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Title DIFFUSION OF SUGAR, ACIDS AND PIGMENTS DURING PROCESSING AND STORAGE OF CANNED BERRIES

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Processing and storage of berry fruits is accompanied by various changes, the important ones being the changes in the soluble solids content, titratable acidity, pH, pigments, and texture. A study was made of these changes in processed strawberries, raspberries, blackberries and blueberries, still cooked and stored at 78° F for one and six months in No. 10 cans. Three samples of the above four berries were analyzed before processing, immediately after processing and after one and six months of storage at 78° F. Five samples of syrups were collected from both center and side of the cans by means of 50 ml pipettes. These five samples were from top, 1 3/4", 3 1/2", and 5 1/4" from the top and from the bottom and a mean sample was taken from the drained syrup. The cans were then drained on an 8 mesh 10" screen. 100 gram samples of the drained solids from top, middle and bottom were collected for texture measurements.

The results indicated the following:

1. There is a decrease in soluble solids of the syrup and drained weight of the fruit immediately after processing. Softening of berries progresses with storage.

2. There is an increase in titratable acidity, pH and pigments of the syrup immediately after processing. Titratable acidity and pigments increase with storage and pH values were lower.

3. There is a tendency to reach an equilibrium in the can with regards to soluble solids in all berries and pigments in case of strawberries with a lower tendency for raspberries. In the case of titratable acidity equilibrium was almost realized in strawberries and blueberries. All berry packs showed no equilibrium in the pH value after six months.

4. No noticeable differences between samples collected from centers and side of the can.

DIFFUSION OF SUGAR, ACIDS AND PIGMENTS DURING PROCESSING AND STORAGE OF CANNED BERRIES

by

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INTRODUCTION

Fruits are important food items for human feeding, giving compounds needed to keep the body in a good nutrition. Canning of fruits is the most widely used method of extended preservation. Canning involves many problems, each commodity presenting its own characteristic problem. Food technologists have to find ways to improve acceptability, uniformity, and maintain nutritive value of the food. Color, flavor, and texture of fruit are three main factors which determine the quality of canned fruits.

The changes which take place during processing and storage of canned fruits, as a matter of diffusion of sugars, pigments, acids and water, comprise the problems of this study. The diffusion problem depends on many factors, such as temperature, time of processing and storage, and the presence of different compounds characteristic of each fruit.

REVIEW OF LITERATURE

1. Fruit Tissue

Fruit from the botanical point of view is usually the ripened ovary of the flower. However, certain accessory flower parts may undergo a development which makes them a part of the fruit. For example, the fleshy edible part of the strawberry is receptacular tissue.

The soft fruits, which belong to the small fruit class called berries, undergo the influence of many factors during processing which produce an effect on the textural characteristics.

Weier and Stocking (119, p. 298) point out that there is often a close relation between the cellular structure of the plant tissue and the quality of the finished product. They concluded that plant tissues are complex and may be considered as myriads of small individual colloidal systems. They demonstrated that parenchyma cells are alive, previous to processing, and the method and rate of killing these cells may have an important influence on the quality of the product. The epidermal layer is of considerable importance in processing.

In conclusion, they summarize the whole picture of cellular structure as follows:

The vacuole of most parenchyma cells is a dilute aqueous solution of various inorganic and organic salts, pigments and food materials separated from the protoplasm by a thin cytoplasmatic membrane. The cell is a complex, organized body. Its very existence is dependent upon a balance maintained by interfaces, between plastids, nucleus, vacuole and the cytoplasm and molecular orientation, such as that mentioned for the chloroplasts.

The food chemist is not dealing with a homogeneous mixture of chemical substances, since cellular organization, even in a dead cell, is complex. The relationship of substances within cells must be of great importance in determining the course of changes in foods during processing and storage.

Physiology of Tissues

a. Normal Cell - The histochemical features of the tissue that result in a loss of turgor may greatly decrease the acceptability of the product. It is necessary to know the function of the absorption, retention and availability of water in living and dead tissue.

Weier and Stocking (119, p. 297-342) say that the living plant cell is an osmotic system which maintains its turgor by literally "sucking itself full of water." During imbibation the vacuole becomes large, pressing the water-rich protoplasm tightly against the partially elastic cell wall, which stretches to a maximum at full turgidity. To say that the cell is an osmotic system implies a differentially permeable membrane enclosing a solution-filled central cavity. Such a system is represented by the living protoplasm which, surrounding the solute-rich vacuole and enclosed within the permeable cellulose wall, acts as a differentially permeable membrane. This allows water to pass through fairly rapidly but prevents or greatly impedes the penetration of most dissolved substances.

Because of their metabolic acitivity, plant cells are able to accumulate and retain quantities of inorganic solutes, greatly in excess of the concentration found in the external normal environment.

