose, ash, and minerals. The amount of pectic substances, sugar, titratable acids, ash, and minerals leaching out of the berries into the reconstituting solution were smaller and were independent of the degree of reconstitution.

6. Individual berries showed a large variation in their chemical constituents, which was responsible for the differences in the thawing and reconstitution behavior of Northwest strawberries.

THE EFFECT OF FREEZING AND FREEZE-DRYING ON THE PHYSICO-CHEMICAL CHANGES IN NORTHWEST STRAWBERRIES

by

AKKINAPALLY VENKETESHWER RAO

A THESIS

submitted to

OREGON STATE UNIVERSITY

in partial fulfillment of
the requirements for the
degree of

DOCTOR OF PHILOSOPHY

June 1967

APPROVED:

Professor of Food Science and Technology
In Charge of Major

Head of Department of Food Science and Technology

Dean of Graduate School

Date thesis is presented June 30, 1966

Typed by Trudie Vallier

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. Robert F. Cain for his interest, helpful suggestions, encouragement and guidance during the course of this investigation.

Appreciation is expressed to Dr. James H. Dietz for suggesting this research problem, to Dr. Clifford E. Samuels for his helpful suggestions in preparing the manuscript, Mr. Kenneth E. Rowe for his suggestions regarding the statistical analysis, Professor Thomas Onsdorf for his assistance with the photographic work, and to several other members of the staff of this University, particularly those of the Department of Food Science and Technology.

Last, but not the least, the author wishes to express his greatfulness to his family who made it possible for him to come to the United States of America for graduate work.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

LIST OF FIGURES

LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF TABLES (Continued)

LIST OF TABLES (Continued)

THE EFFECT OF FREEZING AND FREEZE-DRYING ON THE PHYSICO-CHEMICAL CHANGES IN NORTHWEST STRAWBERRIES

INTRODUCTION

The preservation of food by subjecting them to temperatures below 10°C (50°F) is a well accepted and commonly used method in industrialized countries. Of the two divisions of low temperature preservation, viz. cold storage and freezing (77, p. 336) the last method is of primary interest to the food technologist. The preservation of food by this method is not new and has been practiced by early man. However, it is only during the last 30 years that it has gained prominence and extensive research in all phases of freezing preservation is underway. As a direct result of such research the quality of frozen foods has been greatly improved.

Freezing, as a method of preservation, has several advantages over other methods; the chief among them is that the fresh quality of the raw product is retained extremely well and is the closest to the fresh product in terms of taste, color, aroma, texture and nutritive value (81). Under suitable storage conditions these quality factors can be maintained in the product from one to several years.

Every year in United States of America alone, huge amounts of food are processed and stored this way. For

some food products, like fruits which are easily perishable and contain soft flesh, this method is particularly suited, since other methods such as canning and dehydration inflict significant changes. During the year 1963 in the United States of America, 234.4 million pounds of strawberries were frozen, an increase of almost 590 percent over the year 1936 (55), indicating its growing importance.

The final quality of foods subjected to the freezing method of preservation depends on several factors, such as the raw material being frozen, conditions prior to freezing, during freezing, during storage, and during thawing. The conditions under which a food is thawed are particularly important, as the time required for thawing a normally rigid food material is much slower than freezing (21, p. 287). Fennema and Powrie (21, p. 286) have shown that the thawing curve was not merely a reversal of the freezing curve and stressed the importance of thawing on the quality of the product. They state: "Not only does thawing take longer than freezing, but an additional concern is the temperature at which it occurs. It is of no small importance that all of the additional time required for thawing is spent at the most damaging subfreezing temperature possible, that is just below the melting point." Physico-chemical and bacteriological changes take place in the product during thawing of fruits and

vegetables which effect the final quality.

Several physical and chemical methods, including measurement of drip, have been used as an index of quality in frozen foods (5, 22, 39, 42, 71, 79, 82). Animal and plant tissues commonly lose fluids, referred to as "drip" or "leakage", during thawing. Kaloyereas (39) was probably the first to develop a reliable method for determining "drip" in frozen fruits. Since then better techniques for collection and measurement of drip, both in fruits and vegetables and meats have been developed and the relationship between this and other quality factors such as texture have been well established (3, p. 45-49; 5, 79). A full understanding of thawing and the changes involved is very essential to produce a product of good quality, without which the beneficial effects of better handling prior to freezing, proper freezing and storage will be of no avail.

Dehydration of food products is probably one of the oldest forms of preservation known to man. Until recently this was accomplished by drying the food products under the sun, which is still practiced in some parts of the world; or drying them under controlled conditions of temperature and other factors. During the past few years interest has been increasing in preservation of food by freeze-drying. This process is simple in principle. The material so dried is first frozen and then the water

vapor removed by means of sublimation, usually under vacuum to increase the rate of sublimation (30, p. 172). Many workers (9, 29, 51, p. 212-214; 56) have shown the advantages of this method over the ordinary high temperature dehydration of biological products. Harper and Tappel (30, p. 172) list some of the undesirable changes following conventional dehydration as: (1) shrinkage of solids, (2) migration of dissolved constituents to the surface when drying solids, (3) denaturation of proteins, (4) case-hardening, (5) formation of hard, impervious solids when drying liquids, (6) undesirable chemical reactions in heat sensitive materials, (7) loss of desirable volatile constituents, and (8) difficulty of rehydration.

Although freeze-drying overcomes in whole or in part most of these undesirable characteristics, yet it is not free of problems. The quality of the final reconstituted product depends on the raw material itself and also on the subsequent processing operations such as freezing, sublimation, storage, and reconstitution. Many workers (18, 30, p. 223; 32, 41, p. 179; 54, p. 8; 26, p. 109-112; 69) have shown the presence of adverse chemical and biochemical activities in freeze-dried products. Fruits due to their highly perishable nature pose further problems. Most of the work done so far with food products deals with meat and meat products. Of the 638 references listed

in the library list of selected references on freeze-drying of food (11) only 17 deal with fruits and four with fruit juices indicating the limited work done in this area. However, in recent years more and more attention is being given to this field both by research workers and food industries.

In view of the importance of strawberry production and preservation in Oregon, the present study was undertaken to determine some of the changes brought about by freezing, thawing, freeze-drying, and reconstitution of Northwest strawberries, and in particular, the changes concerned with the textural characteristics and the chemical basis for such changes.

REVIEW OF LITERATURE

Freezing

Mechanism of Freezing

Freezing is a physical phenomenon and the single most important concept in freezing of biological materials is that freezing involves the withdrawal of pure water from solution and its isolation into biologically inert foreign bodies, the ice crystals (52). Tressler and Evers (72, p. 256) point out that when fruits are frozen the water is crystallized as ice. The number and size of these crystals are important in determining the subsequent quality of the product. These factors have been shown to depend on the rate of freezing (52, 53, 81). Upon trying to define freezing rates some confusion arises owing to the usage of several terms like "sharp", "slow", "rapid", or "quick". Universally accepted definitions for these terms are nonexistent as there is a great deal of variation in the methods of expressing the rate associated with each of these terms. Meryman (52) defines the rate of freezing as "the rate of advance of a freezing boundary in a linear direction through the medium". He further describes that the basis for definition of rapid and slow freezing is the location of ice crystal formation in the cell. Many workers (8, 25, 29,

37, 44, 52, 53, 81) have shown that with slow freezing, crystal nucleation is usually confined to the extracellular space and with rapid rates of freezing nucleation occurs throughout the medium, both as extra- and intra-cellular ice crystal formation. Woodroof (81) pointed out that the shape and size of the ice crystals depends greatly upon the rate of freezing. Through histological studies of strawberries, he showed that the size of most of the ice crystals formed range from the size of the fruit cell - 10 x 15 x 20 microns up to 200 x 400 x 800 microns depending upon the rate of freezing, and also that the shape varied from lenticular, in case of rapid freezing, to sharp crystals of irregular shape, in case of slower freezing. Meryman (52) in trying to explain why extracellular crystallization occurs in preference to intracellular crystallization during slow freezing suggest two possibilities; one, higher freezing point of extracellular material compared to the intracellular, and the second, to a lack of heterogeneous nucleation sites in the intracellular material. Thus, upon slow freezing a vapor pressure differential is created between the extracellular ice crystals and the water present at the cell surface causing the water to migrate out of the cell and deposit on the ice crystals, as the rate of freezing is slowed the opportunity for the water to migrate out is greater (21, p. 258). This phenomenon results in the

formation of a few large extracellular ice crystals. Woodroof (81) showed that such ice crystals draw water from a surrounding distance of 12 or more cell diameters. Contrary to this, quick freezing gives very little opportunity for cellular dehydration and hence favors the formation of intracellular ice crystals.

The nature and location of ice crystals is very important in determining the final quality of the food product. Woodroof's (81) pioneering work gives an insight into this. He showed that in the slow freezing of strawberries, the ice crystal could rupture many dozens of cells surrounding it, thus leaving only ten percent of the cells present with intact cell walls. Rapid freezing of individual berries by direct contact with solid carbondioxide showed more than 50 percent of cells with unbroken walls. Similar results of damage due to slow freezing was obtained by McArthur (48). The plasma membrane was shown to be completely destroyed and in extreme cases, a relocation of the cell contents was evident in case of slow freezing. Upon fast freezing the cell contents seemed to collect in the center of the cell adding strength to the cell wall and resisting injury.

Different food products respond differently to freezing treatments. Plant tissues, which differ from animals by having a large vacuole, thicker cell wall and intercellular spaces with entrapped air (8), behave differently

than meat tissue. Most edible tissues of plants consist of parenchyma cells along with interlacing conducting cells. A fresh strawberry consists of a cone of vascular bundles from where a branch bundle extends upward and outwards to each achene. These bundles consist of cambium tissue giving rise to a white or colorless xylem towards the center of the berry and the highly colored and flavored phloem which makes up most of the edible portion of the fruit. They are made up of true parenchyma cells of varying sizes and shapes depending on the intercellular contact and pressures, the ones farther away from the bundles are nearly spherical with large intercellular spaces between them which are filled with gases. These spaces form the site of ice crystal nucleation and growth during freezing of the tissue (21, p. 307; 81). Parenchyma cells consist of thin walls composed of a matrix of cellulose and hemi-cellulose filled with an aqueous fluid containing pectic and other compounds (23, p. 6-7). The cell walls of the parenchyma tissue are made up of three layers: "primary wall", "secondary wall" and "middle lamella". The term "compound middle lamella" is used to refer to both the middle lamella and primary wall of two cells, as differentiation between them is very difficult (20, p. 37). Due to the thin walls of the parenchyma cells they are easily ruptured by ice crystals. Also found in the parenchyma walls are cavities called "pits"

(21, p. 307), which are covered with a very thin, semi-permeable membrane which allows low molecular weight compounds and ions to migrate between cells. This membrane can be easily broken by slight pressures as caused by ice crystal formation during freezing, resulting in a diffusion of cell solutes reducing cell turgor and collapse of the tissue.

Other constituents of the cell wall which are responsible for damage due to freezing are the presence of water itself, in both the free and bound form (12, p. 72), and the presence of polysaccharides such as pectins, cellulose, and hemicellulose which are highly hydrophilic.

In addition, parenchyma cells have prominent vacuoles, which contain water as a major constituent, but also contain sugars, organic acids, proteins, tannins and anthocyanins (21, p. 310). They are separated from the cytoplasm by a vacuolar membrane called the tonoplast. Woodroof (81) noted that upon freezing of fresh tissue, disruption of the intact vacuole occurred. Yeast cells, cooled rapidly to -30°C, showed the lack of vacuoles in contrast to the untreated living cell as observed by Mazur (50), and this was closely correlated with the survival of the yeast cells upon thawing. Analysis of the drip from thawed strawberries showed that not only water but constituents like sugars and anthocyanins were also present.

Changes During Freezing

A highly complex food product consisting of numerous compounds such as proteins, carbohydrates, pigments, enzymes, and salts, undergoes many alterations of physical, chemical and biological nature when frozen. The nature and extent of such changes are important in controlling the quality of the final product.

Physical Changes. Joslyn and March (37) have pointed out that the physical changes that occur during freezing depend mainly on ice formation and osmotic action. Woodroof (81) points out that the movement of water in and out of cells, upon freezing and thawing, involves a diffusional process rather than osmotic process with the cell wall acting as a passive filter. Such physical changes include changes in volume, drained weights and texture. Water upon freezing was observed to increase nine percent in the volume (37). Rates of freezing affect such changes in a food product like strawberry which contains 84 to 89 percent water and also air in the intercellular spaces. When strawberries are frozen at relatively high temperatures, ice is first formed in the intercellular spaces and the fruit contracts in volume, similar contractions in plant materials during freezing have also been observed by Levitt (44). When strawberries are subjected to rapid freezing an expansion in volume

was observed. The authors found an increase in volume of three percent when whole strawberries were frozen rapidly and an increase of four percent with whole raspberries. Crushed strawberries gave an increase of 8.2 percent in the volume. Such expansion of biological material, due to the expansion of water upon freezing together with the contraction of other nonaqueous constituents, results in high local stresses which produce mechanical damage to cellular material (21, p. 274). Callow (7) working with frozen beef demonstrated internal pressures of up to 200 psi.

Decrease in the weight of frozen fruit during and after thawing has been discussed by Joslyn and March (37) and is attributed to the water separated as ice during freezing, which is not reabsorbed during thawing, and also to the leakage of fluids through injured and disrupted tissue by freezing and other osmotic actions of the added sugars and sirups. They showed a decreasing loss of weight in beans, peas, and asparagus with increased rates of freezing. The loss in weight as a consequence of cell disruption and leakage of fluids was closely related to the textural characteristics of the frozen food material upon thawing. These authors (37) did not find any direct relationship between textural changes and weight losses, and showed that, in general, the greater the loss of weight the more severe was the change in texture. They

also showed a relationship between the degree of retention of original shape and turgidity and loss in weight. Woodroof (81) pointed out that the flabiness of frozen berries upon thawing may be due to withdrawal of more water from cells into intercellular spaces during freezing than is reabsorbed on thawing, even though no cell walls are broken. He measured the texture of both frozen and thawed individual strawberries by subjecting them to a pressure between two flat surfaces and compared various treatments as to their effect on texture. He reported his data as the number of grams required to crush the berries. Berries frozen according to the immersion method of Taylor (70) and examined after one month and a year required 167 to 168 grams to crush them. Berries which were similarly frozen by the immersion method in 12 ounce package and allowed to thaw and then refrozen, required 23 grams of pressure. Based on these data he concluded that intimate contact with the refrigerant was much more important than low temperature as such and an extremely low temperature was less desirable for the preservation of firmness than was moderately low temperature with direct contact.

Lee, Gartner and Whitcombe (43) working with strawberries, raspberries and sliced peaches; and Fieger et al. (22) with strawberries observed only slight differences in the physical, chemical, and organoleptic properties of the products when different rates of freezing were

utilized. Other physical changes commonly observed upon freezing are cell plasmolysis and desiccation.

Chemical Changes. The chemical changes that occur during preparation, freezing, and thawing are important in controlling the quality of the final product. These chemical changes include irreversible denaturation of proteins, altered mass action relationship, hydrolysis of pectins and sucrose due to the presence of hydrolytic enzymes, changes in color due to oxidation, and changes in flavor.

Formation of ice crystals in the tissue upon freezing results in a high salt and substrate concentration owing to the removal of water to form ice (21, p. 270; 52, 53, 74). The extent of concentration depends upon the characteristics of the product, rate of freezing and the final temperature. Penderson and Beattie (59) observed that slow freezing caused greater degree of solute concentration than rapid freezing. An inverse relationship between solute concentration and temperature in the subfreezing range was observed.

Such concentration changes usually lead to changes in other factors which are described by Fennema and Powrie (21, p. 270) as changes in "pH, titratable acidity, ionic strength, viscosity, osmotic pressure, vapor pressure, freezing point, surface and interfacial tension, and oxidation-reduction potential". All these changes

excepting the changes in viscosity are associated with changes in the electrolytes. Van den Berg (74) working with frozen cauliflower, green beans and tomatoes measured the changes in pH during storage at -10° and -18°C. He observed changes in pH of 0.3 to 2.0 pH units in all products during the first three months of storage. However tomatoes did not show appreciable changes at -10°C but a sharp increase of 1.5 pH units was observed after 20 days at -18°C returning to its initial value of 4.0 after 10 to 20 days. The pH changes in various products were attributed to the type of salt which precipitates. Tucker (73) observed a decrease in pH value of up to 0.3 pH units and a marked increase in viscosity and titratable acidity in several fruit juices during freezing concentration.

Other than the electrolytes, concentration of non-electrolytes, especially the hydrophilic colloids, during freezing have pronounced effects. Removal of water from such hydrophilic colloids will result in an increase in the viscosity. Joslyn and Marsh (38) reported that relatively little loss in pectin due to hydrolysis occurred upon freezing of blackberry juice extracted by crushing the berries, boiling and pressing in a hand press. However, the results obtained were not consistent. Diehl et al. (16) showed a loss in pectin content of raspberries and strawberries. They believed that the loss was primarily due to the longer period of time required to freeze

the large quantity of fruit mass. In instances where sucrose was added prior to freezing of strawberries and raspberries a considerable inversion of the added sucrose occurred (38). The percent of sucrose inverted was shown to increase with decrease in the amount of added sugar and increase upon prolonged thawing periods. Perkins (60) observed changes in sugar and amino acids of fresh-frozen wheat leaves at -20°C. In some varieties sucrose content of the leaves fell to less than five percent of the original, whereas in others, there was no change in the sucrose but the glucose or fructose content increased or decreased in a random fashion. A doubling of the free amino acid content during the first three months was also observed, indicating a possible breakdown of the proteins. Newton and Brown (57, 58) believed that protein dehydration was the primary cause of its precipitation. They observed higher freezing temperatures to be more determental than lower ones due to the more rapid coagulation at lower temperatures which did not allow colloidal dehydration to proceed to the damaging stage, as was the case when freezing took place more slowly. They observed the protein precipitation by freezing to be irreversible.

Upon freezing of a food material at lower temperatures a decrease in the chemical and enzymatic reactions such as acid hydrolysis, enzymic hydrolysis, metabolism, microbiol growth and oxidation takes place, however the product is not

free from other forms of deterioration, off-color, and off-flavor production. Joslyn and Marsh (38) observed changes in color of fruits when frozen and thawed, and suggested that the injury caused to the tissue upon freezing allows mixing of the cell contents with consequent rapid oxidation upon exposure to air. However, all fruits studied did not show an equal degree of deterioration. They observed that apples, apricots, avocados, peaches, pears, light color-cherries, plums, and grapes are subject to a more severe color deterioration than berries. Peaches frozen in solid carbon dioxide darkened more rapidly and severely than those frozen in air at 0°F, both during freezing, storage, and thawing. The loss of flavor in the berries was shown to be quite significant.

Food products when frozen, undergo further changes during the period of storage, as the food in the frozen state is not inert. The rate of deterioration depends on the temperature of storage, thus as the temperature is decreased the rate of deterioration also decreases. Fennema and Powrie (21, p. 315) in summarizing the changes taking place during frozen storage of food product pointed out that they are mostly chemical and physical in nature rather than bacteriological. They describe the chemical changes as "degradation of chlorophyll and ascorbic acid, denaturation of animal tissue proteins and lipoproteins, hydrolysis of phospholipids, oxidation of

lipids, browning, loss of cloud in juices, and flavor deterioration." Some of the physical changes during frozen storage are "gelation, diffusion and recrystallization". Guadagni, Nimmo and Jensen (28) working with frozen strawberries showed that the rates of deteriorative changes occurring at temperatures above 0°F vary exponentially with temperature and such changes are the direct result of the sum of all the time-temperature conditions the product encounters. Guadagni and Nimmo (27) studied the effect of fluctuating storage temperature on the quality of frozen strawberries and raspberries. They report that fluctuating temperatures do not cause important chemical, physical and organoleptic changes in the fruits other than those which can be predicted on the basis of steady temperatures. Similar observations are also reported by Willis et al. (80) and Hustrulid and Winter (31).

Freezing and Thawing

When a food product is thawed a certain amount of fluid is commonly lost. The amount of fluid lost depends on such factors as the type of product. Plant tissues with their rigid cellular structure are usually flabby upon thawing while in animal tissues, the effect is not so severe (21, p. 317). Woodroof (81) reported that the leakage from plant tissues which has been frozen

and thawed is almost entirely due to the ruptured cell walls. He observed a fairly good relationship between the number of ruptured cells and the amount of leakage. He further stated that a direct relationship exists between the loss of fluids by the cell to the outside, the loss of original turgidity and the degree of fragmentation of the precipitated protoplasm. He pointed out that the water movement in and out of cells upon freezing and thawing is a diffusion phenomenon as the movement of water is rapid and occurs in dead cells as well as live ones. This phenomenon is reversible when the cell walls are intact and not broken. Joslyn and Marsh (37) measured the loss in weight of strawberries with increased concentrations of invert sugar and cane sugar. They observed increase in the weight loss, however, the weight lost was not as large as would be expected from the molecular size of the two sugars. They concluded that other factors besides osmotic pressure are involved in loss of weight upon thawing. In a separate study (38) they pointed out that the loss of weight in fruits which are stored in sirup at room temperature is entirely due to the withdrawal of water from the fruit tissue by osmosis. However, when fruits are frozen without added sirup the loss of weight could be due partly to mechanical injury of the tissue, partly to the loss of semipermeability of the cells and partly to changes brought about in the gels

present to a more dehydrated sols and gels. They conclude by saying that"the loss of weight that occurs upon thawing fruits is due both to the osmotic action of the sugar or sirup and also due to the mechanical injury to the tissue". Diehl et al. (16) suggested that the loss of weight was entirely due to the osmotic action of the sugars. Joslyn and Hohl (36) reported that the loss in weight of frozen fruits occurred both during and after thawing and was caused by the water which separates out as ice during freezing and was not reabsorbed during thawing, the leakage of fluids through tissues, and the osmotic action of the sugar or sirup. Weier and Stocking (77, p. 333) provided further evidence to the reabsorption theory of Joslyn and Hohl (36) and stated that the amount of water reabsorbed by the cell contents upon thawing differs greatly and the determining factors are the number of intact cells and cell contents. They pointed out that peas containing large amounts of storage starch are firm upon thawing due mainly to the closely packed starch grains and their water absorbing properties. Kaloyereas (39) reported a definite relationship between the amount of drip and the bound water of the tissues. He treated pumpkin which contained about 2.46 percent bound water, with substances such as sugar, pectin, gelatin etc. which would effect the capacity of tissues for binding water. He demonstrated an inverse relationship between the amount of bound water and

drip. Pumpkins which were soaked in 55 percent sugar solution for 24 hours gave 8.64 percent bound water and a drip measurement of 0.5 ml for 100 grams of material. Fruits and vegetables which contain less than six percent bound water (14) show greater damage. Fennema and Powrie (21, p. 235) pointed out that bound water influences reactions during freezing and also was an important factor in hindering crystal formation.

Drip as a Quality Measure of Frozen Fruits

A search for convenient and reliable method of measuring the quality of frozen foods has long been underway. Several factors have been used in the past. Tressler (71) described the use of a method to measure the vitamin C content and the peroxide value of the fat along with the count of microorganisms. Lee (42) employed the determination of alcohol insoluble solids in frozen asparagus and correlated it to the toughness of the product. However most of these methods were either too involved or too time consuming. Joslyn and Marsh in 1933 (38) described a method of measuring the free drip or loss in weight of the product during thawing as an index of the change in the colloidal state and degree of disorganization of flesh products. They measured the drip of a number of fruits by allowing them to thaw overnight for about 16 hours and then drained two minutes over a 1/8 inch mesh screen (38).

Their results did not show a definite relationship between quality and drip. Fieger, Dubois and Koloyereas (22) reported their data on drip collected in milliliters. Their work was not conclusive owing to the great variation they obtained between similar samples. They concluded that these variations were due to the lack of proper techniques in determining the drip. They obtained changes in pH and refractive index values of the drip during the time of thawing and pointed out that such abnormal conditions of the product were due to deterioration and fermentation. Later, in 1947, Kaloyereas (39) working with various fruits, overcame the problem of deterioration and fermentation by thawing the frozen product under petroleum ether or Skelly Solve B which was previously saturated with water. After allowing the samples to thaw for a period of 24 hours they were drained over a screen and the aqueous phase read directly in a graduate cylinder. By allowing the frozen product to thaw for various lengths of time he observed that a state was reached when practically no more drip was obtained from the product. He obtained comparable results using this method.

Woodroof and Shelor (82) working with strawberries, blackberries, raspberries and peaches, also used drip as an index of quality. Their technique involved weighing duplicate 125 gram samples into a Buchner funnel and placing them in a rack over graduate cylinder. The

apparatus was then kept at 35°F during the test, which lasted for 24 hours from the time the last ice melted. They minimized deterioration and fermentation spoilage of the product and collected the drip samples without any alterations.

Wierbicki and Deatherage in 1958 (79) studied the water holding capacity of fresh meats by pressing a 400 to 600 mg sample of fresh muscle on No. 1 Whatman filter paper of constant humidity in a specially constructed press which was operated under 500 psi pressure for one minute. They later measured the area of the paper wetted by the expressed juice. They observed a direct proportionality between the area measured and the weight of water in the pressed juice. This method gave a reproducibility of result within two to five percent.

Briskey et al. (5) also measured the expressible water of eight pork muscles. Their apparatus consisted of plexiglass plates which were placed between two one-quarter inch aluminum sheets, which in turn were connected to a steel frame, hydraulic jack and pressure gauge. Just prior to the measurement of sample, a filter paper sheet was singularly removed from a humidifier and placed between the plexiglass plates. The sample was immediately placed on the midportion of the paper. A pressure of 4000 psi was then applied for a period of five minutes. They measured the muscle and water (juice) areas with a

polar planimeter and the amount of expressible water was recorded as percent of the total moisture content of the original sample. They obtained significant correlations between expressible water, pH and muscle class for the two pork muscles studied. They reported that the measurement was influenced by the type of paper used, treatment of paper, amount of pressure and the duration of pressure.

This method offered a convenient and quick procedure for testing the quality of meat. It had the added advantage of collecting the juice and storing it to be measured later at a convenient time without any changes. This method has been used in the current study with certain modifications owing to the different nature of the product under study.

Changes During Thawing

Fennema and Powrie (21, p. 286) pointed out that thawing of a frozen food usually takes a longer time than freezing. They further stated that all of the additional time required for thawing is spent at the subfreezing temperature just below the melting point which also is the most damaging temperature in the subfreezing range. The faster a food product passes through this critical temperature range the less will be the damage to the quality of the product. The rate of thawing acquires an added importance. Achieving rapid thawing is made difficult by

the fact that thawing of normally rigid food materials is slower than freezing and the temperature differentials during thawing are usually less than during freezing (21, p. 287). To add to this, frozen foods are usually thawed by persons who are unaware of proper thawing procedures. The controlling factors in the rate of thawing a food material as described by Fennema and Powrie (21, p. 278) are: (1) the temperature differential between the product and the heating medium, (2) the method of heat transfer to, from, and within the food product, (3) type of package and its size and shape, and (4) the size, shape and thermal properties of the product itself. This is further complicated by the fact that the temperature differential during thawing are subject to limitations. Food materials which are consumed uncooked, such as fruits, are thawed at relatively lower temperatures to avoid heat damage to the product and also to minimize the growth of undesirable microorganisms.

The final quality of a frozen food depends not only on the quality of the raw material itself and the handling prior to freezing but also on the treatment it receives at every stage of the freezing operation. Thawing being the final operation prior to consumption in case of fruits, it reflects the sum total of all the deterioration in quality of the product. A better understanding of the changes taking place during thawing is essential

in controlling the quality without which the beneficial effects of proper handling and freezing will be of no use.

Physical Changes. Restoration of the original properties of frozen fruits and vegetables upon thawing is seldom complete. However, food products vary considerably in this respect. Plant tissue with its normally rigid character undergoes more severe changes upon thawing than animal tissue. The physical changes that occur upon thawing a frozen food product involves changes in volume, weight, shape, and texture. Joslyn and Marsh (37, 38) reported that a decrease in the weight of frozen fruits occurs during and after thawing and depends on the kind and character of the fruit. The method of packing also has an important bearing. They pointed out that in general the loss in weight was greater when the fruits were packed in water and the least in sirups. Strawberries packed in water and allowed to thaw overnight for 16 hours and drained two minutes over a 1/8 inch mesh screen, showed a weight loss of 46.4 percent whereas those packed in 40° Balling sirup showed 16.8 percent weight loss. This situation was not true when strawberries were thawed at room temperature, where the fruits packed in water or dilute sirup gained weight and those packed in concentrated sirup lost weight. Osmotic action of the sirup plays an important role in the extraction of water from the fruit resulting in a high weight loss. Diehl et al. (15)

also reported similar findings. They observed an increase in the percent soluble solids in the fruit when they were packed in increasing concentration of cane sugar, indicating an increase in the amount of water extracted. Aref (3, p. 33) working with loganberries and peaches showed that both fruits lost weight rapidly up to four hours after the start of thawing as measured by the amount of drip collected and eight hours later the fruits had reached their maximum drip.

Besides the changes in the weight of the product, during thawing they occupy considerably less volume than they did prior to freezing. This is attributed to the structural damage, loss of intercellular gases and the loss of water by diffusion in the presence of added sugar or sirup (36). Joslyn and Marsh (37) observed a correlation between the degree of retention of original shape and turgidity to the loss in weight. The greater the loss in weight, the more severe was the change in the shape of the product.

Upon thawing, plant tissue becomes flabby which effects the texture. In fruits and vegetables, firmness of the product upon thawing is an important criterion. Weir and Stocking (77, p. 335) describe four factors which are involved in the firmness of living fruits and vegetables used for freezing: (1) the turgidity of living cell, (2) the type and amount of cell contents, (3) the nature of

the cell wall, and (4) the middle lamella. Changes brought about in any of these factors would effect the textural quality of the product upon thawing. In general there is a complete loss of crispness upon freezing and subsequent thawing, the juicy portion of fruits become very soft, whereas the fibrous portion in case of vegetables, becomes tough.

Rate of freezing has been shown by many workers (37, 38, 43, 52, 81) to effect the quality of the frozen product upon thawing. Woodroof (81) reported that the loss in weight of quick frozen sliced tomatoes, Hale peaches, bananas and pears was less than that for similar products which had been slow frozen. Joslyn and Marsh (37, 38) observed similar behavior in string beans, peas, white asparagus, and tomatoes. Peaches that were slow frozen were shown to lose slightly more than 50 percent in leakage while similar lots quick frozen with solid carbon dioxide lost 31 percent (81). Woodroof and Shelor (82) obtained a decrease of 29 percent in the resistance to crushing of strawberries stored at -10°F for 12 months and an increase of 17 percent in the amount of leakage. Those berries stored at 0° to 10°F were poorer in quality than the ones stored at a constant temperature of 10°F. Kaloyereas (39) stated that in general more rapid freezing causes decreased formation of drip and renders the product firmer after thawing. Storage, on the other hand,

increased the amount of drip. He further explained that the effect of quick freezing upon the drip is not always the same with different products, so even quick freezing does not always reduce the drip as was shown for grapes, pears and potatoes. A definite relationship between the amount of drip and the bound water of the tissues was observed for the products of high bound water content. Low freezing temperatures effect the bound water - free water equilibrium to a greater extent than do high freezing temperatures, consequently, quick freezing would not be as beneficial for such products as for those of low bound water content.

Sistrunk et al. (64) observed that a slower rate of freezing increased the firmness of sliced strawberries as measured by the shear-press, although the viscosity of the sirup decreased. They explained their observation by stating that since more water was withdrawn from the fruit when frozen slowly, it caused a toughening of the tissues, thus firming the slices. In another study Sistrunk et al. (65) studied the relationship of field and processing factors to the quality of frozen strawberries. The rate of freezing did not significantly influence either the firmness or the amount of whole slices retained on a one-half inch screen. Webster, Bensen and Lucas (75) have pointed out that quick freezing of strawberries by liquid nitrogen immersion, considerably improved their

quality compared to other methods. In contrast to these observations Lee, Gortner and Whitcomb (43) studying the effect of freezing on strawberries, raspberries and sliced peaches concluded that very slow, very rapid and intermediate rates of freezing does not result in marked differences in vitamin content, appearance, flavor, or texture and in their retention during a six month storage period at 0°F. They prepared photomicrographs of the frozen samples which did not show any appreciable variations for the different rates of freezing.

Chemical Changes. Deteriorative chemical changes will occur during and after thawing. Higher temperatures will normally result in faster rates of changes. The most common temperature used for thawing frozen fruits is room temperature. Vegetables and small cuts of frozen meat can be cooked without thawing them previously. The quality of the product is at its maximum when thawing is just complete and any further delay in consumption would invariably result in the loss of quality. Thawing is usually preceeded by frozen storage and freezing of the product, thus any damage inflicted during these operations cannot be overcome regardless of how well the thawing operation is performed. Tressler and Evers (72, p. 339) mention the difficulty of differentiating the changes due to freezing and those due to thawing. Joslyn and Marsh (38) describe the chemical changes that occur during

preparation, freezing and thawing as changes in composition such as hydrolysis of pectin and sucrose by the hydrolytic enzymes, changes in color and flavor due to oxidation, by oxidizing enzymes, and changes in flavor due to anaerobic respiration, and other causes. These changes are more pronounced during the thawing period owing to the injury to the tissues during freezing. Kaloyereas (39) observed a direct relationship between the quality of food material as measured by the loss of weight in the form of drip and the water holding capacity of the hydrophilic colloids. Joslyn and Marsh (38) suggest a change in the properties of gels which are present in the fruits to a more dehydrated form. They also mention the loss of semipermeability of the membrane which undoubtedly is due largely to the changes in the properties of protein. No work has been reported in this area.

Freeze-drying and Reconstitution

Many workers (9, 29, 30, p. 172; 51, p. 212; 56) have reported the advantages of using freeze-drying techniques for preservation of foods. Among the advantages listed are the increase in storage stability and acceptance (9, 34). Meryman (54) points out that freeze-drying when carried out under proper conditions permits the maintenance of morphology, solubility and chemical integrity of the product as opposed to drying from a liquid

state. Harper and Tappel (30, p. 173) and Weir (78) describe that keeping the material frozen until it is dry minimizes shrinkage and migration of dissolved materials and inhibits chemical reactions. In addition to these, the low temperature further minimizes loss of volatile constituents. The dry product due to its porous nature reconstitutes faster. Jackson, Richter and Chichester (34) report that when fruit products are reduced to below five percent moisture, a three fold increase in storage stability is obtained at normal storage temperatures. Chichester (9) working with peaches observed that freeze-dried samples were superior in color retention in comparison with conventionally dehydrated peaches, when stored for 120 days at 110°F. Nemitz (56) showed that freeze-dried peas, beans, asparagus, carrots, celery, cauliflower, and mushrooms manifested much faster water uptake upon reconstitution than when they are warm-air-dried. In onions, no differences were observed between the two methods of drying. Hanson (29) also lists similar advantages and goes further to state that freeze-dried products are almost unchanged in flavor, texture and nutrient content because of low temperature of processing.

The primary purpose of freeze-drying is to produce a product which will be stable on storage at normal ambient temperatures and upon reconstitution be as similar to the original product as possible. This depends on several

factors such as the nature of the raw material used, type of freezing, dehydration treatment, length and conditions of storage, and finally on the method of reconstitution itself. Fruit and fruit products which are high in sugars, salts, acids, and flavor components represent more sensitive materials and require greater care in freezing and drying in order to retain these desired organoleptic properties. Burke and Decareau (6, p. 3) stress the importance of the freezing step in freeze-drying of food products. They state that this step may be as important as or even more important than the drying step. Rate of freezing bears an important effect on the quality of the dried products and their reconstitution properties. There is a difference of opinion amongst workers as to the best freezing rate for products that are to be freeze-dried. Smithies (67, p. 192) reports that rapid freezing gave products upon drying which rehydrated slowly and were tough and drier in comparison to samples frozen slowly. Rolfe (62, p. 220) pointed out that fast freezing caused fine pores upon drying and made rehydration of the product more difficult owing to the resistance of water by the air trapped in them. McIlrath, Dekazos and Johnson (51, p. 211) on the other hand working with Swiss chard obtained best rehydration of freeze-dried samples when freezing was rapid. Luyet (47, p. 196-203) described in detail the effect of freezing rates on the structure of

freeze-dried material. His work was with muscle tissue. Upon freezing he obtained a relatively coarse, spongy structured freeze-dried tissue. Rapid freezing gave a finely porous structure of relatively soft consistency and without any appreciable deformation. He also measured the width of the cavities, which are the spaces previously occupied by ice, for four different rates of freezing accomplished at -150°C, -50°C and -29°C. The width measurements corresponding to these rates obtained were 2, 5, 10 and 150 microns. Based on this observation he concluded that a gradual increase in freezing velocity provided ice crystals of gradually decreasing size until a point is reached at which no ice can be detected. The structure of the freeze-dried tissue will affect the rate of rehydration. Air in the very small cavities in the rapidly frozen tissues is expelled quickly, the air in the cavities of intermediate size may cause an obstacle to the completion of rehydration, while the air in the very large channels formed in slowly frozen tissues is expelled at once by the onrush of the flooding water. McIlrath and his coworkers (51, p. 211) working with Swiss chard leaf blades obtained the best quality product, with respect to the degree to which it rehydrated, in rapid frozen samples.

Reconstitution of dehydrated foods has long been used as a factor for evaluating their quality. The terms

"reconstitution" and "rehydration" are used synonymously; however, the former describes the process more accurately than the later as it includes recovery of form and texture and not merely the uptake of water (26, p. 124). The quantity of water taken up by a food product during reconstitution is an important quality measurement. Several factors effect the reconstitution process of food products. Luyet (47, p. 207) describes the factors which pose the main obstacles for successful reconstitution as water repellent surfaces, impermeable membranes, and trapped air bubbles which account for about nine to 26 percent of the total volume of the tissue. Dalgleish (13) also mentions the importance of gases which are present in the porous dry material which cause a delay in reconstitution of sizeable pieces of food products. Simpson and his coworkers (63) described the factors for dehydrated fruits and vegetables as the period of soaking, temperature of water, ratio of water to product, rate of heating, and length of cooking period. Anerback and his coworkers (1) studied the effect of several factors such as sample thickness, rehydration fluid temperature, pH, osmotic pressure and vacuum rehydration, on the reconstitution level of freeze-dried muscle tissue. They observed that as the thickness of the sample increases the rate and level of rehydration decreases. The addition of sodium chloride to the rehydration fluid had an adverse effect

on reconstitution, the best results were obtained with demineralized water. Temperature of the solutions had no effect, however, the greatest rehydration occurred in solutions where the pH was near 7.0 regardless of the osmotic pressure. Rehydration under vacuum was both faster as well as to a higher level. McIlrath and his coworkers (51, p. 212) did similar work with Swiss chard. They observed that freeze-dried tissue absorbed a great portion of its moisture against a very high osmotic pressures than did tissue dried in the vacuum oven. In a solution with an osmotic pressure of 365 atmospheres freeze-dried chard took up about 79 percent of the total water it had a capacity to absorb, while oven dried tissue absorbed only about 67 percent. They suggested that the greater rehydration of the freeze-dried material correlates with the maintenance of the free polar groups in the tissue such that the water binding capacity was not lost. They also studied the rehydration characteristics of various cellular components and observed that none of the components rehydrated to a level comparable to that of the intact tissue and that method of drying the components did not show any differences. They concluded that maintenance of the integrity of cellular structure during the drying process was important in determining the degree of rehydration.

Changes During Freeze-drying and Reconstitution

Changes which occur in the product during dehydration and reconstitution may be considered on a physical, chemical and microbiological basis. As the name suggests freeze-drying in its simplest form is essentially a two step process, that is, freezing of the product followed by dehydration in a frozen state. In the final form, freeze-dried products are reconstituted prior to consumption. The final quality of the product is a cumulative effect of various steps involved. Meryman (54, p. 8) describes the injuries caused to the product during freezing as mechanical and chemical. According to his definition mechanical injury is "physical rupture or displacement of tissue or cell components as a result of the growth of ice crystals". In tissues with a rigid cell wall such as plant tissues, mechanical injury caused by the formation of ice crystals during freezing is an important factor. The major chemical effect is that of solute concentration due to the removal of water to form ice. He further outlines the injuries caused to the product during the drying process due to the removal of free water. When a cell is frozen prior to drying all free water is removed, which results in a maximum concentration of solutes. The drying operation is then carried out with maximum potential for chemical injury. In addition to this when

drying is extensive, the bound water of the product is also removed which causes changes in the configuration of proteins and other constituents of the cell. During reconstitution the concentration of solutes decreases rapidly but not uniformly (54, p. 11) resulting in different osmotic pressure gradients between the reconstituting solution and the product as well as between different parts of the product itself. The large forces involved due to these osmotic imbalances could cause disruption of less soluble components of cell. Failure to replace the bound water properly and immediately upon reconstitution can also create an injurious effect on the product. These deteriorative changes during processing of the product become more pronounced during storage. In fruits, information on the storage stability is not extensive. The early work on peaches and apricots (30, p. 223) shows that these products have a superior storage stability when sulfured before freeze-drying. A storage stability of more than six months at 100°F was observed. Harper and Tappel (30, p. 224) and Weir (78) describe the main deteriorative reaction in dried fruits as active carbonyl-amine browning. Freeze-dried peaches in storage show an increase in brown color and a corresponding increase in carbonyl compounds. Ingles and Reynolds (32) detected mono-esters of glucose, fructose, sorbitol and sucrose with malic and citric acids in browned freeze-dried

apricots and peaches. Anet and Reynolds (2) examined the water soluble constituents of apricot purees before and after storage for 4 to 16 months at 25°C and 70 percent relative humidity. The stored samples contained, in addition, esters of glucose and fructose, unknown products formed from the reaction between glucose and aspartic acid and also glucose and asparagine, mono-esters of malic acid with sucrose, glucose and fructose, compounds formed from ammonia and glucose and also traces of sorbitol mono-ester of malic acid and some sugar mono-esters of citric acid. They observed that the loss of free amino acids or organic acids was equal on a molar basis to the amino acid-deoxy fructoses and sugar esters formed.

The deteriorative reactions of dehydrated foods in storage have been described as oxidative and nonoxidative (26, p. 109). In food products such as meats and fish where fat is an important constituent, oxidative rancidity due to autoxidation of the unsaturated compounds is an important factor. Dehydrated meats have been shown to develop noticeable rancidity within a week or two of exposure to the air. Similarly, dehydrated potatoes which are low in fat content develop a rancid odor when stored in air (26, p. 109; 41, p. 179). Oxidation is also important in discoloration of pigments. Dehydrated carrots were shown to lose color due to oxidation of carotenoid pigments (26, p. 110). Similarly, it has been shown that

the pink oxymyoglobin of freshly freeze-dried beef is rapidly oxidized by atmospheric oxygen to the brown metmyoglobin (69). In addition, due to oxidation, the ascorbic acid is rapidly lost in green vegetables and fruits. Among the major nonoxidative deterioration reaction is the development of brown discoloration. In food products such as fruits, which are not heat processed prior to freeze-drying, the enzymes survive the freeze-drying process. Thus apples, peaches, pear slices, and other fruits along with unblanched mushrooms darken upon freeze-drying and reconstitution (6, p. 73). Draudt and his coworkers (18) working with freeze-dried and frozen peaches at various moisture levels measured the activity of polyphenol oxidase, peroxidase, sucrase, α and β amylase, pectinesterase and ascorbic acid oxidase in relation to browning. They observed that upon drying and also during the early stages of storage α and β amylase, pectinesterase and ascorbic acid oxidase were destroyed. Sucrase activity was detected throughout the storage period at all moisture levels. Prior treatment with sulfur dioxide seemed to inhibit sucrase, polyphenol oxidase and peroxidase.

MATERIALS AND METHODS

The purpose of this investigation consisted of studying the effects of freezing, thawing and freeze-drying on the physico-chemical changes in Northwest strawberries, with particular reference to the texture.

The investigation of the effect of thawing and reconstitution were carried out on the basis of an individual berry for a better understanding of the major factors involved in textural changes.

Raw Material

Northwest strawberries used in this study were obtained from a local commercial freezing plant and represented those of normal physical properties as used in commercial packs. Three replications of the fruits were studied.

Processing Methods

Freezing Process

The berries were precooled overnight at 35°F (1.7°C) prior to processing. Then they were washed in a McLauchlan vibratory washer, sorted to remove dirty and damaged berries on an Allen vibrating table and drained on eight mesh stainless steel trays to remove excess water before freezing. The berries were then evenly spread on the

screens which were arranged on a portable cart with a clearing of five and one-half inches between trays. The cart was then wheeled into freezing rooms at 0°F (17.8°C) and -20°F (-29°C) blast freezer. For measuring the freezing rates three berries were selected on the basis of their weight. Small berries ranged in weight from three to seven grams, while medium berries from seven to nine grams and large berries weighed greater than nine grams. Fine gauge thermocouple wire made of copper and constantan were used. One end of the wire was carefully inserted into the berry from the calyx end so that the temperature at the center of the berry could be recorded. Thermocouples attached to a Brown Electronik recorder were used to measure the freezing rates.

The frozen berries were then sealed in a polyethylene plastic bag, which was placed in a can, sealed and stored in the same freezing room.

Freeze-drying Process

The frozen berries were subsequently freeze-dried in the pilot plant of the Department of Food Science and Technology, Oregon State University. The individually frozen berries were evenly spread on stainless steel trays, which were placed in a chamber of 18"x24"x48" dimensions connected to a Stokes Microvac high vacuum pump Model No. 148 F. A vacuum of 300 to 400 microns of

mercury was maintained throughout the drying cycle. Although a much lower vacuum of 50 to 100 microns of mercury is preferable owing to the nature of strawberries, the equipment available could not provide pressures less than 300 microns of mercury; this was quite satisfactory as long as the pressure was not more than 400 microns. Heat was applied to the platens in the chamber by means of hot water maintained at 125°F (51.6°C). The time required to freeze-dry the strawberries varied with the size of the berries, the large size berries being the limiting factor. The total time for the drying process was 24 hours. At the end of this period, the vacuum was broken with air and the berries were removed from the chamber, placed in one gallon wide mouth jars, sealed tightly and stored at 0°F (17.8°C).

Product Examination

A schematic representation is shown in Figure 1.