A diffusion pressure of the water will exist in regions where the activity of its molecules is high towards regions of lower activity. Pure water has a higher diffusion pressure than water in any other system under the same condition of pressure and temperature. The diffusion pressure of water may be increased: (1) by increasing external pressure (hydrostatic) or (2) by increasing the temperature. The opposite phenomenon of decreasing the diffusion pressure of water may take place by decreasing one of the above mentioned factors or by the addition of solutes or the addition of colloidally active material which may become more or less hydrated.

If a nonturgid, living parenchyma cell is placed in water, the diffusion pressure of water within the cell will be less than the pure water outside and water will diffuse into the cell, causing an increase in volume. Concomitant with this increase in volume, there will be an increase in hydrostatic pressure within the cell as the wall approaches its elastic limit. This turgor or hydrostatic pressure will increase the diffusion pressure of water within the cell and equilibrium will be attained when the increase in diffusion pressure due to turgor is just counterbalanced by the decrease due to the presence of solutes within the cell. At equilibrium, any addition of solute to the external water would cause a reduction in diffusion pressure of that water and water will diffuse out of the cell resulting in loss in turgor. The more solute added to the external solution, the more water will be lost from the cell and greater will be the loss of turgor.

Swanson (111, p. 21) writing about the studies of the cells said that "it is impossible to imagine any biological activity that does not involve a chemical reaction." Breathing, walking, seeing, tasting, even just existing, requires energy. This energy, in turn, is derived from chemical reactions that take place within cells.

The cell, therefore, can be considered as a chemical factory. Regardless of its nature, however, a cell, like a factory, must possess a certain organization in order to be efficient, it must contain a controlling or directing center, a source of supplies, a source of energy, and the machinery for making its product or performing its service. It is not surpirsing, then, that cells, despite their great variety of shapes, sizes, and function, share many common features.

If a cell becomes specialized, we might expect to find a change in organization and, possibly, the appearance of new parts but not at the sacrifice of basic features. For this reason, the biologist considers that "form and function are inseparable biological phenomena" to express it in another way, an organized activity is associated with an organized arrangement of parts.

The cell surface is bound by a cell or plasma membrane. This is the living outer boundary in all cells, but plant cells generally have an additional wall, exterior to the membrane and of variable composition, which serves for support. All materials coming into the cell must enter through the membrane and the wall. It is a living portion of the cell and the screen through which all substances taken into the cell must pass; it is elastic and pliable in some cells, quite rigid and unyielding in others, and it is capable of limited repair if punctured.

The membrane is also said to be semi-permeable, i.e. it permits the entry of some molecules into the cell but not others. Amino acids and glucose pass more easily through the membrane than do many other smaller molecules; size of molecule, therefore, does not always determine ease of passage. Potassium moves across the membrane rapidly and can accumulate in the cell; sodium does not. Water diffuses easily in or out of the cell, depending on whether solutions exterior to the cell are hypotonic or hypertonic.

Meyer (79, p. 225-226) summarized the idea of texture of fruits and vegetables saying that the texture depends on the turgor of the living cells as well as on the occurrence of supporting tissues and the cohesiveness of the cells. Turgor is the pressure of the cell contents on the partially elastic wall of a cell, tending to produce rigidity. It is produced by a delicate balance of forces which maintains the cell at a normal volume yet allows the exchange of substances. Cell tugor depends on a number of factors. (1) The concentration of osmotically active substances in the vacuole, in both true solution and colloidally dispersed. (2) The permeability of the protoplasm. (3) Elasticity of the cell walls.

b. Dead Cell - Weiber and Stocking (119, p. 297-342) said,

> Any food processing technique which alters the permeability of the protoplasm, the ability of solutes to be retained within the cell, the elasticity of the cell wall, or the colloidal nature of the contents, will alter the water retaining power of the cell, and possibly the crispness of the final product.

Death of the cell results in an increase in permeability of the protoplasm and if the cell is in a dilute aqueous medium, there will be a rapid diffusion of solutes out of the cell to regions of lower concentration. Accompnaying this loss of solutes, water will be lost and cell turgidity reduced. If the stored food in the parenchyma cell is chiefly soluble, there will be a great loss of solutes and the flabbiness of the tissue will be apparent. In the normal parenchyma tissue the large intercellular spaces are filled with air. Upon death of the tissue in a humid atmosphere, many of these spaces may become filled with solution pressed out of the cells by contraction of the cell wall.

If the tissue is of a type having highly elastic walls, full turgor will represent a highly distended condition and a large water content. Upon death of this type of tissue, water and solution will be forced out in large amounts due to the contraction of the distended walls. On the other hand, should the tissue be composed of cells having walls of little elasticity and great rigidity, full turgor will be represented by a relatively small change in volume over a placid condition and consequently, death will result in a smaller contraction of the wall and a smaller solution loss, although the solution will be held within the lumen of the cell in a much more loose state than when the cell was alive.