Fresh Berries

Texture. Berries after washing, sorting and draining were measured for texture using a modified Lee-Kramer Shear Press, fitted with an X-Y recorder (61, p. 18-22); as shown in Figure 2. A thousand pound ring with a transducer value of 0.0025, giving a maximum deflection of five inches was used. Total area and peak heights of the work diagrams were measured by plenimeter. Total area

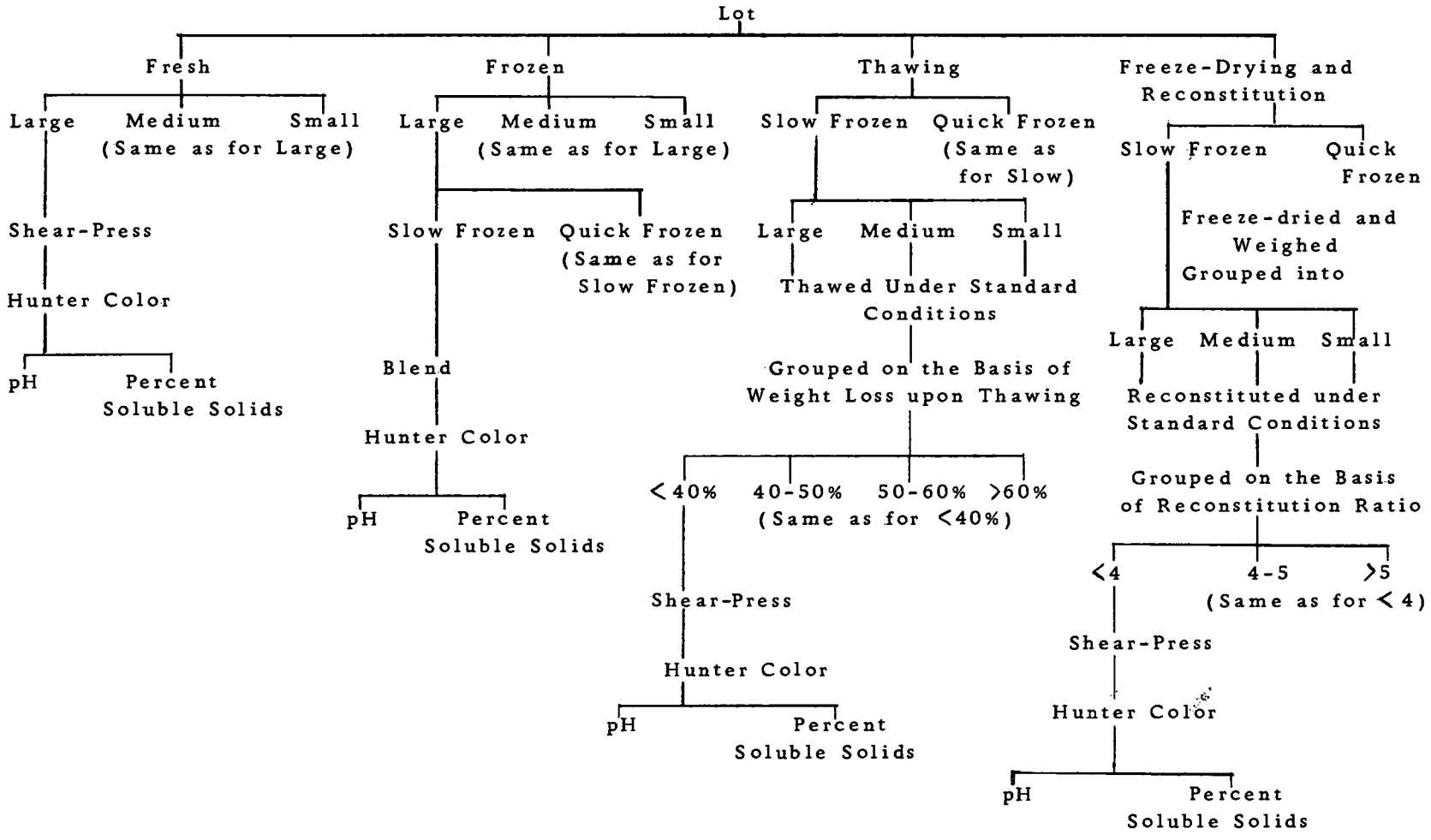


Figure 1. Schematic Representation of Product Examination.

Figure 2. Modified Lee-Kramer Shear Press.

in square inches was then converted to inch pounds by multiplying with a factor of 20. Peak hights were similarly converted to pounds of force by multiplying with the same factor.

Color. The samples after obtaining the shear-press data were subjected to color measurement using the Hunter Color difference meter. The meter was standardized with Panel L 70 red with L, a_L and b_L values of 29.2, 47.7 and 17.7 respectively. A plastic dish of 3.25" x 2.5" x 1.25" measurements was used to contain the sample.

pH. Measurements were made on a Beckman Zeromatic pH meter fitted with an extension arm to hold the electrodes away from the unit for carrying out titratable acid determinations in a beaker supported on a magnetic stirrer. The pH meter was double standardized using a saturated solution of potasium tartrate of pH 3.57 and a buffer of pH 7.

Soluble Solids. Measured with a Bausch and Lomb Abbe type refractometer at room temperature. The values were recorded as percent soluble solids.

Frozen Berries

Frozen berries were brought from the freezer just prior to examination. Two groups of 60 berries each for fruit size and freezing rate and each replication were used. The berries were first crushed while frozen with

the aid of a mortar and pestle. They were then transferred into a Waring blender and blended for one minute at full speed to obtain a well mixed sample. The samples were transferred to a No. 303 glass bottle, sealed, and allowed to thaw at room temperature. Hunter color, pH and total soluble solid measurements were made as described before.

Berries for Thawing

The method as described by Briskey et al. (5) formed the basis for this study. However, due to the inherent differences in the nature of the product under study, a few modifications to the above method were in order. After preliminary tests the following procedure was adapted.

Forty-two berries for each size of fruit, the two rates of freezing and each replication were used to determine the effect of thawing on the quality of Northwest strawberries. The berries were individually weighed in the cold room at 40°F (4.5°C) to minimize condensation and prevent thawing. Thawing occurred in a room under standardized conditions of temperature and relative humidity. The temperature was maintained at 70°F (21°C), and the relative humidity at 60 percent. Whatman No. 32 filter papers (15 cm) were used to collect the drip. The filter papers were allowed to remain in the room to obtain

uniform moisture content. They were then arranged in three rows of seven filter papers each on a flat board covered with aluminum foil. Weighed berries were then placed at the center of the paper and allowed to thaw for one hour, at the end of which the filter paper was removed and replaced with a fresh equilibrated paper. The berries were allowed to thaw for an additional hour. Typical drip patterns are shown in Figure 3. At the end of two hours of thawing the berries were transferred into previously weighed six ounce bottles and reweighed. The filter papers were dried at room temperature, wrapped in plastic sheets and stored in sealed cans till the time they could be analyzed. Percent weight loss of the berries were calculated and the berries were regrouped on this basis. With slow frozen berries they were grouped into four groups as follows: Below 40 percent weight loss, between 40 and 50 percent, between 50 and 60 percent and above 60 percent. In quick frozen berries, the groups were; below 30 percent, between 30 and 40 percent, between 40 and 50 percent and above 50 percent. The weight of the regrouped berries was taken. They were then subjected to texture measurement using a modified Lee-Kramer Shear-press as described for fresh berries. Hunter color, pH and soluble solids were similarly measured.

The filter papers were measured for the area of the drip with a planimeter. They were then regrouped as for

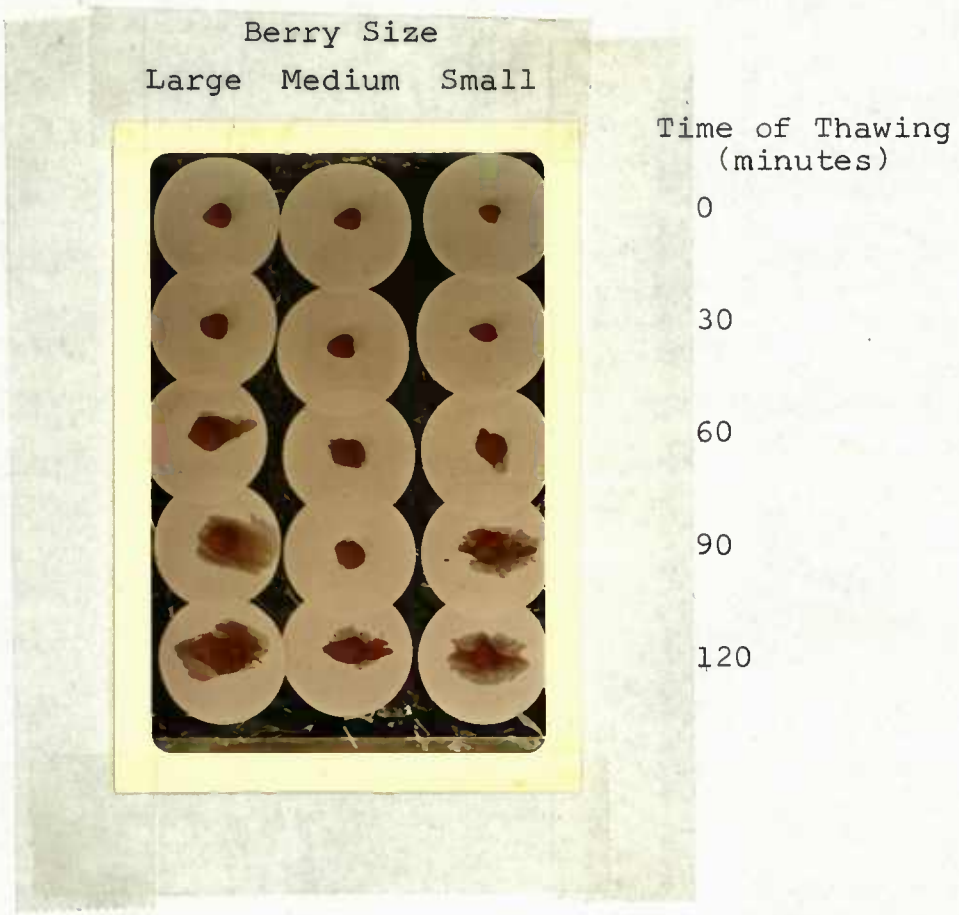


Figure 3. Thawing of Northwest Strawberries.

the berries. The area of drip was cut out with scissors. The combined weight of the drip areas for each group was measured. The resulting papers were then cut into small pieces and a weighed sample of the filter paper containing the drip was then transferred into a 250 ml centrifuge tube. One hundred milliliters of distilled water was added and they were left to stand at room temperature for one hour with occasional stirring. At the end of one hour they were centrifuged at 2100 r.p.m. for 15 minutes using an International centrifuge, Universal Model UV. The supernatant was carefully poured into 250 ml volumetric flasks. To the residue, 75 ml of distilled water was added and well mixed. This was allowed to stand at room temperature for 30 minutes and centrifuged as before. The supernatant was decanted into the same 250 ml volumetric flask. This procedure was repeated once more with 50 ml distilled water. The extracts were then made to volume and reserved for the determination of titratable acids, sugars, pectins, ash and minerals.

Berries for Reconstitution

A preliminary study was made to determine the optimum conditions for reconstitution of the berries. The factors studied were: (1) ratio of berry to reconstituting water; (2) time of reconstitution; (3) temperature of reconstituting water.

Ratio of Berry to Reconstituting Water

Five groups of ten berries for each replication of two were weighed separately. They were placed in 600 ml beakers and varying amounts of water at 25°C (77°F) were added to the beaker to obtain ratios between berries and water of 1:10, 1:20, 1:30 and 1:40. The berries were allowed to reconstitute for 15 minutes, at room temperature. At the end of this time they were drained over a No. 8 (1/8 inch mesh) screen for one minute to remove excess water and reweighed. The ratios of reconstitution were calculated as follows:

$$\text{Reconstitution Ratio} = \frac{\text{Weight of reconstituted material}}{\text{Weight of dehydrated sample}}$$

The results obtained are shown in Tables 1, 2 and 3 and Figures 4, 5 and 6.

Table 1. Effect of Ratio of Berry to Reconstituting Water on Reconstitution Ratio. (averages of two replications)

No.	Ratio of Berry to Water	Weight of Berry	Weight of Recon. Berry	Ratio
		g	g	
1	1:10	6.82	34.37	5.04
2	1:15	6.74	35.59	5.28
3	1:20	8.08	39.27	4.86
4	1:30	6.50	30.81	4.74
5	1:40	7.39	34.44	4.66

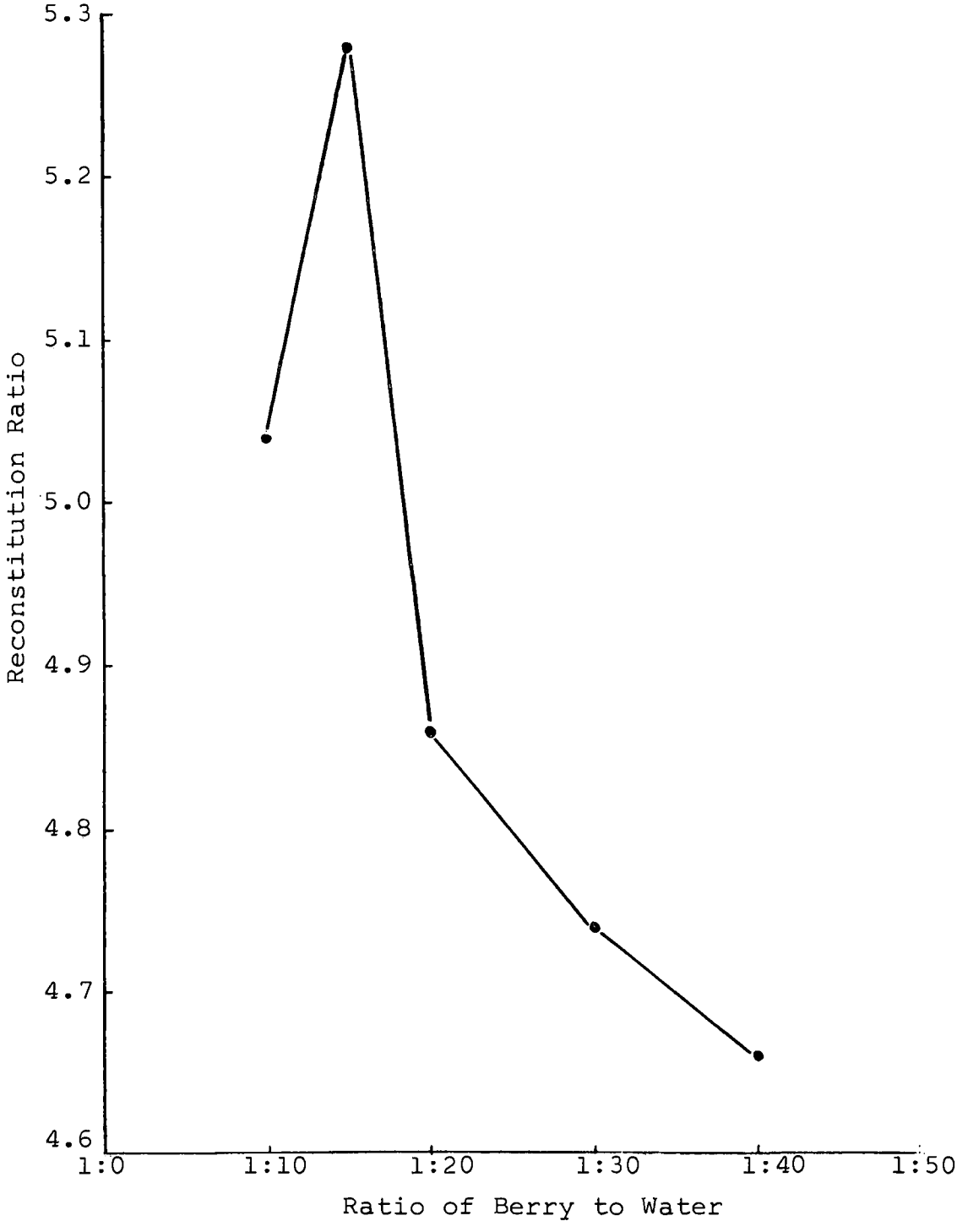


Figure 4. Effect of ratio of berry to water on reconstitution ratio.

Time of Reconstitution

A similar procedure as described before was used for reconstitution of the berries. The ratio of freeze-dried berry to water was 1:15 and the temperature of the reconstituting water was maintained at 25°C (77°F). The times of reconstitution used were 10, 15, 20 and 30 minutes respectively.

Table 2. Effect of Time of Reconstitution on Reconstitution Ratio.

No.	Time of Recon. Minutes	Weight of Berry	Weight of Recon. Berry	Ratio
		g	g	
1	10	7.46	33.42	4.48
2	15	8.21	43.18	5.26
3	20	6.74	35.72	5.30
4	30	6.83	36.06	5.28

Temperature of Reconstituting Water

The ratio of berry to water used was 1:15 and the time of reconstitution was 15 minutes. Three different temperatures of reconstituting water were used viz. 20°C (68°F), 25°C (77°F), and 30°C (86°F). The data obtained are shown in the following table.

Based on these observations it was decided that reconstitution of the experimental berries would be

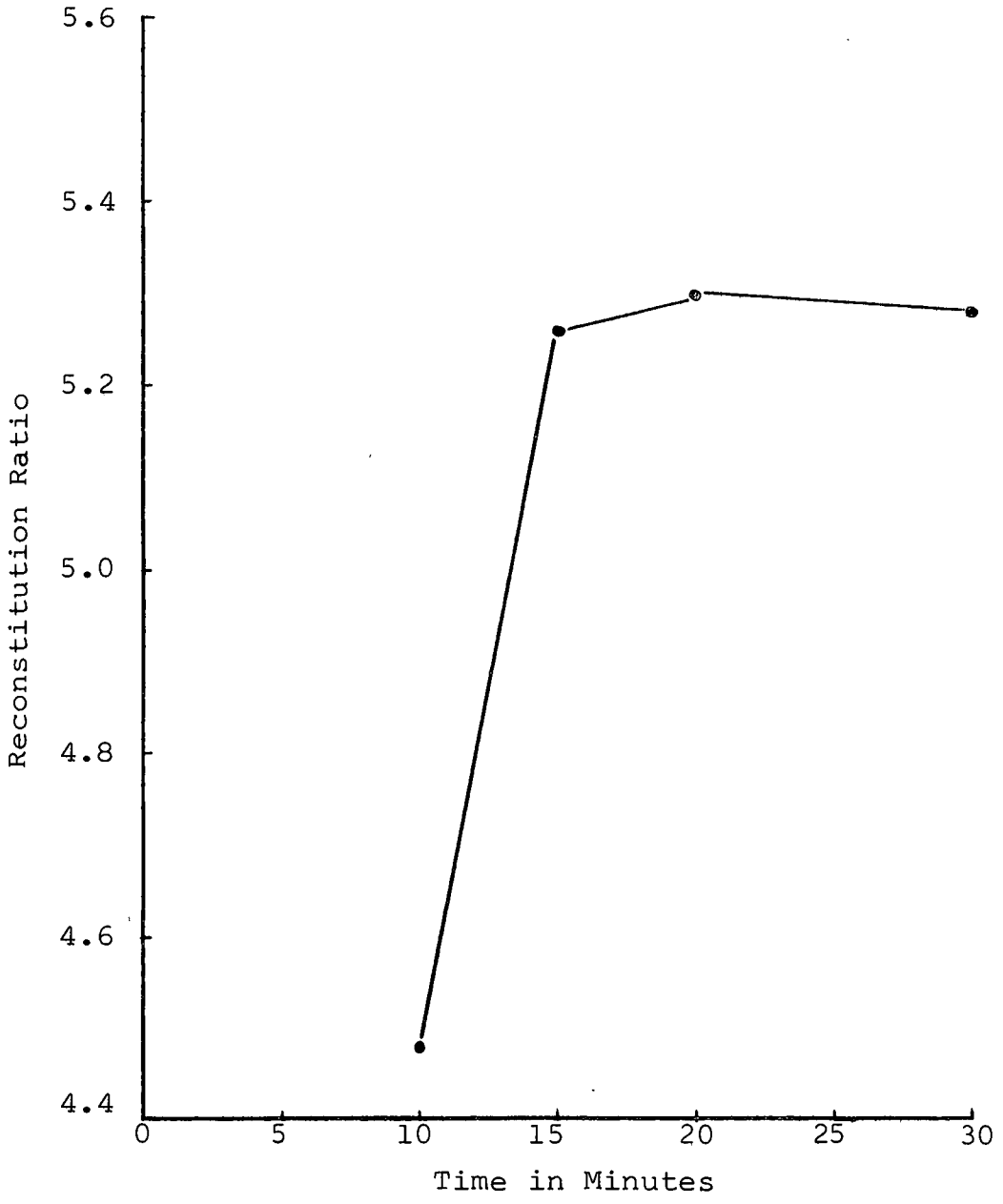


Figure 5. Effect of time of reconstitution on reconstitution ratio.

Table 3. Effect of Temperature of Reconstituting Water on Reconstitution Ratio.

No.	Temp. of Recon. °C	Weight of Berry	Weight of Recon. Berry	Ratio
		g	g	
1	20	6.93	29.59	4.27
2	25	7.52	40.16	5.34
3	30	7.96	42.66	5.36

accomplished as follows: a ratio of dehydrated material to water of 1:15, reconstituting water temperature of 25°C (77°F) for a total time of 15 minutes.

Freeze-dried berries were brought from the freezer and allowed to stand at room temperature for four hours. Thirty berries for each size and each freezing rate, of each replication were individually weighed. They were then placed in 100 ml beakers and appropriate amounts of distilled water at 25°C (77°F) was pipetted into each beaker. At the end of five minutes of reconstitution the berries were gently turned to the other side with a micro spatula and allowed to reconstitute further for ten minutes. At the end of 15 minutes the excess liquid was poured into small bottles, capped, and the berries drained over a No. 8 mesh screen for one minute. The reconstituted berries were transferred into previously weighed six ounce bottles and reweighed. The ratios of reconstitution were calculated as described previously. They

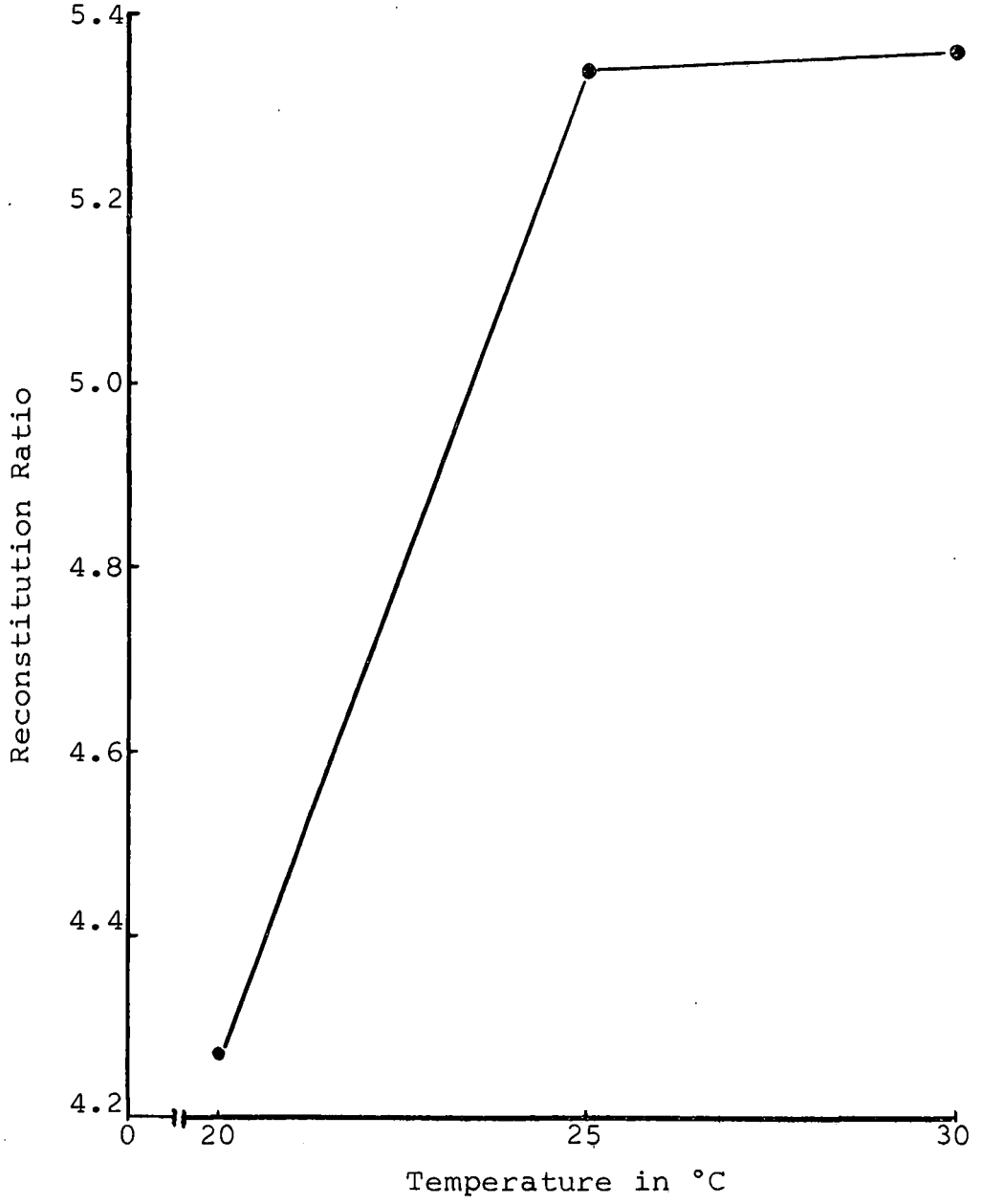


Figure 6. Effect of temperature of reconstitution water.

were then regrouped on this basis as follows:

No.	Rate of Freezing	Reconstitution Ratio Group I	Group II	Group III
1	Slow	< 4	4 - 5	> 5
2	Quick	< 5	5 - 6	> 6

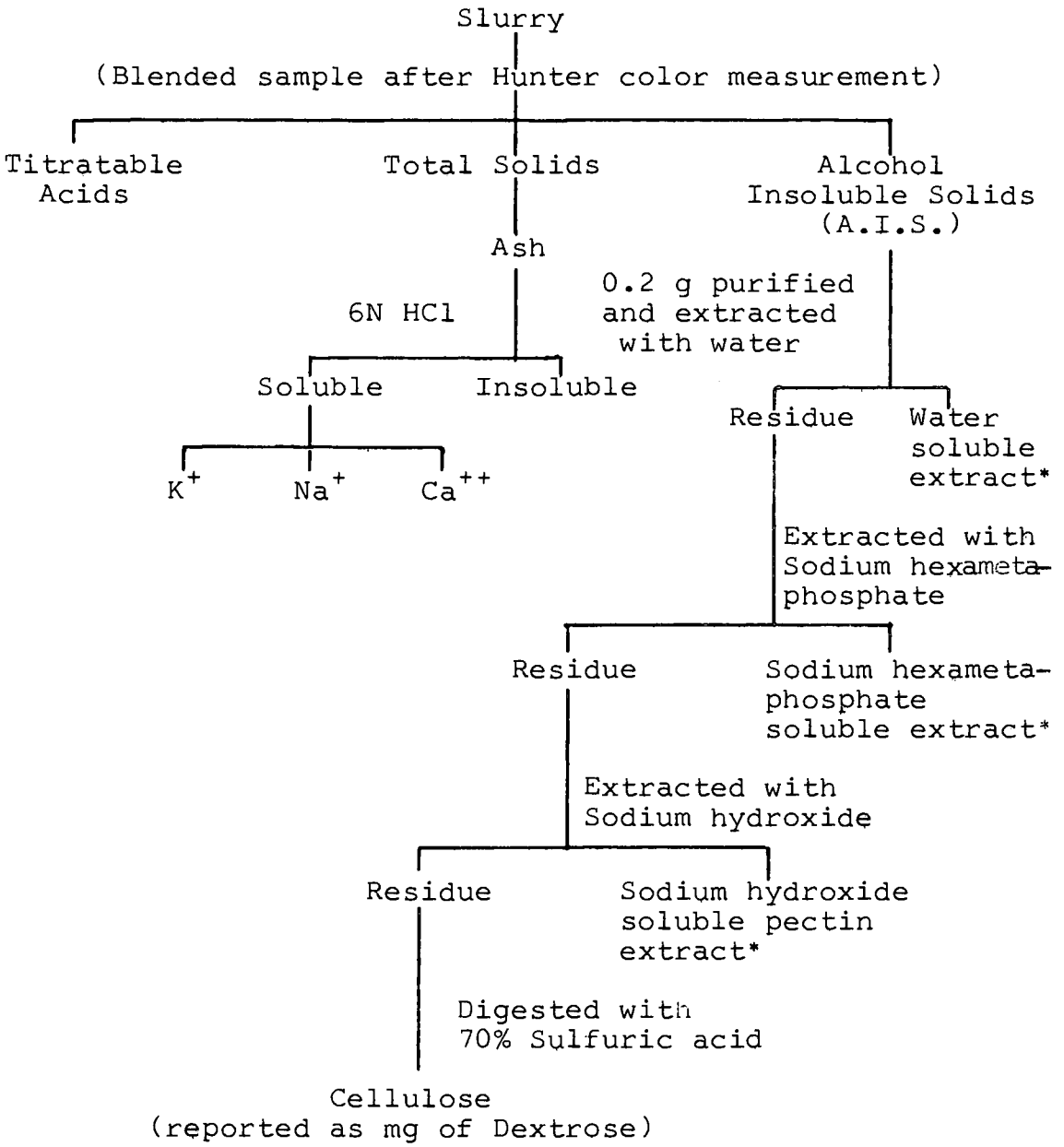
The regrouped berries for each ratio were weighed and texture determination carried out according to the previously described procedure. They were then measured for color, pH and percent soluble solids.

Analytical Procedure

A schematic representation of the procedure used for analytical work is shown in Figure 7 and Figure 8. All the analytical determinations were made on the samples collected after the shear-press measurement. The samples after measuring the color were placed in a Waring blender and blended at full speed for one minute. This formed the basis for further analytical work with the exception of the freeze-dried and reconstituted berries, where distilled water was added to the sample prior to blending. The amount of water added was twice the weight of the fruits.

Total Solids

Ten gram samples of the blended material were weighed



*Extracts analyzed for pectin using modified methods of Dietz and Rouse (17).

Figure 7. Schematic representation of analysis.

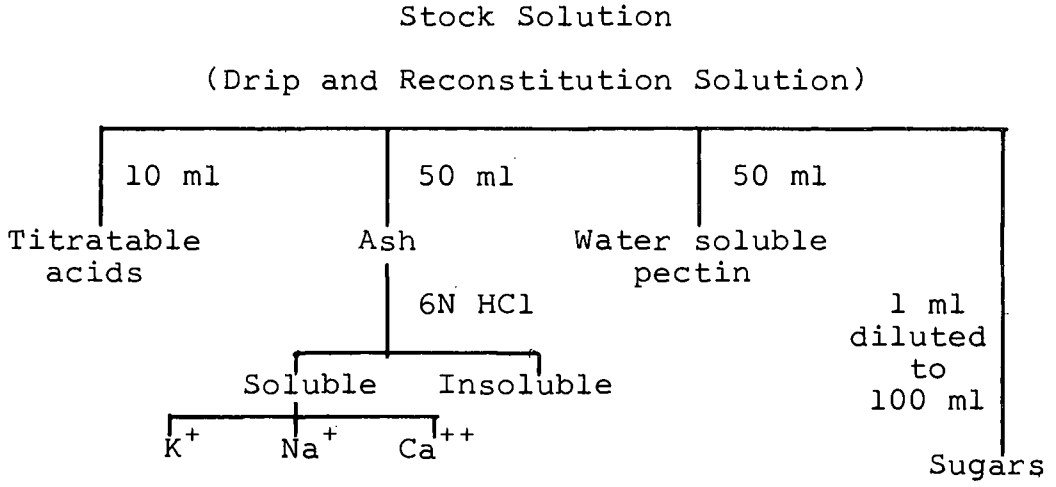


Figure 8. Schematic representation of analysis for drip and reconstitution solution.

into 50 ml pyrex beakers and dried over a steam bath until apparently dry. They were then dried in a vacuum oven maintained at 60°C (140°F) under 30 inches of vacuum for 16 hours, cooled in a desiccator and weighed. The total solids were then calculated on the basis of 100 grams of fresh weight.

Titratable Acids

Five gram samples were weighed into 250 ml beakers. To this 50 ml of distilled water was added. They were titrated against 0.05 N NaOH to a pH of 8.3, using a Beckman Zeromatic pH meter. The samples were constantly stirred by means of a magnetic stirrer. The results were reported as percent citric acid.

Titratable Acids in Drip and Reconstitution Solution

Ten ml of the stock drip solution and reconstitution solutions were pipetted into 250 ml beakers. To this 50 ml of distilled water was added and titrated against 0.05 N NaOH as previously described.

Alcohol Insoluble Solids (AIS)

Forty to 50 grams of material were weighed into 600 ml beakers, 200 ml of boiling 95 percent ethyl alcohol was added and the mixture well stirred. This mixture was quickly brought to boiling again and heated in water bath

at 80°C (176°F) for ten minutes. The samples were then transferred to a Waring blender and blended at full speed for one minute, washed into 250 ml centrifuge tubes with hot 70 percent ethanol and heated in a water bath at 80°C (176°F) for ten minutes. They were cooled to room temperature and centrifuged at 2100 r.p.m using an International Centrifuge, Universal Model UV. The supernatant was decanted and discarded. To the residue in each centrifuge tube, 50 ml of hot 70 percent ethanol were added, the mixture stirred, heated in a water bath at 80°C (176°F) for ten minutes and after cooling centrifuged as before. This procedure was repeated once more with hot 70 percent ethanol and once with cold 70 percent ethanol, without any heating. The sediment was stirred every time before heating and centrifuging. The final decanted supernatent was colorless. The residue was then transferred into previously weighed evaporating dishes with 95 percent ethanol. The dishes were initially dried over a water bath and then dried in a vacuum oven under a vacuum of 30 inches at 60°C (140°F) for 16 hours. They were cooled in a desiccator and weighed. The difference between the weights of evaporating dish containing AIS sample and the original weight of the dish were calculated and reported as percent AIS based on original fresh weight.

Fractionation of Alcohol Insoluble Solids

Removal of Interfering Substances. To further use the AIS samples for pectin and cellulose determination it was necessary to remove interfering substances which were extractable with 70 percent ethanol. The following procedure was adopted for purifying the AIS samples.

The samples were ground with the help of a mortar and pestle to a fine powder. These samples were further ground in a Wiley mill using a 20 mesh sieve. The ground samples were then redried in a vacuum oven at 60°C (140°F) and 30 inches of vacuum for four hours, cooled in a desiccator and 0.2 g of sample weighed into 50 ml conical centrifuge tubes. Ten ml of distilled water were added to each tube and the tube heated in a boiling water bath for five minutes. To this, 30 ml of hot 95 percent ethanol and 0.05 g of Dicalite filter aid (grade 40) were added. They were mixed well, cooled to room temperature and centrifuged at 2100 r.p.m for ten minutes. The supernatant was decanted and discarded. Following this, 40 ml of 70 percent ethanol were added to the residue, the mixture stirred and heated in a water bath at 80°C (176°F) for ten minutes. The tubes were then cooled and centrifuged as before, discarding the supernatant fraction. This procedure was repeated once more with hot 70 percent ethanol and twice with cold 70 percent ethanol, without

heating. At this stage almost all the interfering substances were removed.

Extraction of Water Soluble Pectins. The method as described by Dietz and Rouse (17) formed the basis for this procedure. Forty ml of distilled water were added to each centrifuge tube containing the purified sample of AIS. The contents were stirred well, the mixture allowed to stand for ten minutes and stirred once again. The tubes were then centrifuged as before. The supernatant was decanted into 100 ml volumetric flask. This water extraction was repeated once more using 40 ml of distilled water. The supernatant was decanted into the same volumetric flask, to which five ml of one N NaOH were added and made to volume with distilled water.

Extraction of Sodium Hexametaphosphate Soluble Pectins. To the above residue 40 ml of 0.4 percent sodium hexametaphosphate were added, which was well mixed and permitted to stand for ten minutes at room temperature. It was centrifuged as before and the supernatant collected into a 100 volumetric flask. This extraction procedure was repeated once more using 40 ml of 0.4 percent sodium hexametaphosphate. The supernatant was decanted into the same 100 ml volumetric flask. Five ml of one N NaOH were added to the extract and it was diluted to volume, with distilled water.

Extraction of Sodium Hydroxide Soluble Pectin. To

The remaining residue in the centrifuge tubes 40 ml of 0.05 N NaOH were added, the mixture stirred well and allowed to stand for 15 minutes at room temperature. The mixture was occasionally stirred. The tube was centrifuged as before and the extract decanted into a 100 ml volumetric flask, which was diluted to volume with distilled water.

Extraction of Water Soluble Pectins in Drip and Reconstitution Solution. Fifty ml of the solutions were pipetted into 250 ml centrifuge tubes. To this, 150 ml of 95 percent ethanol were added and the mixture stirred. This caused the pectins to gel. The mixture was heated in a water bath at 80°C (176°F) for ten minutes with occasional stirring. After cooling the mixture to room temperature it was centrifuged at 2100 r.p.m for 15 minutes. The supernatant was decanted and discarded. Fifty ml of 70 percent ethanol were added to the residue and the procedure repeated as described above. To the final residue 50 ml of distilled water were added and mixed well, all the residue went into solution. It was then quantitatively transferred into a 100 ml volumetric flask, five ml of one N NaOH were added and diluted to volume with distilled water.

Colorimetric Procedure for Pectin Determination. For the analysis one ml aliquots of each of the above extracts after proper dilution were pipetted into 6" x 1" test

tubes. To this 0.5 ml of 0.1 percent alcoholic carbazole solution was added and 6 ml of concentrated sulfuric acid were run into each tube with constant agitation by means of a 100 ml buret. The color was allowed to develop for 15 minutes. Exactly 15 minutes after adding the sulfuric acid, the percent transmittance at a wavelength of 525 mu was determined, using a Bausch and Lomb Spectronic 20 spectrophotometer. The instrument was nulled using a blank where one ml distilled water and 0.5 ml of purified ethanol was added instead of aliquots and 0.1 percent carbazol solution. The percent transmittance was then read off a standard curve which was constructed by using known amounts of vacuum dried Eastman Practical grade d-Galacturonic acid and the readings converted to mg of galacturonic acid.

Preliminary Steps for Cellulose Determination. To the residue after extracting with 0.05 N NaOH, as shown in Figure 7, 30 ml of acetone were added, heated in a water bath at 55°C (131°F) for ten minutes with occasional stirring. They were then centrifuged at 2100 r.p.m for ten minutes. The supernatant was decanted and discarded. This procedure was repeated once more and the residue allowed to dry overnight at room temperature. One ml of distilled water was added to the residue and tubes were heated in a warm water bath for 30 minutes with stirring to disperse the solids. The mixture was allowed to cool

and 25 ml of 70 percent sulfuric acid (v/v) were added, and the mixture was allowed to digest at room temperature for three hours with occasional stirring. Most of the residue dissolved except for a few particles of seeds and skin. The solutions were then transferred into 100 ml of distilled water in 250 ml volumetric flasks. The tubes were washed out into the volumetric flasks with distilled water. After cooling, the solutions were diluted to volume with distilled water and filtered through No. 31 Whatman papers. Five ml of the filtrates were further diluted to 100 ml in a volumetric flask. Assuming that all the cellulose had been hydrolyzed to glucose units the diluted solution was analyzed for glucose and the cellulose reported as percent of the original fresh weight.

Colorimetric Procedure for Sugar Determination. The sugars were determined by a modification of the method of Dubois et al. (19). Two ml aliquots of the above solutions were pipetted into 6" x 1" pyrex test tubes. To this, one ml of five percent phenol solution and five ml of concentrated sulfuric acid were added, the tubes mixed well and heated in a boiling water bath for five minutes. After cooling in running water the color was measured in a Bausch and Lomb Spectronic 20 Spectrophotometer at 490 mu.

A standard curve was run using vacuum dried reagent grade dextrose.

Estimation of Sugars in Drip and Reconstitution Solution

One ml of the stock solutions of the drip and reconstitution solution were diluted to 25 ml in a volumetric flask. An aliquot of 0.1 ml was used for the sugar estimation. To the 0.1 ml sample, 1.9 ml of distilled water, one ml of five percent phenol solution and five ml of concentrated sulfuric acid were added. A procedure as described under colorimetric procedure for sugar determination was used to estimate the sugar content.

Ash Determination

Total Ash. The dried samples after determination of the total solids were used for the ash determination. They were carefully charred over a burner and subsequently ashed in a muffle furnace at 525°C (977°F) to 550°C (1022°F) overnight and then cooled. For even ashing, two ml of distilled water was added to the samples and any lumps present were broken with a glass rod. They were redried, reashed, cooled in a desiccator and weighed. The difference between the weight of ashed sample and original beaker were reported as percent total ash.

Acid Insoluble Ash. Into each of the beakers containing ash samples, ten ml of six N Hydrochloric acid were pipetted. They were heated on a steam bath for 30 minutes with occasional stirring. At the end of the

heating period they were filtered through a seven cm Whatman No. 40 ashless paper into 50 ml volumetric flasks. The beakers and filter papers were washed well with hot distilled water, collecting the washings into the same volumetric flasks and the filter paper returned to the respective beaker. The acid extracts were cooled and made to volume and held for mineral assays. The beakers containing filter papers were returned to the muffle furnace where they were reashed, cooled and weighed. The difference between the weight of reashed samples and original beakers were reported as percent acid insoluble ash. Controls consisting of 50 ml pyrex beaker and filter papers without any sample were also run. No increase in the weight of the beaker was observed.

Mineral Determination

Twenty-five ml aliquots of the ash extracts were evaporated to dryness in 50 ml beakers over a steam bath. Five ml of hot 0.1 N hydrochloric acid was added to the dried residue, mixed well and transferred to ten ml volumetric flasks. The solutions were allowed to cool and made up to volume. Mineral determinations were made using a Coleman Flame Photometer, Model 21 A, with appropriate filters, attached to a Coleman, Model 6A, Junior Spectrophotometer. The recommended procedure for preparation of standard reagents as given in the Coleman Model

21 Flame photometer instruction manual was followed (10).

Sodium. One ml of the stock solution was further diluted to ten ml in a volumetric flask. The sodium filter was used. A standard curve was prepared according to the procedure described in the manual (10, p. 24). The percent transmittance values were then converted to meq/liter of sodium.

Potassium. A 0.1 ml aliquot of the stock solution was further diluted to ten ml. The potassium filter and direct reading scale were used.

Calcium. One ml of the stock solution was diluted to ten ml and used for determination of calcium. The calcium filter was used and the measurements were made in the presence of excess phosphate ion by adding one drop of 50 percent H_3PO_4 prior to the dilution of stock solution. The direct reading scale was used.

Ash and Mineral Determination in Drip and Reconstitution Solution

Fifty ml of the stock solutions were pipetted into previously dried and weighed 50 ml pyrex beakers. The solutions were evaporated to dryness over a steam bath and ashed in a muffle furnace at 525°C (977°F) to 550°C (1022°F) overnight, cooled and weighed. The differences in weights were reported as percent total ash. Six N hydrochloric acid insoluble ash and the minerals were

determined according to the procedure described on pages 67 to 69.

RESULTS AND DISCUSSION

The work will be presented in four parts, covering the rates of freezing (I), effect of freezing on the physicochemical characteristics of the berries (II), changes observed upon thawing (III), and changes upon freeze-drying and reconstitution (IV).

All the data were calculated on the basis of 100 grams of original fresh weight of the berries. The experimental results were subjected to statistical analysis to study the effect of rate of freezing and also to evaluate the level of significance of observed effects.

I. Rates of Freezing

The typical freezing curves obtained for small, medium, and large berries are shown in Figure 9 and Figure 10. At the completion of the freezing period, thermocouple wires were removed from the berries and these berries were measured for percent soluble solids, using a Bausch and Lomb refractometer. The average values for the three replications were as follows:

Size of Berry	Percent Soluble Solids Rate of Freezing	
	Slow	Quick
Small	7.63	7.57
Medium	8.07	8.63
Large	7.70	7.70

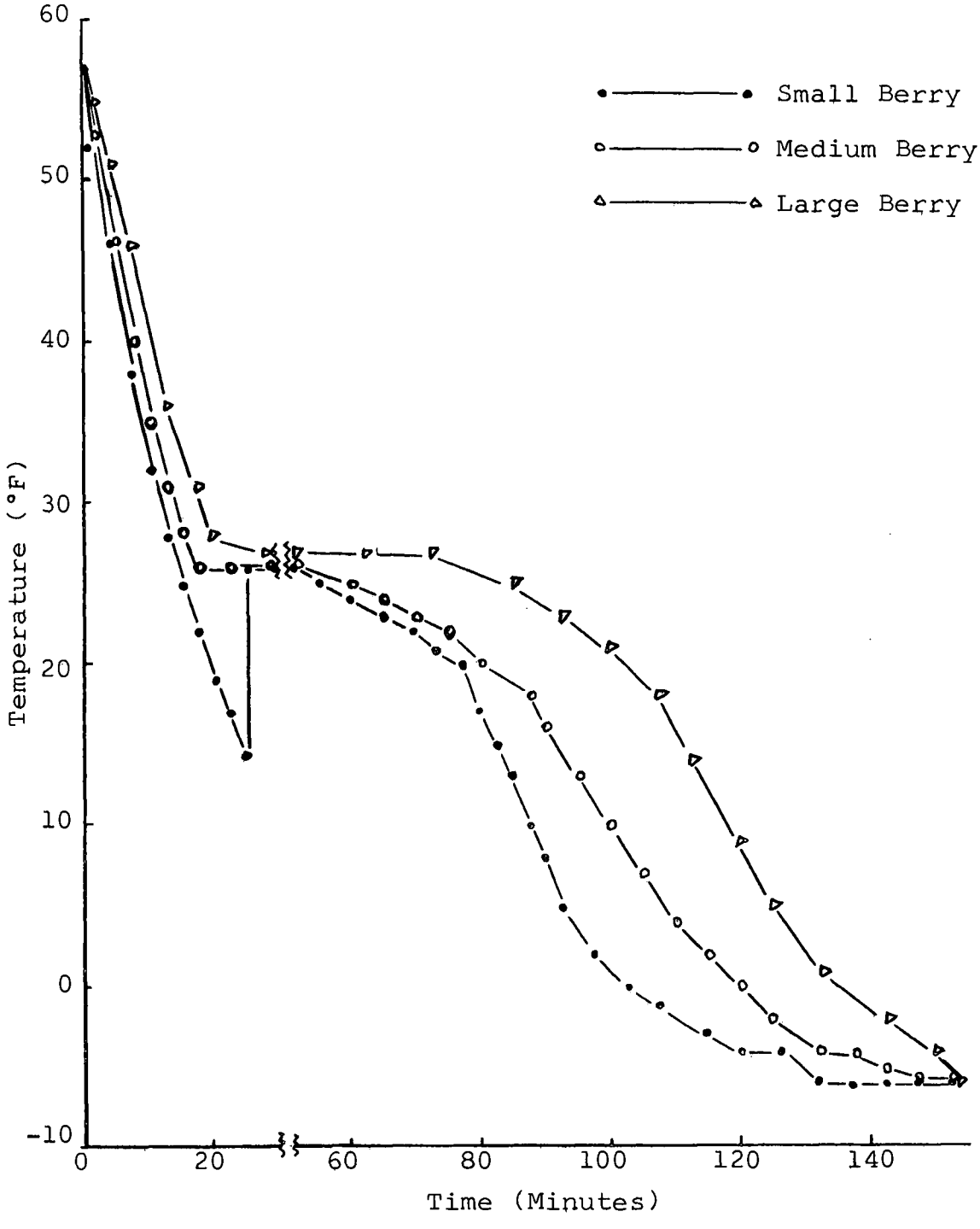


Figure 9. Freezing curves for strawberries slow frozen.

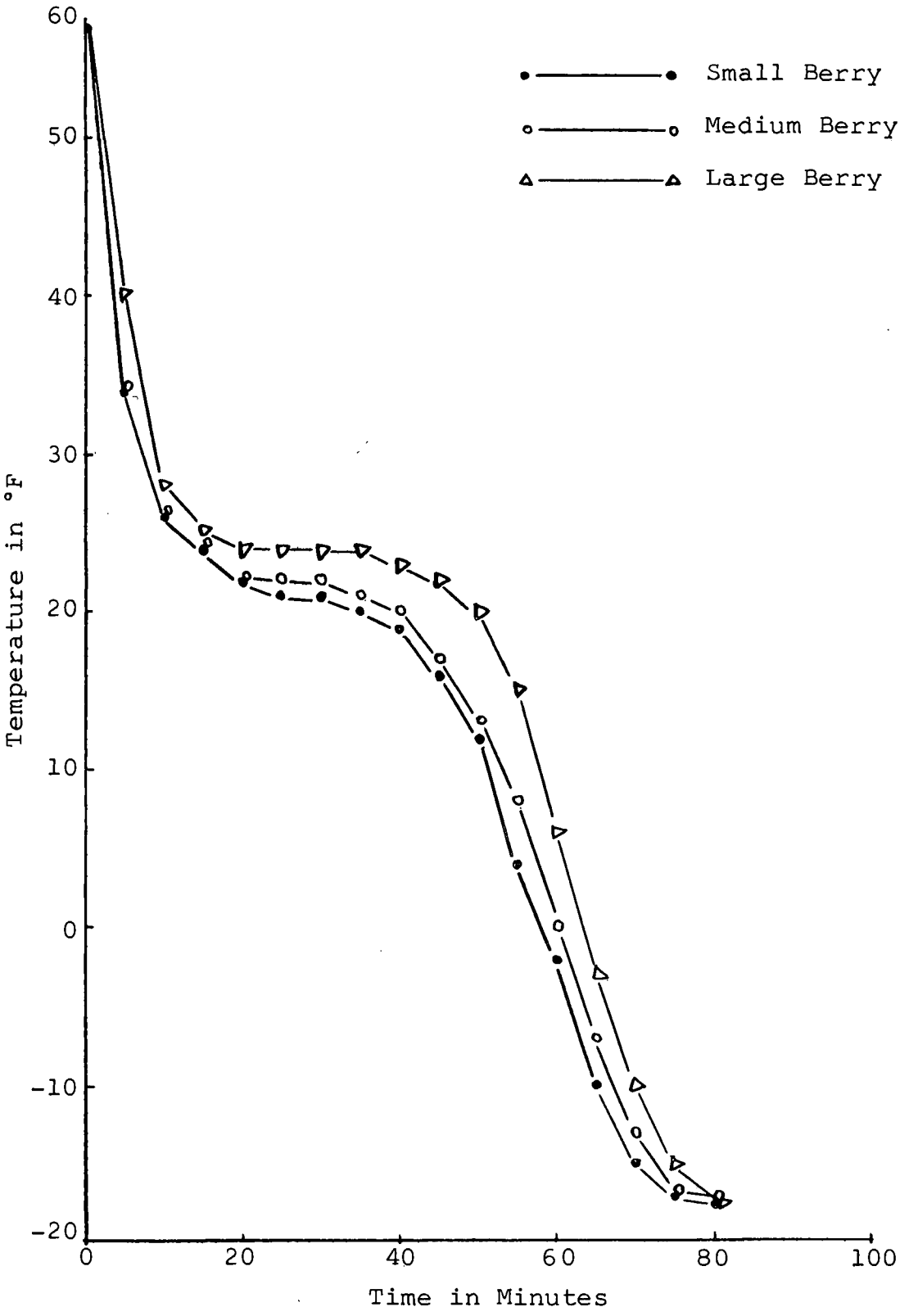


Figure 10. Freezing curves for strawberries quick frozen.

In general, it took less time for the smaller berries to reach the freezing room temperature than medium or large size berries. Upon slow freezing, small size berries showed supercooling which confirms the observation of Fennema and Powrie (21, p. 265) who state that small samples are more prone to supercooling than are large samples.

II. The Effect of Freezing on the Physicochemical Characteristics of Northwest Strawberries

Color

The data obtained for Hunter color determination are presented in Table 4. F values for various treatments are shown in Table 5. No significant differences were observed between size of berries and freezing treatments at the 0.01 level of significance. Hunter L values showed significant differences as a consequence of freezing at the 0.05 level of significance. There was a decrease in a_L and b_L values upon freezing, with slow freezing showing the most change. Also significant differences between a_L values were observed between size of berries. Smaller berries gave low a_L values. The overall color changes as a result of freezing treatments were small as indicated by ΔE values of 3.23 and 2.75 between fresh fruits and slow frozen and quick frozen fruits, respectively. Average a/b values for fresh, slow frozen and

Table 4. Hunter Color Measurement of Fresh and Frozen Northwest Strawberries.

Rep.	Size of Berry	Hunter Color Measurement								
		Fresh			Slow Frozen			Quick Frozen		
		L	a_L	b_L	L	a_L	b_L	L	a_L	b_L
1	Small	22.6	23.1	11.7	21.3	12.5	8.8	23.0	18.1	12.2
	Medium	21.6	24.3	11.3	21.8	17.5	9.9	21.3	20.4	13.7
	Large	21.4	24.0	11.0	22.5	21.0	10.8	21.9	21.3	13.5
2	Small	22.3	19.1	10.4	19.4	11.1	7.6	22.9	16.2	9.2
	Medium	21.0	20.2	9.8	20.6	18.3	9.3	22.6	18.5	10.5
	Large	21.2	22.6	10.5	22.1	22.9	11.0	23.7	18.5	10.9
3	Small	24.5	20.3	12.1	25.1	22.8	12.2	26.1	20.5	11.5
	Medium	25.2	22.3	13.0	26.7	23.5	13.4	25.6	22.0	12.9
	Large	26.9	22.9	14.3	25.1	22.2	12.3	27.2	22.8	12.7

Table 5. Analysis of Variance of Hunter Color Measurements.

Source of Variation	df	L			a_L			b_L		
			Level			Level			Level	
		F	0.05	0.01	F	0.05	0.01	F	0.05	0.01
Replication	2	58.35	S	S	8.50	S	S	17.39	S	S
Treatments	8	1.77	NS	NS	2.87	S	NS	2.30	NS	NS
Size of Berry	2	1.24	NS	NS	6.05	S	NS	3.58	NS	NS
Freezing	2	3.64	S	NS	3.88	S	NS	4.23	S	NS
Size vs. Freezing	4	1.09	NS	NS	0.77	NS	NS	0.70	NS	NS
Error	16									

df = Degrees of freedom
S = Significant
NS = Not significant

quick frozen berries were 1.91, 1.79 and 1.66 respectively.

pH and Percent Soluble Solids

The data obtained are presented in Table 6. F values are shown in Table 7. Significant differences in the pH values with size of berry and freezing treatment were obtained. The average pH value for large berries was 3.58 while for small and medium berries they were 3.52 and 3.51, respectively. The average pH for fresh berries was 3.46, while for slow frozen and quick frozen berries pH values of 3.62 and 3.52 were obtained, giving an increase of 0.16 and 0.06 pH units above the control. Van den Berg (74), working with tomatoes, observed a sharp increase of 1.5 pH units above the control after 20 days at -18°C (0.4°F) which returned to its initial value after 10 to 20 days. A similar phenomenon is likely to operate in strawberries. The samples observed here were processed and stored for more than a month before analyzing, thus the differences observed were not high.

A significant increase in the percent soluble solids was observed with both slow and quick frozen berries. As was pointed out by Fennema and Powrie (21, p. 329), constant changes take place in food products during freezing and subsequent storage, as they are not inert in such conditions, although the biochemical processes are slowed

Table 6. The Effect of Freezing on pH and Percent Soluble Solids.

Rep.	Size of Berry	Percent Soluble Solids			pH		
		Fresh	SF	QF	Fresh	SF	QF
1	Small	7.9	8.2	8.6	3.40	3.55	3.50
	Medium	8.1	8.6	9.0	3.40	3.60	3.50
	Large	8.2	8.6	8.9	3.45	3.68	3.53
2	Small	9.2	9.3	10.6	3.50	3.55	3.50
	Medium	9.8	10.4	10.2	3.53	3.55	3.50
	Large	9.6	10.1	10.4	3.50	3.75	3.55
3	Small	7.2	8.5	8.0	3.50	3.65	3.55
	Medium	7.2	8.3	8.2	3.40	3.58	3.50
	Large	7.2	8.3	8.1	3.50	3.70	3.55

SF = Slow frozen
QF = Quick frozen

Table 7. Analysis of Variance of pH and Percent Soluble Solids.

Source of Variation	df	pH			Per. Soluble Solids		
		F	Level 0.05	Level 0.01	F	Level 0.05	Level 0.01
Replication	2	2.48	NS	NS	111.44	S	S
Treatment	8	12.75	S	S	5.40	S	NS
Size of Berry	2	8.56	S	S	1.82	NS	NS
Freezing	2	3.83	S	NS	19.19	S	S
Size vs. Freezing	4	2.16	NS	NS	0.30	NS	NS
Error	16						

df = Degrees of freedom
S = Significant
NS = Not significant

down considerably. Thus, the hydrolytic enzyme systems within the cell are still active as shown by Diehl et al. (16). Due to the action of such enzyme activity, high molecular weight polysaccharides and other insoluble fractions of the cell like cellulose, pectins, hemicellulose etc. may be hydrolysed to lower molecular weight compounds which account for an increase of the percent soluble solids of the berries upon freezing. Slow freezing rates have been shown to have an adverse effect on cell protein (16, 35) as irreversible coagulation takes place due to colloidal dehydration with increased temperatures. Apart from the enzymatic hydrolysis of higher molecular weight compounds, acid hydrolysis also occurs to a certain extent due to the presence of natural acids in the fruit. The table on effects of freezing upon percent titratable acids shows an increase of such acids with freezing as compared to the fresh tissue. This also could result in an increase of total soluble solids upon freezing. Size of berries did not show significant differences in the percent soluble solids present.

Titratable Acids

The data are presented in Table 8. F values are shown in Table 9. Processed berries showed a significant increase in the percent titratable acids over that of control. There was no significant difference between the

Table 8. Effect of Freezing on Percent Titratable Acids.

Rep.	Size of Berry	Percent Titratable Acids (Citric) Fresh	Slow Frozen	Quick Frozen
1	Small	0.820	0.925	0.880
	Medium	0.948	0.883	0.858
	Large	0.749	0.810	0.897
2	Small	0.845	0.864	0.823
	Medium	0.794	0.896	0.821
	Large	0.807	0.829	0.897
3	Small	0.807	0.941	0.820
	Medium	0.788	0.836	0.861
	Large	0.717	0.819	0.925

Table 9. Analysis of Variance of Titratable Acids.

Source of Variation	df	Percent Titratable Acids (Citric) F	Level of Significance 0.05	0.01
Replication	2	1.16	NS	NS
Treatment	8	3.80	S	NS
Size of Berry	2	1.43	NS	NS
Freezing	2	5.79	S	S
Size vs. Freezing	4	4.00	S	NS
Error	16			

df = Degrees of freedom
S = Significant
NS = Not significant

two rates of freezing. The percent increase over the control was 10.5 and 9.1 in case of slow frozen and quick frozen berries respectively. Size of berries did not show differences in the percent titratable acids present.

Percent Total Solids and Alcohol Insoluble Solids

The data obtained are presented in Table 10. F values obtained are shown in Table 11. Both percent total solids and alcohol insoluble solids showed significant decrease with freezing compared to fresh. The decrease was greater with slow freezing. Both the total solids and alcohol insoluble solid fractions of a fruit are commonly associated with its textural characteristics. An inverse relationship exists between the texture of a fruit and the rate of freezing, thus when they are subjected to slow freezing the extent of flabiness and overall loss of texture is greater than when quick frozen. Woodroof (81) pointed out that the loss of texture in strawberries upon freezing and subsequent thawing may be due to the withdrawal of more water from cells into the intercellular spaces during freezing than is reabsorbed upon thawing, even though the cell walls were not broken. With slow rates of freezing the mechanical injury to the cell has been clearly demonstrated, which results in the mixing of the cell constituents and making the polysaccharides, etc. more vulnerable to breakdown by enzymes. Greater loss of

Table 10. Effect of Freezing on Percent Total Solids and AIS Fractions.

Rep.	Size of Berry	Percent Total Solids			Percent AIS		
		Fresh	SF	QF	Fresh	SF	QF
	Small	10.00	9.30	9.78	2.84	2.10	2.52
1	Medium	9.63	9.10	9.38	2.82	1.86	2.48
	Large	9.76	9.01	9.50	2.27	1.59	2.34
	Small	11.43	9.38	10.68	3.26	2.29	2.86
2	Medium	11.22	9.70	10.40	2.70	2.01	2.36
	Large	10.62	9.43	10.10	2.44	1.77	2.13
	Small	10.11	9.62	10.00	2.80	2.30	2.41
3	Medium	9.30	9.47	9.45	2.48	1.89	2.14
	Large	9.20	9.12	9.18	2.52	1.74	1.67

SF = Slow frozen
QF = Quick frozen

Table 11. Analysis of Variance of Percent Total Solids and AIS.

Source of Variation	df	Percent Total Solids			Percent AIS		
			Level			Level	
		F	0.05	0.01	F	0.05	0.01
Replication	2	16.01	S	S	3.19	NS	NS
Treatments	8	4.01	S	S	15.37	S	S
Size of Berry	2	4.59	S	NS	22.00	S	S
Freezing	2	11.04	S	S	39.44	S	S
Size vs. Freezing	4	0.20	NS	NS	0.03	NS	NS
Error	16						

df = Degrees of freedom
S = Significant
NS = Not significant

both total solids and alcohol insoluble solids with slow rate of freezing probably will account for the severe effects on the texture by this process.

Pectins

The data are shown in Table 12. No significant differences in percent total pectin and its fractions were observed between fresh and processed berries at both 0.05 and 0.01 level of significance. Size of the berries also did not show significant differences in their effect.

Cellulose

The data obtained are presented in Table 13. Statistical analysis of the data did not show any significant differences between fresh and frozen samples or between the different sizes of berries. Although there was an increase in the percent soluble solids upon freezing (Table 6), cellulose hydrolysis was not evident.

Ash and Minerals

The data for percent total ash and 6 N hydrochloric acid insoluble ash are presented in Table 14. Table 15 gives the percent of sodium, potassium, and calcium present in the berries. Statistical analysis did not reveal any significant differences in these factors between the fresh berries and frozen one at either the 0.05 or 0.01

Table 12. Effect of Freezing on Percent Pectic Constituents of Northwest Strawberries.

Rep.	Size of Berry	Fresh				Slow Frozen				Quick Frozen			
		WSP	VSP	SSP	TP	WSP	VSP	SSP	TP	WSP	VSP	SSP	TP
1	Small	0.186	0.106	0.129	0.421	0.180	0.068	0.108	0.356	0.207	0.144	0.055	0.376
	Medium	0.194	0.084	0.119	0.397	0.185	0.084	0.146	0.415	0.188	0.084	0.143	0.415
	Large	0.184	0.093	0.125	0.402	0.166	0.088	0.114	0.368	0.166	0.082	0.141	0.389
2	Small	0.192	0.085	0.098	0.375	0.175	0.092	0.115	0.382	0.185	0.073	0.153	0.411
	Medium	0.176	0.102	0.114	0.392	0.163	0.104	0.101	0.368	0.170	0.095	0.105	0.370
	Large	0.185	0.076	0.157	0.418	0.190	0.095	0.120	0.405	0.183	0.106	0.131	0.420
3	Small	0.180	0.087	0.119	0.386	0.164	0.100	0.161	0.425	0.178	0.070	0.133	0.381
	Medium	0.185	0.112	0.128	0.425	0.182	0.079	0.127	0.388	0.167	0.100	0.128	0.395
	Large	0.204	0.103	0.086	0.393	0.165	0.074	0.161	0.400	0.195	0.096	0.144	0.405

WSP = Water soluble pectin
VSP = 0.4% Sodium hexametaphosphate soluble pectin
SSP = 0.05% Sodium hydroxide soluble pectin
TP = Total pectin

Table 13. Effect of Freezing on Cellulose Content of Northwest Strawberries.

Rep.	Size of Berry	Percent Cellulose		
		Fresh	Slow Frozen	Quick Frozen
1	Small	0.183	0.202	0.156
	Medium	0.172	0.167	0.189
	Large	0.214	0.200	0.160
2	Small	0.220	0.195	0.234
	Medium	0.196	0.224	0.200
	Large	0.203	0.186	0.215
3	Small	0.176	0.186	0.185
	Medium	0.188	0.180	0.175
	Large	0.165	0.164	0.183

level of significance. No significant differences were observed between the three sizes of berries.

III. The Effect of Freezing and Thawing on the Physicochemical Properties of Northwest Strawberries

Loss of Weight Upon Thawing

Strawberries lost weight upon thawing under the previously mentioned conditions. The weight loss for slow frozen and quick frozen berries averaged to 48.15 and 37.58 percent respectively. Table 16 shows these data on loss of weight for the different sizes of berries.

Smaller berries lost the least weight which increased

Table 14. Effect of Freezing on Percent Total Ash and 6 N HCl Insoluble Ash.

Rep.	Size of Berry	Fresh		Slow Frozen		Quick Frozen	
		Total Ash	6 N Hcl Insoluble Ash	Total Ash	6 N Hcl Insoluble Ash	Total Ash	6 N Hcl Insoluble Ash
		%	%	%	%	%	%
1	Small	0.286	0.031	0.272	0.029	0.321	0.025
	Medium	0.295	0.030	0.282	0.026	0.288	0.032
	Large	0.292	0.025	0.311	0.042	0.267	0.033
2	Small	0.315	0.043	0.330	0.040	0.308	0.036
	Medium	0.286	0.036	0.295	0.033	0.301	0.027
	Large	0.310	0.052	0.286	0.036	0.285	0.041
3	Small	0.292	0.022	0.287	0.028	0.274	0.032
	Medium	0.320	0.024	0.306	0.029	0.292	0.028
	Large	0.304	0.031	0.299	0.024	0.324	0.037

Table 15. Effect of Freezing on Percent Sodium, Potassium and Calcium Content of Northwest Strawberries.

Rep.	Size of Berry	Fresh			Slow Frozen			Quick Frozen		
		Na^+	K^+	Ca^{++}	Na^+	K^+	Ca^{++}	Na^+	K^+	Ca^{++}
		%	%	%	%	%	%	%	%	%
1	Small	0.040	0.036	0.013	0.053	0.061	0.010	0.034	0.051	0.023
	Medium	0.046	0.046	0.018	0.039	0.054	0.007	0.045	0.042	0.006
	Large	0.060	0.043	0.020	0.065	0.032	0.014	0.055	0.056	0.014
2	Small	0.063	0.058	0.018	0.048	0.043	0.015	0.058	0.043	0.012
	Medium	0.043	0.062	0.011	0.042	0.056	0.012	0.063	0.063	0.013
	Large	0.052	0.052	0.016	0.044	0.062	0.007	0.048	0.048	0.010
3	Small	0.037	0.050	0.008	0.045	0.047	0.012	0.052	0.045	0.013
	Medium	0.054	0.034	0.014	0.055	0.045	0.013	0.040	0.048	0.011
	Large	0.045	0.056	0.013	0.045	0.050	0.016	0.043	0.042	0.012

Table 16. Percent Loss of Weight of Northwest Strawberries Upon Thawing.

Size of Berry	Rep.	Slow Frozen	Average	Quick Frozen	Average
	1	43.13		34.48	
Small	2	45.57	45.25	33.23	34.10
	3	47.04		34.58	
	1	51.43		39.58	
Medium	2	47.38	48.71	37.31	38.25
	3	47.32		37.87	
	1	53.68		39.00	
Large	2	48.94	50.50	40.29	40.39
	3	48.88		41.88	

gradually as the size of the berries increased. Explanation for the lower weight loss with smaller berries seems to be due to the smaller surface area in contact with the filter paper upon thawing. Also with a smaller volume to surface ratio in case of small berries the likelihood of ice formation in the cell is less as the surface through which the smaller amount of water can pass to the outside is more. Gallop (24, p. 72) and Armbruster (4) observed that berries with smaller size cells withstood freezing treatment better than others.

Area of Drip

The drip lost during thawing of the berries was

absorbed on a Whatmann No. 32 filter paper (15 cm). After drying, at room temperature, the area covered by the drip was measured with a planimeter. The data obtained are presented in Tables 17 and 18.

A linear relationship was obtained between percent weight loss of the berry and the area of the drip. These observations are in agreement with the work reported by Brisky et al. (5), who, working with pork muscle, observed significant correlations between expressible water, pH and the muscle class. They employed a similar technique of collecting the expressible water on filter papers and measured the area. The regression coefficients between percent weight loss of the berry upon thawing and area of the drip collected the first hour, second hour and the total for slow frozen berries are 0.272, 0.085 and 0.360 respectively. In case of quick frozen berries they are 0.136, 0.085 and 0.221 respectively.

Joslyn and Marsh (38), Kaloyereas (39), Woodroof and Shelor (82), and Aref (3) used drip as a quality measure of frozen fruits. The procedure used by these workers gave good indication as to the quality, yet it was time consuming and inconvenient. The present method offers a convenient and quick procedure with the added advantage of collecting the drip and storing it for further analysis without any appreciable changes under proper storage conditions.

Table 17. The Effect of Weight Loss Upon Thawing on Area of Drip - Slow Frozen.

Size of Berry	Percent Weight Loss < 40			40-50			50-60			> 60		
	1st Hour sq. in.	2nd Hour sq. in.	Total sq. in.	1st Hour sq. in.	2nd Hour sq. in.	Total sq. in.	1st Hour sq. in.	2nd Hour sq. in.	Total sq. in.	1st Hour sq. in.	2nd Hour sq. in.	Total sq. in.
Small	2.506	1.233	3.739	4.857	1.692	6.549	6.895	2.423	9.319	10.871	3.638	14.509
Medium	2.673	1.324	3.997	4.901	1.911	6.811	7.039	2.663	9.702	10.892	3.796	14.688
Large	3.312	1.410	4.722	5.363	2.190	7.552	8.040	2.633	10.683	11.655	4.345	16.000

Table 18. The Effect of Weight Loss Upon Thawing on Area of Drip - Quick Frozen.

Size of Berry	Percent Weight Loss < 30			30-40			40-50			> 50		
	1st Hour sq. in.	2nd Hour sq. in.	Total sq. in.	1st Hour sq. in.	2nd Hour sq. in.	Total sq. in.	1st Hour sq. in.	2nd Hour sq. in.	Total sq. in.	1st Hour sq. in.	2nd Hour sq. in.	Total sq. in.
Small	2.317	1.454	3.767	3.406	1.903	5.308	4.405	2.670	7.075	6.714	3.873	10.587
Medium	2.524	1.697	4.222	3.621	2.386	6.006	5.366	3.137	8.503	7.326	4.733	12.060
Large	4.358	2.571	6.929	5.318	3.855	9.173	6.600	4.489	11.088	7.442	4.884	12.326

Texture

The berries after thawing were grouped into four groups based on the percent weight loss. The samples were weighed and measured for texture. The data obtained are shown in Table 19. The F values obtained and their significance are shown in Table 20. The statistical analysis of the data shows that maximum force measurements did not show any significant differences either at the 0.05 or 0.01 level of significance. On the other hand, total work data shows softening of the berries with increasing loss of weight upon thawing and also that slow frozen berries were softer compared to quick frozen ones. The maximum force values showed a gradual decrease but when more than 60 percent of the weight was lost in case of slow freezing and more than 50 percent in case of quick freezing, an increase in the shear press value was observed. Upon withdrawal of water as drip from the fruit, the insoluble solids, which consists mainly of skin and seeds, show toughening which is reflected in an increased value of maximum force.

Color

The average values of the Hunter color determinations are presented in Table 21. No significant differences were observed between treatments or within treatments.

Table 19. Average Shear-press Values of Thawed Berries.

Rate of Freezing	Percent Weight Loss	Texture Measurement*	
		Total Work**	Maximum Force***
Slow	< 40	33.65	44.49
	40-50	27.39	38.27
	50-60	25.83	32.65
	> 60	22.72	45.45
Quick	< 30	35.24	44.40
	30-40	30.64	40.81
	40-50	27.47	38.83
	> 50	25.29	45.10

* All samples on 100 g original fresh weight
** Inches converted to pounds force by multiplying with 20
*** Square inches converted to inch pounds by multiplying with 20

Hunter color measurements for fresh berries were presented in Table 4. ΔE values were calculated to study the overall color changes between fresh strawberries and thawed berries. The values obtained for slow frozen and quick frozen berries are 8.19 and 8.14 respectively. The average a/b value for fresh berries was 1.943. There was a decrease in this value upon freezing and thawing. The average values obtained for four groups of slow frozen berries and also quick frozen berries are 1.325 and 1.341 respectively.

Table 20. Analysis of Variance of Shear-press Values.

Source of Variation	df	Total Work			Maximum Force		
		F	Level of Sig.		F	Level of Sig.	
			0.05	0.01		0.05	0.01
Replication	2	0.074	NS	NS	0.115	NS	NS
Freezing Treatment	1	6.446	S	NS	0.531	NS	NS
Thaws vs. Freezing Treatment	6	12.519	S	S	1.374	NS	NS
Thaws vs. Slow Frozen	3	13.294	S	S	2.202	NS	NS
Thaws vs. Quick Frozen	3	11.744	S	S	0.547	NS	NS
Error	14						

df = Degrees of freedom
S = Significant
NS = Not significant

Table 21. Average Hunter Color Values of Thawed Berries.

Slow Frozen					Quick Frozen				
Percent Wt. Loss	L	a_L	b_L	a/b	Percent Wt. Loss	L	a_L	b_L	a/b
< 40	25.07	14.96	10.87	1.376	< 30	27.90	15.35	12.07	1.272
40-50	24.49	15.25	10.82	1.409	30-40	27.10	15.18	10.92	1.390
50-60	24.28	14.58	10.46	1.394	40-50	26.02	14.45	10.75	1.344
> 60	26.52	12.10	10.78	1.122	> 50	26.33	14.78	10.90	1.356

pH and Percent Soluble Solids

The data obtained for pH and percent soluble solids are presented in Table 22. The F values obtained are shown in Table 23. There was a significantly greater increase in the pH values when the strawberries were slow frozen. The pH value for fresh berries was 3.45 with a range from 3.40 to 3.50. There was an initial drop in the pH for both slow frozen and quick frozen berries respectively. Following this a gradual increase was observed with progressive increase in the weight loss. In case of slow frozen berries the pH values for the 60 percent and above weight loss group exceeded that of the fresh berries. Van den Berg (74) working with frozen cauliflower, green beans and tomatoes observed similar changes in pH of 0.3 to 2.0 pH units in all products during the first three months of storage. He attributed these changes in pH to the type of salt which was precipitated. A significant increase in the percent soluble solids was observed in case of slow frozen berries, while quick frozen fruits showed only a slight change, being significant at only the 0.05 level. The percent soluble solids for fresh berries was 7.978 with a range from 7.80 to 8.20. The increase in percent soluble solids is due partly to the concentration of cell contents as a consequence of weight loss upon thawing and partly to the hydrolytic products of

Table 22. Average pH and Percent Soluble Solids of Thawed Berries.

Slow Frozen			Quick Frozen		
Percent Weight Loss	pH	Per. Sol. Solids	Percent Weight Loss	pH	Per. Sol. Solids
< 40	3.283	8.00	< 30	3.217	8.10
40-50	3.350	8.50	30-40	3.250	8.20
50-60	3.450	9.40	40-50	3.317	8.53
> 60	3.583	10.53	> 50	3.383	9.10

insoluble materials of the cell. Significant differences were also observed between the freezing treatments, slow freezing being responsible for a greater increase.

Titratable Acids

The average values for the percent titratable acids in the berry and the drip are shown in Table 24. Statistical analysis of the data showed significant differences between freezing treatments. Slow frozen berries showed a greater loss of titratable acids than the quick frozen ones. Also a significant reduction in the titratable acids and a simultaneous increase in the drip, with increasing loss of weight upon thawing was observed for both rates of freezing. However, the percent loss of acids in the drip in case of quick frozen berries was less than for slow frozen berries as shown in Table 24.

Table 23. Analysis of Variance of pH and Percent Soluble Solids.

Source of Variation	df	pH			Percent Soluble Solids		
		F	Level of Sig.		F	Level of Sig.	
			0.05	0.01		0.05	0.01
Replication	2	0.259	NS	NS	0.212	NS	NS
Freezing Treatment	1	0	NS	NS	13.137	S	S
Thawing vs. Freezing	6	30.721	S	S	12.119	S	S
Thawing vs. Slow Frozen	3	31.801	S	S	20.820	S	S
Thawing vs. Quick Frozen	3	10.197	S	S	3.419	S	NS
Error	14						

df = Degrees of freedom
S = Significant
NS = Not significant

Table 24. Average Percent Titratable Acid of Thawed Berries and Drip.

Item	Slow Frozen Percent Weight Loss				Quick Frozen Percent Weight Loss			
	< 40	40-50	50-60	>60	< 30	30-40	40-50	>50
Berry	0.6300	0.4913	0.3600	0.2597	0.7057	0.5207	0.4400	0.2977
Drip	0.2683	0.3105	0.3426	0.3508	0.1531	0.2323	0.2742	0.2905
Per. Total Titratable Acids in Drip	29.87	38.73	48.76	57.46	17.83	30.85	38.39	49.39

Total Solids

The average percent total solids of the strawberries is tabulated in Table 25. F values obtained for various treatments are shown in Table 26, along with their significance. The percent total solids decreased significantly at both 0.05 and 0.01 level, upon slow freezing as compared to quick freezing. Significant differences in total solids were also obtained for different weight loss groups between the two rates of freezing and within a given freezing rate. As the percent loss in weight increased, a decrease in the total solids was observed. This would indicate that the water holding capacity of the berries is related to the total solid content, thus berries with higher total solids would tend to lose less weight upon thawing than the ones with lower total solids content as would be expected.

Table 25. Average Percent Total Solids Content of Thawed Berries.

Slow Frozen				Quick Frozen			
Percent Weight Loss				Percent Weight Loss			
< 40	40-50	50-60	>60	< 30	30-40	40-50	>50
%	%	%	%	%	%	%	%
7.328	7.266	5.890	4.509	7.983	7.062	6.428	5.230

Alcohol Insoluble Solids

The data obtained for AIS are presented in Table 27.

Table 26. Analysis of Variance of Percent Total Solids.

Source of Variation	df	F	Level of Significance 0.05	0.01
Replication	2	0.652	NS	NS
Freezing Treatment	1	16.149	S	S
Thawing vs. Freezing	6	68.967	S	S
Thawing vs. Slow Frozen	3	78.876	S	S
Thawing vs. Quick Frozen	3	59.056	S	S
Error	14			

df = Degrees of freedom
S = Significant
NS = Not significant

F values for various treatments are shown in Table 28. Rate of freezing did not have a significant effect on the AIS fraction. However the percent of AIS between the various weight loss groups for freezing treatments showed significant differences both at 0.05 and 0.01 level of significance and also within a given rate of freezing.

AIS fraction of fruit cells consists mainly of polysaccharides like cellulose, xylans, araban, galactan, polygalacturonic acid (pectic acid), mannan and to a certain extent proteins (33, p. 137; 76). All of these compounds are capable of binding water owing to their hydrophilic nature. As would be expected a higher content of AIS materials in a tissue would prevent loss of drip when it is frozen and thawed.

Table 27. Average Percent Alcohol Insoluble Solids Content of Thawed Berries.

Slow Frozen				Quick Frozen			
Percent Weight Loss				Percent Weight Loss			
<40	40-50	50-60	>60	<30	30-40	40-50	>50
%	%	%	%	%	%	%	%
2.797	2.495	2.110	1.772	2.508	2.365	2.281	1.967

Table 28. Analysis of Variance of Percent Alcohol Insoluble Solids.

Source of Variation	df	F	Level of Significance 0.05	0.01
Replication	2	1.980	NS	NS
Freezing Treatment	1	0.269	NS	NS
Thawing vs. Freezing	6	92.543	S	S
Thawing vs. Slow Frozen	3	146.65	S	S
Thawing vs. Quick Frozen	3	38.44	S	S
Error	14			

df = Degrees of freedom
S = Significant
NS = Not significant

Pectins

The average values for percent total pectin and its fractions in the berries are shown in Table 29. The

Table 29. Effect of Freezing and Thawing on Percent Pectic Constituents of Northwest Strawberries.

Rate of Freezing	Per. Wt. Loss	Fractions of Pectin			
		WSP	CSP	SSP	TP
		%	%	%	%
Slow	< 40	0.0298	0.0733	0.2159	0.3190
	40-50	0.0192	0.0749	0.1749	0.2688
	50-60	0.0103	0.0557	0.1511	0.2171
	> 60	0.0091	0.0450	0.1345	0.1886
Quick	30	0.0496	0.0723	0.1905	0.3123
	30-40	0.0272	0.0653	0.1640	0.2565
	40-50	0.0212	0.0591	0.1592	0.2395
	> 50	0.0111	0.0614	0.1275	0.2000

WSP = Water soluble pectin
CSP = 0.4% sodium hexametaphosphate soluble pectin
SSP = 0.05% sodium hydroxide soluble pectin
TP = Total pectin

F values for various treatments are given in Table 30. Water soluble pectins gave significant differences between slow frozen and quick frozen berries at both 0.05 and 0.01 level of significance. However 0.4 percent sodium hexametaphosphate soluble pectin and total pectin did not show significant differences while 0.05 percent sodium hydroxide soluble pectin gave significant differences only at 0.05 level of significance. With gradual increase in weight loss of the berries upon thawing there was a decrease in all the fractions of pectin for both rates of freezing and also for a given freezing rate.

The amount of total pectin in the drip increased with increasing loss of weight of the berries upon thawing for both rates of freezing as shown in Table 31. The berries which lost the least weight had the highest amount of total pectin in them. Table 32 shows the percent of total pectin in the drip.

The berries with lower percent weight loss had higher total pectin and lost less in the drip. In contrast to this the ones which lost more weight showed lower total pectin, while a higher percentage of this was lost in the drip.

Pectic substances which are present mainly in the middle lamella of cells, act as cementing material in holding adjacent cells together (40, p. 279). They are strongly hydrophilic in nature and can take up and retain several

Table 30. Analysis of Variance of Pectic Constituents.

Source of Variation	df	Fractions of Pectin											
		WSP			CSP			SSP			TP		
		F	Level of Sig. 0.05	0.01	F	Level of Sig. 0.05	0.01	F	Level of Sig. 0.05	0.01	F	Level of Sig. 0.05	0.01
Replication	2	1.987	NS	NS	0.322	NS	NS	1.977	NS	NS	2.137	NS	NS
Freezing Treatment	1	27.679	S	S	1.174	NS	NS	5.105	S	NS	0.722	NS	NS
Thawing vs. Freezing	6	23.938	S	S	13.705	S	S	31.819	S	S	72.627	S	S
Thawing vs. Slow Frozen	3	12.335	S	S	23.625	S	S	41.445	S	S	87.780	S	S
Thawing vs. Quick Frozen	3	35.549	S	S	3.788	S	NS	22.178	S	S	57.480	S	S
Error	14												

df = Degrees of freedom
S = Significant
NS = Not significant
WSP = Water soluble pectin
CSP = 0.4% Sodium hexametaphosphate soluble pectin
SSP = 0.05% sodium hydroxide soluble pectin
TP = Total pectin

Table 31. Distribution of Pectic Substances in Thawed Berry and Drip.

Rate of Freezing	Per. Wt. Loss	Factor					
		TP	WSP In Berries After Thawing	WSP In Drip	Total WSP	Per. WSP of TP	Texture Inch Pounds
		%	%	%	%		
Slow	< 40	0.4150	0.0298	0.0960	0.1258	30.31	33.65
	40-50	0.3785	0.0192	0.1097	0.1289	34.05	27.39
	50-60	0.3301	0.0103	0.1130	0.1233	37.35	25.83
	> 60	0.3087	0.0091	0.1201	0.1292	41.85	22.72
Quick	< 30	0.3775	0.0496	0.0652	0.1148	30.41	35.24
	30-40	0.3560	0.0272	0.0995	0.1267	35.58	30.64
	40-50	0.3504	0.0212	0.1109	0.1321	37.70	27.47
	> 50	0.3165	0.0111	0.1165	0.1276	40.32	25.29

TP = Total pectin
WSP = Water soluble pectin

Table 32. Effect of Freezing and Thawing on Pectic Substances in Drip.

Slow Frozen					Quick Frozen				
Percent Weight Loss	TP in Berry	TP in Drip	TP in Original Berry	WSP in Drip	Percent Weight Loss	TP in Berry After Thaw	TP in Drip	TP in Original Berry	WSP in Drip
	%	%	%	%		%	%	%	%
< 40	0.3190	0.0960	0.4150	23.13	< 30	0.3123	0.0652	0.3775	17.27
40-50	0.2688	0.1097	0.3785	28.98	30-40	0.2565	0.0995	0.3560	27.95
50-60	0.2171	0.1130	0.3301	34.23	40-50	0.2395	0.1109	0.3504	31.64
> 60	0.1866	0.1201	0.3087	38.91	> 50	0.2000	0.1165	0.3165	36.80

TP = Total pectin
WSP = Water soluble pectin

times their weight of water (40, p. 184). Thus, berries with higher total pectin content would tend to lose less weight upon thawing. Strawberries with higher amount of water soluble pectin showed not only higher amount of drip but also softer texture as measured by a shear press. These data are presented in Table 31.

Cellulose

The data are presented in Table 33. F values for various treatments are shown in Table 34. A significant decrease in the amount of cellulose was observed at both 0.05 and 0.01 level of significance for slow frozen berries as compared to the quick frozen ones. The different weight loss groups between the two rates of freezing and within a given freezing rate also showed significant differences. Weight loss of the berries upon thawing was a direct function of amount of cellulose. Cellulose like pectins are highly hydrophilic in nature and are capable of swelling by imbibing water. In the edible portion of the fruit, cellulose constitutes one of the major component of cell wall along with other polysaccharides such as xylans, arabans, galactan, polygalacturonic acid (pectic acid) and mannan (33, p. 137). Any changes in the amounts and properties of these polysaccharides will consequently effect the texture of the fruits. Correlation coefficients between cellulose content of the berries for

Table 33. Average Percent Cellulose of Thawed Berries.

Slow Frozen				Quick Frozen			
Percent Weight Loss				Percent Weight Loss			
<40	40-50	50-60	>60	<30	30-40	40-50	>50
%	%	%	%	%	%	%	%
0.214	0.187	0.184	0.134	0.239	0.230	0.199	0.184

Table 34. Analysis of Variance of Cellulose.

Source of Variation	df	F	Level of Significance 0.05	0.01
Replication	2	1.042	NS	NS
Freezing Treatment	1	80.974	S	S
Thawing vs. Freezing	6	32.488	S	S
Thawing vs. Slow Frozen	3	40.514	S	S
Thawing vs. Quick Frozen	3	24.460	S	S
Error	14			

df = Degrees of freedom
S = Significant
NS = Not significant

various weight loss groups and texture as measured by total work were 0.828 in case of slowfrozen berries and 0.754 in case of quick frozen berries, which were significant at the one and five percent levels, respectively.

Ash

The total percent ash and acid insoluble ash of the berries and drip were determined and calculated on the basis of 100 g of original weight of berries prior to thawing. The average values are shown in Tables 35 and 36. Both percent total ash and acid insoluble ash decreased significantly with increased weight loss of the berry upon thawing. Slow freezing significantly decreased the ash content of berries as compared to quick freezing. Percent total ash and six N hydrochloric acid insoluble ash in the drip increased with an increase in percent loss of weight of the berry as shown in Tables 35 and 36 and Figures 11 and 12 for both rates of freezing. This would indicate that in berries which tend to lose more weight upon thawing, the minerals are not in a bound state and thus are extracted from the tissue.

Sodium, Potassium and Calcium

The amount of these cations present in berries after thawing and in the drip is presented in Table 37. It is observed that the amount of these cations found in the drip increased with an increase in the loss of weight of the berries upon thawing, for both rates of freezing as shown in Figure 13 and 14. Also berries which tend to lose more weight contained lower amount of sodium,

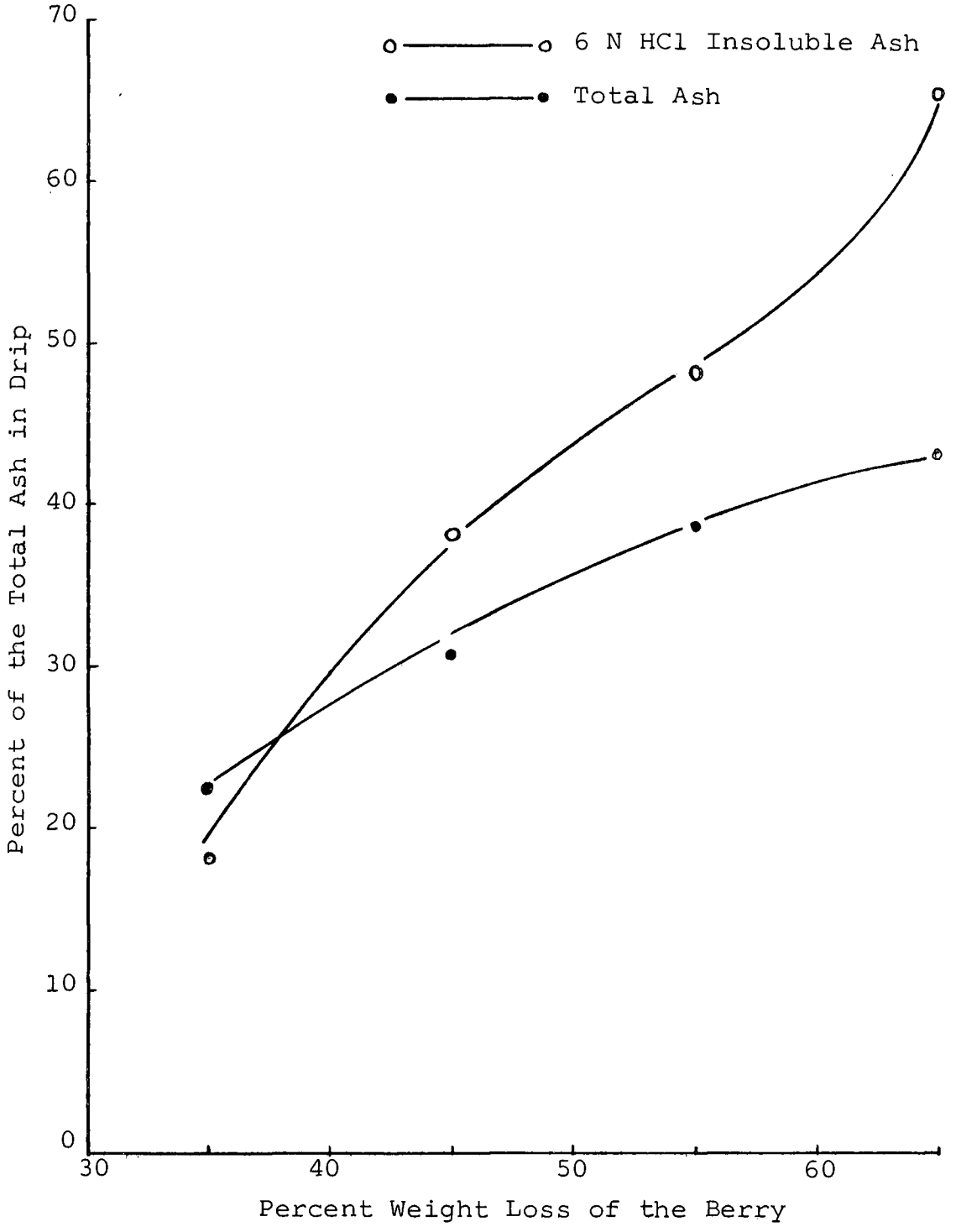


Figure 11. Effect of freezing and thawing on percent total ash and 6 N hydrochloric acid insoluble ash content of drip - slow frozen.

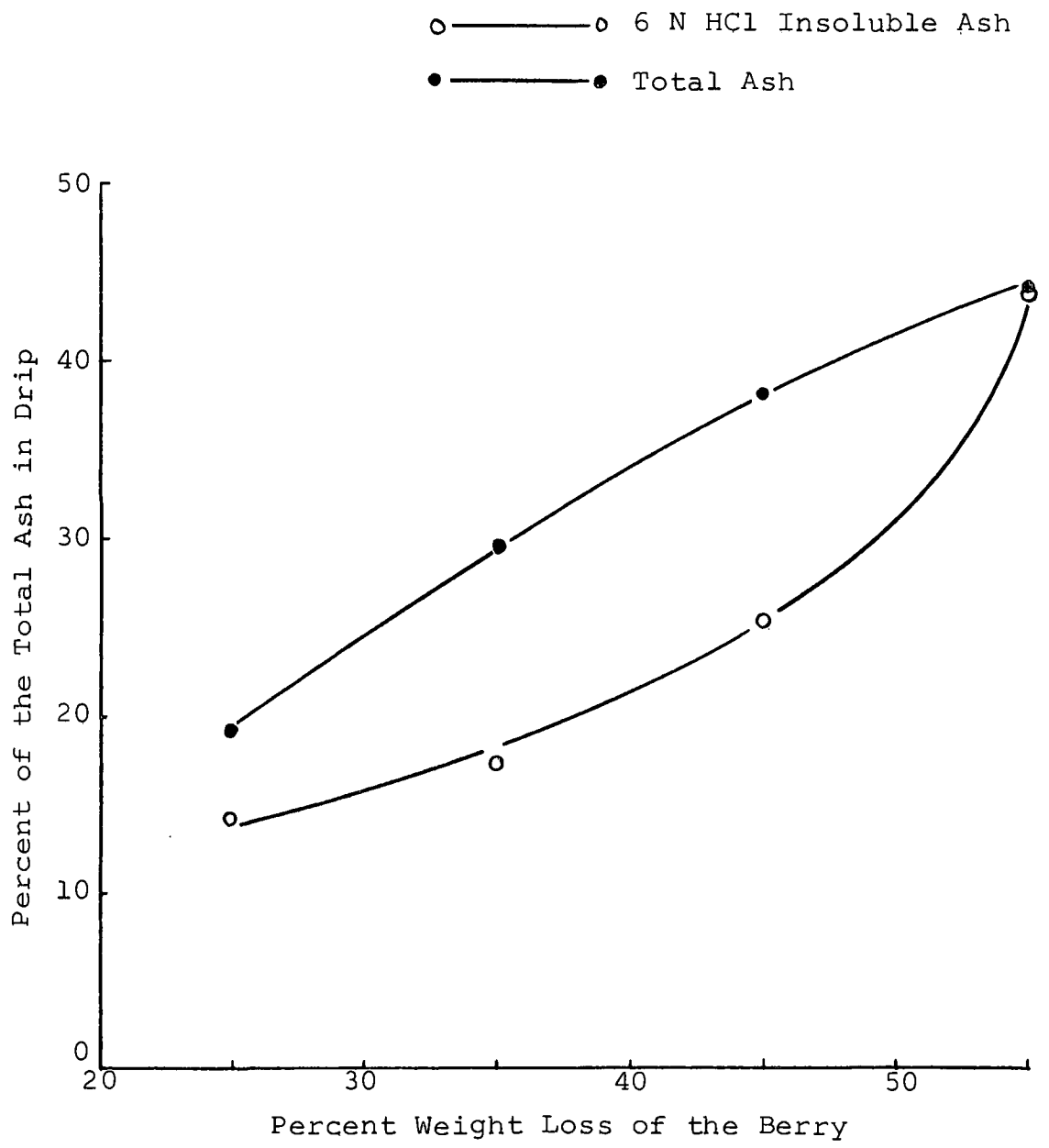


Figure 12. Effect of freezing and thawing on percent total ash and 6 N hydrochloric acid insoluble ash content of drip - quick frozen.

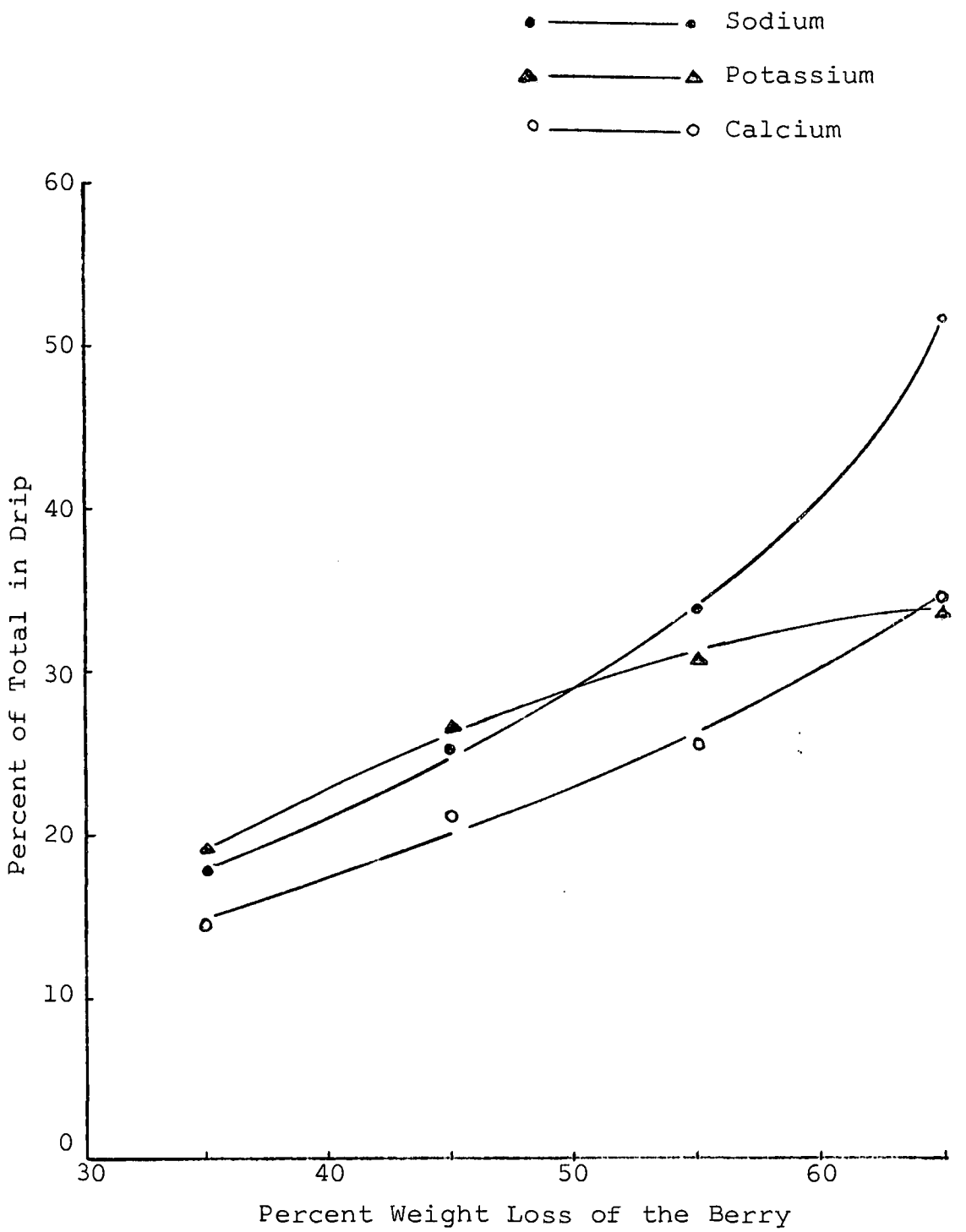


Figure 13. Effect of freezing and thawing on percent cations of drip - slow frozen.

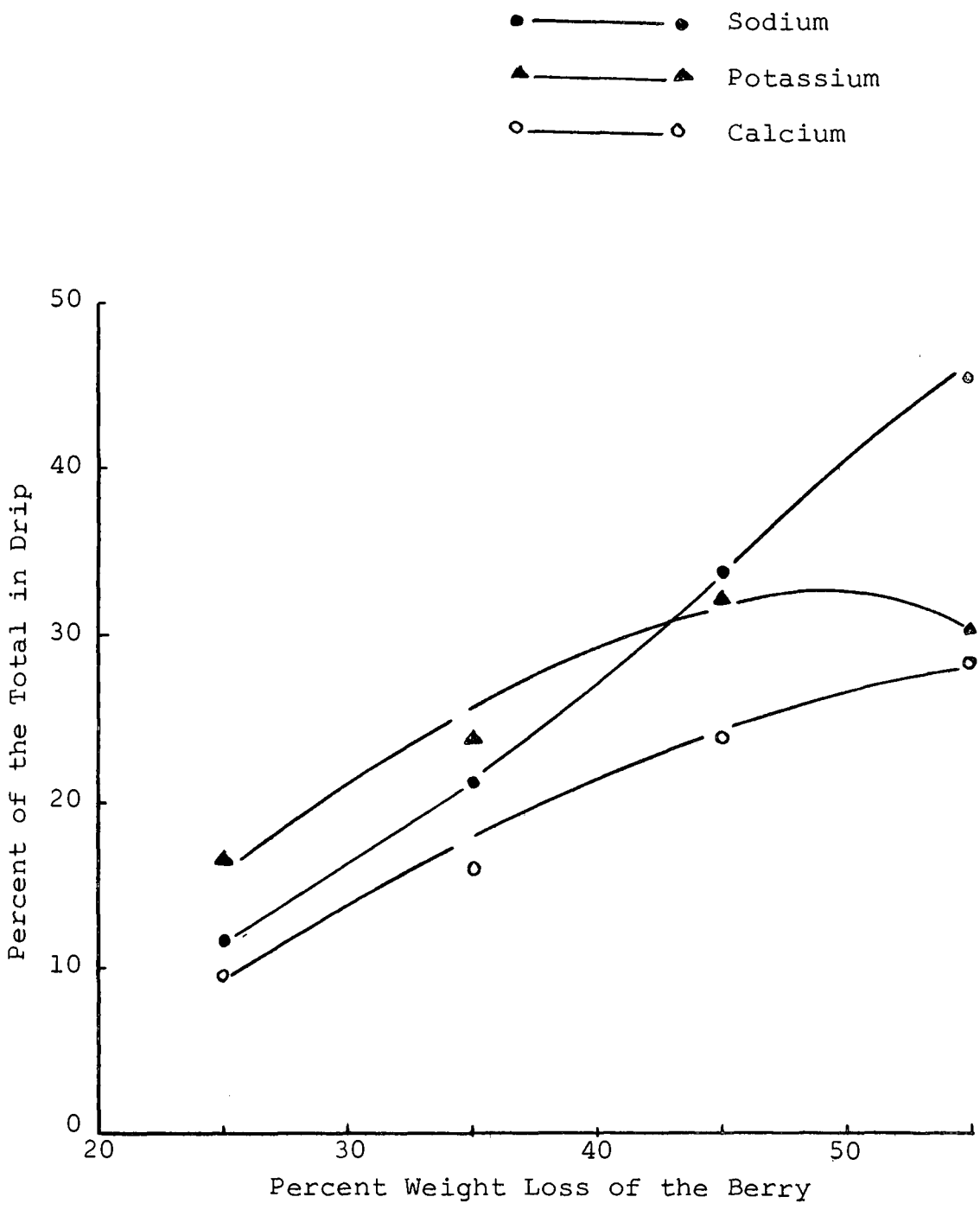


Figure 14. Effect of freezing and thawing on percent cations of drip - quick frozen.

Table 35. Distribution of Percent Total Ash and 6 N Hcl Insoluble Ash in Thawed Berries and Drip - Slow Frozen.

Item	Percent Weight Loss							
	< 40		40-50		50-60		> 60	
	TA ($\times 10^{-1}$)	AIA ($\times 10^{-2}$)	TA ($\times 10^{-1}$)	AIA ($\times 10^{-2}$)	TA ($\times 10^{-1}$)	AIA ($\times 10^{-2}$)	TA ($\times 10^{-1}$)	AIA ($\times 10^{-2}$)
	%	%	%	%	%	%	%	%
Berry After Thawing	2.06	2.55	1.63	0.58	1.39	0.38	1.26	0.49
Drip	0.60	0.57	0.73	0.36	0.88	0.26	0.96	0.93
Per. of Total Ash in Drip	22.56	18.27	30.93	38.30	38.77	48.15	43.24	65.49

TA = Total ash
AIA = 6 N hydrochloric acid insoluble ash

Table 36. Distribution of Percent Total Ash and 6 N HCl Insoluble Ash in Thawed Berries and Drip - Quick Frozen.

Item	Percent Weight Loss < 30		30-40		40-50		> 50	
	TA ($\times 10^{-1}$)	AIA ($\times 10^{-2}$)	TA ($\times 10^{-1}$)	AIA ($\times 10^{-2}$)	TA ($\times 10^{-1}$)	AIA ($\times 10^{-2}$)	TA ($\times 10^{-1}$)	AIA ($\times 10^{-2}$)
	%	%	%	%	%	%	%	%
Berry After Thawing	2.27	4.46	2.10	4.08	1.72	3.78	1.42	2.24
Drip	0.54	0.73	0.89	0.85	1.06	1.29	1.13	1.80
Per. of Total Ash in Drip	19.22	14.07	29.83	17.24	38.13	25.44	44.31	44.55

TA = Total ash
AIA = 6 N hydrochloric acid insoluble ash

Table 37. Distribution of Cations in Thawed Berries and Drip.

Cation	Item	Slow Frozen Percent Weight Loss				Quick Frozen Percent Weight Loss			
		< 40	40-50	50-60	>60	< 30	30-40	40-50	>50
		%	%	%	%	%	%	%	%
Sodium	Berry	0.0390	0.0370	0.0300	0.0150	0.0474	0.0418	0.0389	0.0283
	Drip	0.0085	0.0125	0.0154	0.0160	0.0069	0.0114	0.0199	0.0236
	Per. of Total in Drip	17.89	25.25	33.92	51.61	12.71	21.43	33.84	45.47
Potassium	Berry	0.0350	0.0300	0.0350	0.0360	0.0532	0.0424	0.0465	0.0379
	Drip	0.0082	0.0110	0.0156	0.0183	0.0106	0.0133	0.0223	0.0166
	Per. of Total in Drip	18.98	26.83	30.83	33.70	16.61	23.88	32.41	30.46
Calcium	Berry	0.0124	0.0101	0.0082	0.0077	0.0138	0.0126	0.0112	0.0081
	Drip	0.0021	0.0027	0.0028	0.0041	0.0015	0.0024	0.0035	0.0032
	Per. of Total in Drip	14.48	21.09	25.45	34.75	9.80	16.00	23.81	28.32

potassium and calcium than the ones which lost less weight. Comparison of Table 37 with Table 29 shows that the increase of these metals in the drip parallels the decrease of total pectin as well as 0.4 percent sodium hexametaphosphate soluble pectin and sodium hydroxide soluble pectin of the berries. Pectic substances in a cell have been shown to exist in the form of salts, mainly as calcium and magnesium pectates (40, p. 74). These high molecular weight pectins are insoluble in water and are related to the texture of fruits and vegetables. Joslyn (35, p. 3-7) in his review article on the chemistry of protopectin presents several possible models for protopectin, showing the involvement of calcium and magnesium. Pectin is present as a linear polymer of α-1, 4-linked D-galacturonic acid units, which are either fully or partially esterified with methanol and also some of the available OH groups acetylated by acetic acid. The extent of esterification with methanol and acetylation varies with the source of pectin and also with the maturity of fruit itself. As indicated by these data, the extent of methylation between individual berries is considerable. Thus, berries which showed greater amount of water soluble pectin in the drip and also a greater percentage of the total calcium, potassium and sodium, probably contain highly esterified pectins which would account for the higher percentage of these cations in free form

and which are readily extracted into the drip. These berries were also softer in texture as measured by shear press.

IV. The Effect of Freeze-drying and Reconstitution on the Physicochemical Properties of Northwest Strawberries

Reconstitution of Northwest Strawberries

Strawberries were reconstituted according to the procedure described on page 55. The reconstitution ratios for slow frozen and quick frozen berries averaged to 4.776 and 5.633 respectively. Table 38 presents the data of reconstitution ratio for the different size berries. Smaller berries showed slightly higher reconstitution ratios.

Table 38. Effect of Size of Berries on the Reconstitution Ratios.

Size of Berry	Rep.	Reconstitution Ratio			
		Slow Frozen	Ave.	Quick Frozen	Ave.
	1	4.990		6.121	
Small	2	5.061	5.020	5.638	5.776
	3	5.010		5.570	
	1	5.176		5.280	
Medium	2	4.779	4.999	5.811	5.599
	3	5.042		5.706	
	1	4.418		5.171	
Large	2	4.379	4.309	5.811	5.525
	3	4.131		5.594	

Texture

Strawberries after reconstitution were grouped into three groups based on their reconstitution ratios and their texture determined with the use of a shear-press. Area under the curves were measured and converted to inch pounds. These data are presented in Table 39. F values are shown in Table 40. Significantly higher values are obtained for berries which had higher reconstitution ratios in case of both slow and quick frozen berries. Quick frozen berries gave slightly higher values than slow frozen ones, but the difference was not significant at the levels tested.

Color

The average values for Hunter color determination are shown in Table 41. Significant differences were not observed between rates of freezing and between the reconstitution groups within a given rate of freezing. ΔE values between fresh and the two rates of freezing were 2.61 for slow frozen berries and 4.13 for quick frozen ones. a/b values did not show great deviation from fresh berries.

pH and Percent Soluble Solids

The data are presented in Table 42. The statistical

Table 39. Effect of Reconstitution on Texture - Total Work.*

Slow Frozen Reconstitution Ratio			Quick Frozen Reconstitution Ratio		
< 4	4-5	> 5	< 5	5-6	> 6
14.55	14.62	23.74	15.46	16.24	26.37

*Data presented as inch pounds/100 gms of fresh weight

Table 40. Analysis of Variance of Shear-press Values.

Source of Variation	df	F	Level of Significance	
			0.05	0.01
Replication	2	0.46	NS	NS
Freezing Treatment	1	2.42	NS	NS
Reconstitution vs. Freezing	4	17.74	S	S
Reconstitution vs. Slow Frozen	2	15.25	S	S
Reconstitution vs. Quick Frozen	2	20.22	S	S
Error	10			

df = Degrees of freedom
S = Significant
NS = Not significant

Table 41. Average Hunter Color Values of Reconstituted Berries.

Slow Frozen					Quick Frozen				
Rec. Ratio	L	a_L	b_L	a/b	Rec. Ratio	L	a_L	b_L	a/b
< 4	24.6	18.6	10.2	1.824	< 5	24.3	18.0	10.9	1.651
4-5	22.7	20.3	9.9	2.051	5-6	23.6	18.1	10.2	1.775
> 5	22.1	20.7	10.7	1.935	> 6	23.0	18.2	11.1	1.640

Rec. Ratio = Reconstitution ratio

Table 42. Average pH and Percent Soluble Solids of Reconstituted Berries.

Slow Frozen			Quick Frozen		
Rec. Ratio	pH	Percent Soluble Solids	Rec. Ratio	pH	Percent Soluble Solids
< 4	3.30	24.7	< 5	3.31	19.5
4-5	3.32	19.6	5-6	3.31	14.8
> 5	3.33	14.0	> 6	3.32	11.7

Rec. Ratio = Reconstitution ratio

analysis of these data did not show any significant differences in pH between the rate of freezing or between the different reconstitution groups within a given rate of freezing, either at 0.05 or 0.01 level of significance (Table 43).

The F values for percent soluble solids are presented in Table 43. Highly significant differences were observed between the two rates of freezing, with slow frozen berries showing higher values. Within a given rate of freezing the reconstitution ratio had an inverse relationship with percent soluble solids. As would be expected berries which had higher reconstitution ratio showed lower percent soluble solids. The average value for fresh berries was 8.27 while the values for slow frozen and quick frozen berries upon reconstitution were 19.41 and 15.36 respectively. The difference between fresh berries and reconstituted berries is probably due to the incomplete reconstitution. McIlrath, Dekazos and Johnson (51, p. 214) working with Swiss chard showed that freeze-dried samples reconstituted to a greater extent than any other method of freezing, however when various cellular components were isolated and their rehydration characteristics examined it was found that none of the components rehydrated to the level of intact tissue and also that the type of dehydration had no effect on their rehydration. Based on these observations they concluded that minimum disruption

Table 43. Analysis of Variance of pH and Percent Soluble Solids.

Source of Variation	df	pH			Percent Soluble Solids		
		F	Level of Sig.		F	Level of Sig.	
			0.05	0.01		0.05	0.01
Replication	2	0.19	NS	NS	17.78	S	S
Freezing Treatment	1	0.13	NS	NS	211.02	S	S
Reconstitution vs. Freezing	4	0.56	NS	NS	188.32	S	S
Reconstitution vs. Slow Frozen	2	0.94	NS	NS	246.10	S	S
Reconstitution vs. Quick Frozen	2	0.17	NS	NS	130.53	S	S
Error	10						

df = Degrees of freedom
S = Significant
NS = Not significant

of the tissue during the dehydration process results in a high degree of rehydration. During freezing of biological products several physical and chemical changes occur in the product, which result in the disruption of cells and cellular constituents which probably account for the incomplete reconstitution of the strawberries under observation herein reported.

Titratable Acids

The data obtained are presented in Table 44. F values and the levels of significance are shown in Table 45. Rates of freezing did not show significant differences in the titratable acid content of the reconstituted berries. Significant differences were observed between the various reconstitution groups within a given rate of freezing. Loss of titratable acids from the berries to the reconstitution solution, as shown in Table 44, was small and no differences were observed between the groups of reconstitution.

Total Solids and Alcohol Insoluble Solids

Data are presented in Table 46 and F values are presented in Table 47. A direct relationship was observed between degree of reconstitution and amount of total solids as well as AIS. Rates of freezing did not show significant differences at the levels of significance tested,

Table 44. Distribution of Percent Titratable Acids and Reconstituted Berries and Reconstituting Solution.

Item	Slow Frozen			Quick Frozen		
	Reconstitution Ratio			Reconstitution Ratio		
	< 4	4-5	>5	< 5	5-6	>6
	%	%	%	%	%	%
Berry	0.764	0.723	0.705	0.752	0.728	0.677
Rec. Sol.	0.139	0.126	0.120	0.137	0.128	0.109
Per. of the Total Titratable Acid in Rec. Sol.	15.39	14.84	14.54	15.41	14.95	13.86

Rec. Sol. = Reconstitution solution

Table 45. Analysis of Variance of Percent Titratable Acids.

Source of Variation	df	F	Level of Significance	
			0.05	0.01
Replication	2	5.70	S	NS
Freezing Treatment	1	1.20	NS	NS
Reconstitution vs. Freezing	4	7.10	S	S
Reconstitution vs. Slow Frozen	2	5.40	S	NS
Reconstitution vs. Quick Frozen	2	8.80	S	S
Error	10			

df = Degrees of freedom
S = Significant
NS = Not significant

Table 46. Average Percent Total Solids and Alcohol in Soluble Solid Content of Reconstituted Berries.

Item	Slow Frozen Reconstitution Ratio			Quick Frozen Reconstitution Ratio		
	<4	4-5	>5	<5	5-6	>6
	%	%	%	%	%	%
Total Solids	11.48	11.69	12.68	10.97	12.47	13.23
AIS	2.23	2.36	3.20	2.35	2.58	3.34

although slight differences were noticed.

Pectins

The average values for percent total pectin and its fractions are shown in Table 48. F values are presented in Table 49. Significant differences in the water soluble and total pectin were observed between freezing treatments and also between different reconstitution groups within a given rate of freezing. A direct relationship between ratio of reconstitution and pectin in the original berry was observed. McIlrath, Dekazos and Johnson (51, p. 215) showed a direct correlation between rehydration and maintenance of free polar groups in the tissue. Pectic substances being highly hydrophilic in nature have the capacity to bind water. The higher the pectic substances in a tissue the greater will be the sites for holding water. It is likely that such a mechanism is in

Table 47. Analysis of Variance of Percent Total Solids and Alcohol Insoluble Solids.

Source of Variation	df	Total Solids			AIS		
		F	Level of Sig.		F	Level of Sig.	
			0.05	0.01		0.05	0.01
Replication	2	1.28	NS	NS	0.72	NS	NS
Freezing Treatment	1	1.25	NS	NS	2.25	NS	NS
Reconstitution vs. Freezing	4	9.71	S	S	15.98	S	S
Reconstitution vs. Slow Frozen	2	4.61	S	NS	16.16	S	S
Reconstitution vs. Quick Frozen	2	14.82	S	S	15.79	S	S
Error	10						

df = Degrees of freedom
S = Significant
NS = Not significant

Table 48. Pectic Constituents of Reconstituted Berries.

Rate of Freezing	Rec. Ratio	Fractions of Pectin as AGA			
		WSP	CSP	SSP	TP
		%	%	%	%
Slow	< 4	0.107	0.089	0.102	0.289
	4-5	0.126	0.097	0.123	0.347
	> 5	0.159	0.112	0.131	0.402
Quick	< 5	0.130	0.110	0.125	0.365
	5-6	0.155	0.107	0.129	0.392
	> 6	0.171	0.130	0.140	0.440

WSP = Water soluble pectin
CSP = 0.4% Sodium hexametaphosphate soluble pectin
SSP = 0.05% Sodium hydroxide soluble pectin
TP = Total pectin

operation in strawberries. The percent of the total pectin found in reconstituting solution was small as shown in Table 50. Also the amount of pectin leached out of the berries did not greatly vary between the various groups of reconstituted berries.

Cellulose

Values obtained are for percent cellulose shown in Table 51 and the F values are presented in Table 52. Significant differences in the cellulose content of strawberries were not observed with different rates of freezing

Table 49. Analysis of Variance of Pectic Constituents.

Source of Variation	df	Fractions of Pectin											
		WSP			CSP			SSP			TP		
		F	0.05	0.01	F	0.05	0.01	F	0.05	0.01	F	0.05	0.01
Replication	2	1.25	NS	NS	3.13	NS	NS	0.87	NS	NS	0.48	NS	NS
Freezing Treatment	1	50.00	S	S	13.75	S	S	6.70	S	NS	59.52	S	S
Reconstitution vs. Freezing	4	41.25	S	S	5.31	S	NS	4.18	S	NS	33.48	S	S
Rec. vs. Slow Frozen	2	51.25	S	S	2.50	NS	NS	6.50	S	NS	45.95	S	S
Rec. vs. Quick Frozen	2	32.50	S	S	5.63	S	NS	1.85	NS	NS	20.95	S	S
Error	10												

df = Degrees of freedom
WSP = Water soluble pectin
CSP = 0.4% Sodium hexametaphosphate soluble pectin
SSP = 0.05% Sodium hydroxide soluble pectin
TP = Total pectin
S = Significant
NS = Not significant

Table 50. Distribution of Pectic Substance in Reconstituted Berries and Reconstituting Solution.

Slow Frozen					Quick Frozen				
Rec. Ratio	TP in Berry	TP in Rec. Sol.	TP	WSP in Rec. Sol.	Rec. Ratio	TP in Berry	TP in Rec. Sol.	TP	WSP in Rec. Sol.
	%	%	%	%		%	%	%	%
< 4	0.289	0.027	0.316	8.54	< 5	0.365	0.031	0.396	7.83
4-5	0.347	0.032	0.379	8.44	5-6	0.392	0.028	0.420	6.67
> 5	0.402	0.030	0.432	6.94	> 6	0.440	0.028	0.468	5.98

Rec. Ratio = Reconstitution ratio
TP = Total pectin
Rec. Sol. = Reconstitution solution
WSP = Water soluble pectin

Table 51. Average Percent Cellulose Content of Reconstituted Berries.

Slow Frozen Reconstitution Ratio			Quick Frozen Reconstitution Ratio		
<4	4-5	>5	<5	5-6	>6
%	%	%	%	%	%
0.194	0.226	0.238	0.199	0.241	0.255

Table 52. Analysis of Variance of Percent Cellulose.

Source of Variation	df	F	Level of Significance	
			0.05	0.01
Replication	2	1.41	NS	NS
Freezing Treatment	1	1.09	NS	NS
Reconstitution vs. Freezing	4	6.41	S	S
Reconstitution vs. Slow Frozen	2	4.84	S	NS
Reconstitution vs. Quick Frozen	2	7.97	S	S
Error	10			

df = Degrees of freedom
S = Significant
NS = Not significant

however, it was significantly different between the various reconstitution groups. Like pectic substance, cellulose compounds are capable of binding large amounts of water. A direct relationship exists between degree of reconstitution of the freeze-dried berries and their cellulose content.

Ash and Minerals

The data obtained for total ash, 6N HCl insoluble ash and minerals are presented in Tables 53 and 54. Only total ash showed a significant increase with increasing ratio of reconstitution for both slow frozen and quick frozen berries. The rate of freezing did not show significant differences. Total ash and mineral content of the reconstituting solution are shown in Table 55. Total ash and the three cations leaching out of the berries during reconstitution were small and no differences were observed between the various groups of reconstituted berries.

Table 53. Distribution of Percent Total Ash in Reconstituted Berries and Reconstituting Solution.

Item	Slow Frozen Reconstitution Ratio			Quick Frozen Reconstitution Ratio		
	< 4	4-5	>5	< 5	5-6	>6
	%	%	%	%	%	%
Berry after Reconstitution	2.46	2.60	2.98	2.49	2.85	3.02
Reconstituting Solution	0.29	0.30	0.27	0.26	0.30	0.28
Per. Total Ash in Rec. Sol.	10.55	10.38	8.31	9.45	9.52	8.48

Rec. Sol. = Reconstituting solution

Table 54. Average Percent 6 N Hydrochloric Acid in Soluble Ash Values of Reconstituted Berries.

Slow Frozen Reconstitution Ratio			Quick Frozen Reconstitution Ratio		
< 4	4-5	> 5	< 5	5-6	> 6
%	%	%	%	%	%
2.6	3.1	3.3	2.8	3.4	3.5

Table 55. Distribution of Cations in Reconstituted Berries and Reconstituting Solution.

Cation	Item	Slow Frozen			Quick Frozen		
		Reconstitution Ratio			Reconstitution Ratio		
		<4	4-5	>5	<5	5-6	>6
		%	%	%	%	%	%
	Berry	0.0403	0.0473	0.0470	0.0370	0.0420	0.0477
Sodium	Rec. Sol.	0.0430	0.0040	0.0029	0.0031	0.0030	0.0028
	Per. of Total in Rec. Sol.	6.93	7.79	5.81	7.73	6.67	5.54
	Berry	0.0403	0.0410	0.0443	0.0513	0.0490	0.0583
Potassium	Rec. Sol.	0.0045	0.0039	0.0033	0.0052	0.0053	0.0043
	Per. of Total in Rec. Sol.	10.04	8.69	6.93	9.20	10.76	6.87
	Berry	0.0110	0.0120	0.0143	0.0107	0.0127	0.0157
Calcium	Rec. Sol.	0.0014	0.0012	0.0012	0.0013	0.0012	0.0013
	Per. of Total in Rec. Sol.	11.29	9.09	7.74	10.83	8.63	7.65

Rec. Sol. = Reconstitution solution

SUMMARY AND CONCLUSIONS

In this thesis a study was made on the effects of freezing, thawing, freeze-drying, and reconstitution on the physicochemical properties of Northwest strawberries with particular reference to their textural characteristics. The work was carried out on the basis of an individual berry to study the effects of thawing and reconstitution. The results indicated the following conclusions:

1. Individual berries vary in their chemical constituents which are responsible for the differences in the properties of the berries upon thawing and reconstitution.

2. Rate of freezing is affected by the size of berries. Smaller the size, faster is the rate of freezing. Smaller berries also show characteristic supercooling effect upon show freezing.

3. Overall loss of color upon freezing is small and is independent of the size of berries. There is an increase in pH values and percent soluble solids of the berries upon freezing, owing to the breakdown of higher molecular weight substances like cellulose and proteins among other higher molecular weight constituents. A similar increase in the titratable acids upon freezing occurs, which is independent of the rate of freezing.

4. As a consequence of freezing and storage there is a decrease in total solids and AIS fractions of the fruit. The effect is more pronounced in slow frozen berries. An indirect relationship exists between the size of berries, total solids and AIS. Smaller berries are affected least due to freezing.

5. Freezing treatment and size of berries have no effect on pectic substances, cellulose, total ash, 6 N hydrochloric acid insoluble ash and potassium, sodium and calcium.

6. Strawberries lose weight upon thawing depending on the rate of freezing; the slower the rate, the greater is the loss. The relationship between size of berries and loss of weight upon thawing is direct, smaller the berry lower is the loss of weight for both rates of freezing.

7. A linear relationship exists between weight loss of the berry upon thawing and the area of drip, collected on filter papers. This method offers a convenient and quick procedure for quality evaluation of frozen strawberries.

8. Strawberries lose their original texture upon freezing and thawing, which is dependent on the amount of weight lost. With increased loss of weight upon thawing there is a parallel decrease in the texture.

9. Loss of weight of berries upon thawing is

dependent upon the total solids, AIS, pectic substances, cellulose, ash and mineral content of the berries. An inverse relationship exists between loss of weight and these components of the cell.

10. With increasing loss of weight of strawberries upon thawing there is an increase of total pectic substances, sugars, titratable acids, ash and minerals found in the drip.

11. Individual strawberries show variation in their ability to reconstitute. Quick frozen berries, on an average, reconstitute better than the slow frozen berries. Also, the size of the berry affects the rehydratability. The smaller the size, the higher is the reconstitution ratio, probably owing to a better penetration of water.

12. Strawberries with a higher reconstitution ratio are significantly better in texture. The degree of reconstitution depends on the amount of total solids, AIS, pectic substances, cellulose, ash and mineral content of the berries. A direct relationship exists between these factors. No significant differences are present in the leaching out of pectin, titratable acids, ash and minerals, between the various groups of reconstituted berries. Only a smaller percentage of these compounds are found in the reconstituting solution.

13. Variation in the chemical composition of the berries could be a result of various factors. Luh and

Dastur in a recent article (46) pointed out that variations in the raw fruit could be due to varietal characteristics, soil properties, horticultural practices, climatic conditions, and some other unknown factors like air pollution, nutrient levels, irrigation practices and chemical sprays. The strawberries obtained for this investigation were from a local processing plant where berries from several different geographic locations and perhaps of different level of maturity are combined together prior to processing. Any effort, either on the part of growers or processors to minimize such differences would be an advantage in preserving the quality of berries, which is the primary objective. In general, quick freezing resulted in a better product than slow freezing, hence this would offer a better processing technique.

BIBLIOGRAPHY

1. Anerback, E. et al. A histological and histochemical study of beef dehydration. V. Some factors influencing the rehydration level of frozen dried muscle tissue. Food Research 19:557-563. 1954.

2. Anet, E.F.L.J. and T.M. Reynolds. Chemistry of non-enzymic browning-I. Reactions between amino acids, organic acids, and sugars in freeze-dried apricots and peaches. Australian Journal of Chemistry 10: 182-192. 1957.

3. Aref, M. The viscosity of pectin extracts of loganberries and peaches as related to the quality of the frozen product. Master's thesis. Corvallis, Oregon State College, 1949. 56 numb. leaves.

4. Armbruster, G. Microscopic, physical and sensory measurements of characteristics of texture of fresh and frozen strawberries. Ph.D. thesis. Pullman, Washington State University, 1965. 86 numb. leaves.

5. Briskey, E.J. et al. A comparison of certain physical and chemical characteristics of eight pork muscles. Journal of Animal Science 19:214-225. 1960.

6. Burke, R.F. and R.V. Decareau. Recent advances in the freeze-drying of food products. Advances in Food Research 13:1-88. 1964.

7. Callow, E.H. Frozen meat. Journal of the Science of Food and Agriculture 3:145-150. 1952.

8. Chambers, R. and H.P. Hale. The formation of ice in protoplasm. Proceedings of the Royal Society of London, Ser. B, 110:336-352. 1932.

9. Chichester, C.O. The storage stability of freeze-dried peaches. (Abstract) Food Technology 10 (Sup. 5):22. 1956.

10. Coleman Instruments, Inc. Operating directions for the Model 21 Coleman Flame Photometer (D-332). Maywood, Illinois, March, 1962. 45 p.

11. Corridon, G.A. Freeze-drying of foods. A list of selected references. Washington, 1963. 79 p. (U.S. Department of Agriculture. National Agricultural Library. Library List no. 77)

12. Crafts, A.S., H.D. Currier and C.R. Stocking. Water in the physiology of plants. Waltham, Massachusetts, Chronica Botanica, 1949. 240 p.

13. Dalgleish, J.M. A short guide to freeze-drying. Food Manufacture 37:148, 151-156. 1962.

14. Daughters, M.R. and G.S. Glenn. The role of water in freezing foods. Refrigeration Engineering 52: 137-140. 1946.

15. Diehl, H.C. A physiological view of freezing preservation. Industrial and Engineering Chemistry 24: 661-665. 1932.

16. Diehl, H.C. et al. The frozen-pack method of preserving berries in the Pacific northwest. Washington, 1930. 37 p. (U.S. Department of Agriculture. Technical Bulletin no. 148)

17. Dietz, J.H. and A.H. Rouse. A rapid method for estimating pectic substances in citrus juices. Food Research 18:169-177. 1953.

18. Draudt, N.H. et al. Enzyme activity in freeze-dried foods. Washington, 1962. n.p. (U.S. Army. Quartermaster Contract Report DA 19-129-QM-1503)

19. Dubois, M. et al. Colorimetric method for determination of sugars and related substances. Analytical Chemistry 28:350-356. 1956.

20. Esau, K. Plant anatomy. New York, Wiley, 1953. 735 p.

21. Fennema, O. and W.D. Powrie. Fundamentals of low-temperature food preservation. Advances in Food Research 13:219-347. 1964.

22. Fieger, E.A., C.W. Du Bois and S. Kaloyereas. Freezing experiments on strawberries. The Fruit Products Journal 25:297-301. 1946.

23. Frey-Wyssling, A. Die Pflanzliche Zellwand. Berlin, Springer-Verlag, 1959. 367 p.

24. Gallop, R.A. The relationship of processing method to the physicochemical changes which occur in processed soft fruits. Ph.D. thesis. Corvallis, Oregon State University, 1963. 133 numb. leaves.

25. Gane, R. Chemical engineering methods in food industry. Some problems in cooling and freezing foodstuffs. Chemistry and Industry, 1955, p. 78-80.

26. Great Britain. Ministry of Agriculture, Fisheries and Food. The Accelerated Freeze-Drying (AFD) method of food preservation. London, 1961. 169 p.

27. Guadagni, D.G. and C.C. Nimmo. Time-temperature tolerance of frozen foods. XIII. Effect of regularly fluctuating temperatures in retail packages of frozen strawberries and raspberries. Food Technology 12:306-310. 1958.

28. Guadagni, D.G., C.C. Nimmo and E.F. Jansen. Time-temperature tolerance of frozen foods. VI. Retail packages of frozen strawberries. Food Technology 11: 389-397. 1957.

29. Hanson, S.W.F. Accelerated freeze-drying of food. Great Britain. Ministry of Agriculture, Fisheries and Food. Agriculture 68:499-500. 1961.

30. Harper, J.C. and A.L. Tappel. Freeze-drying of food products. Advances in Food Research 7:171-234. 1957.

31. Hustrulid, A. and J.D. Winter. The effect of fluctuating temperatures on frozen foods. Industrial and Engineering Chemistry 40:1423-1426. 1948.

32. Ingles, D.L. and T.M. Reynolds. Chemistry of non-enzymatic browning. IX. Studies of sugar monoesters of malic acid found in browned freeze-dried apricots. Australian Journal of Chemistry 12:483-490. 1959.

33. Isherwood, F.A. Some factors involved in the texture of plant tissues. In: Texture in Foods. London, 1960. p. 135-143. (Society of Chemical Industry. S.C.I. Monograph no. 7)

34. Jackson, S., S.L. Richter and C.O. Chichester. Freeze-drying of fruit. Food Technology 11:468-470. 1957.

35. Joslyn, M.A. The chemistry of protopectin: A critical review of historical data and recent developments. Advances in Food Research 11:1-107. 1962.

36. Joslyn, M.A. and L.A. Hohl. The commercial freezing of fruit products. Berkeley, 1948. 108 p. (California. Agricultural Experiment Station. Bulletin no. 703)

37. Joslyn, M.A. and G.L. Marsh. Observation on certain changes occurring during freezing and subsequent thawing of fruits and vegetables. The Fruit Products Journal 12:203-205, 220. 1933.

38. _____ Changes occurring during freezing storage and thawing of fruits and vegetables. Berkeley, 1933. 40 p. (California. Agricultural Experiment Station. Bulletin no. 551)

39. Kaloyereas, S.A. Drip as a constant for quality control of frozen foods. Food Research 12:419-428. 1947.

40. Kertesz, Z.I. The pectic substances. New York, Interscience, 1951. 628 p.

41. Lea, C.H. Chemical changes in the preparation and storage of dehydrated foods. In: Fundamental aspects of the dehydration of foodstuffs. London, Society of Chemical Industry, 1958. p. 178-194.

42. Lee, F.A. Determination of toughness of frozen asparagus. Food Research 8:249-253. 1943.

43. Lee, F.A., W.A. Gortner and J. Whitcombe. Effect of freezing rate on fruit. Food Technology 3:164-169. 1949.

44. Levitt, J. Freezing injury of plant tissue. Annals of the New York Academy of Science 85:570-575. 1960.

45. Li, Jerome C.R. Introduction to statistical inference. Ann Arbor, Michigan, Edwards Brothers, Inc., 1957. 553 p.

46. Luh, B.S. and K.D. Dastur. The texture and pectic changes in canned apricots. Journal of Food Science 31:178-183. 1966.

47. Luyet, B.J. Effect of freezing rates on the structure of freeze-dried materials and on the mechanism of rehydration. In: A symposium on Freeze-Drying of Foods, ed. by Frank R. Fisher. Washington, D.C., National Academy of Sciences, National Research Council, 1962. p. 194-211.

48. Mac Arthur, M. Freezing of commercially packed asparagus, strawberries and corn. The Fruit Products Journal 24:238-240. 1945.

49. Matz, S.A. Food texture. Westport, Connecticut, Avi, 1962. 286 p.

50. Mazur, P. Manifestation of injury in yeast cells exposed to subzero temperatures. 1. Morphological changes in freeze-substituted and in frozen-thawed cells. Journal of Bacteriology 82:662-672. 1961.

51. McIlrath, W.J., E.D. Dekazos and K.R. Johnson. Rehydration characteristics of freeze-dried plant tissue. In: A symposium on freeze-drying of foods, ed. by Frank R. Fisher. Washington, D.C., National Academy of Sciences-National Research Council, 1962. p. 211-217.

52. Meryman, H.T. Mechanics of freezing in living cells and tissues. Science 124:515-521. 1956.

53. _____ General principles of freezing and freezing injury in cellular materials. Annals of the New York Academy of Science 85:503-509. 1960.

54. _____ Introductory survey of biophysical and biochemical aspects of freeze-drying. In: A symposium on freeze-drying of foods, ed. by Frank R. Fisher. Washington, D.C., National Academy of Sciences-National Research Council, 1962. p. 1-13.

55. National Frozen Food Association. Frozen food fact book and directory. New York, 1965. 196 p.

56. Nemitz, G. Vergleichende Untersuchungen uber die Wasserwiederaufnahme grfriergetrockneter und warmluft getrockneter Gemuse. Die Industrielle Obst-und Gemuseverwertung 47:409-412. 1962.

57. Newton, R. and W.R. Brown. Seasonal changes in the composition of winter wheat plants in relation to frost resistance. Journal of Agricultural Science 16:522-538. 1926.

58. _____ Frost precipitation of plant juice. Canadian Journal of Research 5:87-110. 1931.

59. Penderson, C.S. and H.G. Beattie. Concentration of fruit juices by freezing. Geneva, 1947. 27 p. (New York. Agricultural Experiment Station. Bulletin no. 727)

60. Perkins, H.J. Note on chemical changes occurring in freeze-dried and fresh frozen wheat leaves during storage. Canadian Journal of Plant Sciences 41: 689-691. 1961.

61. Rao, A.V. The effect of processing and storage on the texture of canned berries. Master's thesis. Corvallis, Oregon State University, 1963. 72 numb. leaves.

62. Rolfe, F.J. The influence of the conditions of dehydration on the quality of vacuum dried meat. In: Fundamental aspects of the dehydration of foodstuffs. London, Society of Chemical Industry, 1958. p. 211-224.

63. Simpson, J. I. et al. A histological and histochemical study of beef dehydration. V. Some factors influencing the rehydration level of frozen dried muscle tissue. Food Research 19:557-563. 194.

64. Sistrunk, W.A. et al. Factors contributing to the breakdown of frozen sliced strawberries. Food Technology 14:640-644. 1960.

65. _____ Relationship of field and processing factors to the quality of frozen strawberries. Corvallis, 1962. 23 p. (Oregon. Agricultural Experiment Station. Special Report no. 138)

66. Smith, A.U. Biological effects of freezing and supercooling. Baltimore, Williams and Wilkins, 1961. 462 p.

67. Smithies, W.R. The influence of processing conditions on the rehydration of freeze-dried foods. In: A symposium on freeze-drying of foods, ed. by Frank R. Fisher. Washington, D.C., National Academy of Sciences-National Research Council, 1962. p. 191-193.

68. Szezesniah, A.S. and D.H. Kleyn. Consumer awareness of texture and other food attributes. Food Technology 17:74-77. 1963.

69. Tappel, A.L. Freeze-dried meat. II. The mechanism of oxidative deterioration of freeze-dried beef. Food Research 21:195-206. 1956.

70. Taylor, R.B. New method of quick freezing. Food Industries 9:701-704. 1937.

71. Tressler, D.K. Quality control in frozen industry. Proceedings of the Institute of Food Technology 6: 146-153. 1945.

72. Tressler, D.K. and C.F. Evers. The freezing preservation of foods. 2d ed. New York, Avi. 1947. 932 p.

73. Tucker, L.R. Fruit juice concentration by freezing and centrifuging. Proceedings of the American Society of Horticultural Science 38:225-230. 1940.

74. van den Berg, L. Changes in pH of some frozen foods during storage. Food Technology 15:434-437. 1961.

☆ 75. Webster, R.C., E.J. Benson and W.H. Lucas. Liquid nitrogen immersion freezing may upgrade frozen berry quality. Quick Frozen Foods 25:35-37. 1962.

76. Weckel, K.G. Tenderometer, shearpress and AIS values of Alaska and Perfection peas. Food Packer 35:24-26. 1954.

77. Weier, T.E. and C.R. Stocking. Histological changes induced in fruits and vegetables by processing. Advances in Food Research 2:297-342. 1949.

78. Weir, C.E. Frozen-dried and dehydrofrozen foods. Chicago, Illinois, 1960. 9 p. (American Meat Institute Foundation. Circular no. 60)

79. Wierbicki, E. and F.E. Deathrage. Determination of water-holding capacity of fresh meats. Journal of Agriculture and Food Chemistry 6:387-392. 1958.

☆ 80. Willis, A.G. et al. Effect of fluctuating storage temperatures on quality of frozen foods. Industrial and Engineering Chemistry 40:1423-1426. 1948.

81. Woodroof, J.G. Microscopic studies of frozen fruits and vegetables. Athens, Georgia, 1938. 46 p. (Georgia. Agricultural Experiment Station. Bulletin no. 201)

82. Woodroof, J.G. and E. Shelor. Effect of freezing storage on strawberries, blackberries, raspberries and peaches. Food Freezing 2:387-392. 1958.