2. Processing of Fruits

a. Effect of Heat on the Texture of Fruits - Heat processing is the most common and successful method for commercial large scale food preservation. Heat, besides its effects on microorganisms and enzymes, changes the texture, color and flavor of the product and generally some physico-chemical and histo-chemical changes take place during processing and storage. Acceptability of a product is based to an extent on the texture of the fruit. Changes in cellular adhesion are of primary importance in determining the final texture of the product.

Adams (1, p. 36) in his discussion on effects of temperature on canned fruits said that the heat treatment serves two purposes: it destroys microorganisms present, thus preventing decomposition by yeasts, molds, or bacteria, and it softens the texture of the fruit, making it more easily digested.

The acidity of the fruit not only plays a part in the destruction of bacteria but also helps to bring about the softening which is one of the most obvious results of the cooking process.

Apart from seeds and stones, the insoluble material in fruits rarely exceeds 2-3 percent of the total weight, and the firmness of structure depends largely on the presence of certain relatively tough-textured substances, such as the pectates which are found in the middle lamella of the cell walls. During ripening these substances swell and soften so that the fruit, if left long enough, becomes mushy.

Somewhat similar changes take place during the process of cooking where the high temperature and acidity bring about hydrolysis and extraction of the less readily soluble substances. A result of such action is that the fruit collapses and its subsequent drained weight is reduced considerably. Over-ripeness, over-exhausting and over-processing tend to weaken the semi-solid structure of the fruit and to give a soft texture to the final product.

In the edible portions of fruits, the cell membrane materials which are found most abundantly are cellulose, hemicellulose and the pectic substances. Lignin is found to an extent in some portions, but this constituent is not affected by the mild conditions during processing. Esau (17, p. 30-35), Reeve and Leinbach (93, p. 602), Swanson (111, p. 20-22), Weier and Stocking (119, p. 300).

Cell membrane materials are subject to metabolic changes in these constituents under various conditions. Softening of the tissues of fruits and vegetables during ripening and storage has been shown to involve changes in the pectic substances.

Simpson and Halliday (100, p. 189-206) working on problems of "sloppy" pack in tomatoes and "rotting" of potatoes during storage have shown that these were mostly changes in the pectic substances. Careful examination of the cell walls revealed the fact that the loss of pectic substances was particularly evident in the regions of the primary wall and the intercellular areas. This was correlated with the hydrolysis of protopectin to pectin and as a result an increase in softness. Hydrolysis of insoluble protopectin to soluble pectin is favored by heat and by a pH of 3 or lower. They also found a decided difference between the cellulose of the raw samples and that of the steamed ones in the case of carrots and parsnips. In the raw samples a large portion of the cell walls were relatively thick and continuous, whereas in the steamed ones the walls were thin and broken.

Reeve and Leinbach (93, p. 602) in their investigations of texture in apples said that it does not seem likely that the slight differences in total acidity between two crop years were sufficient, on the basis of hydrolytic action alone, to explain differences in texture when these apples were heated. Correlation of acidity with sloughing upon heating is even less satisfactory if other varieties are compared. The pH of juices of these varieties ranged from 3.5 to 4.1 and this, a priori, does not seem a sufficient difference to explain the textural qualities observed. Delicious, intermediate in sloughing tendency, is a low-acid apple; Winesap, the firmest of the varieties here, has a high acid content and did not slough when boiled in 0.1 percent hydrochloric acid. It is not suggested, however, that pH changes in storage may not relate to subsequent changes in texture. Comparisons here are between apples "as received" and do not apply to metabolic changes in storage.

Reeve (93, p. 21) in his discussion on the texture in seed coats of peas, said that there were "inherent" histological and "environmental" factors which caused changes of the texture.

b. Effect of Heat on the Intercellular Air-Weier and Stocking (119, p. 330, 333) reported that the presence of intercellular spaces filled with air is common in parechyma tissue in fresh fruits and vegetables. After processing the proportion of air-filled spaces is changed resulting in a change of appearance of the product.

Crafts (13, p. 184-185) stated that in high-quality fruits and vegetables, the vascular tissues are small in amount and contain little lignified fiber tissue which constitutes the "strings" or "fibers" of the preserved product. Heat is a way to displace intercellular air from the tissues. In cooking, the cells, which initially were turgid, are rapidly killed. Sap, pressed from them, is available to displace intercellular air. Softening of the cell walls further alters the inherent structural properties of the tissue, allowing them to distort and to fit more closely together.

Reeve and Leinbach (93, p. 599-602) discuss the size of cells and intercellular spaces, the intercellular gas and physiological conditions of cell turgor in apples which may contribute to textural changes. Escape of expanding intercellular gases during heating appears to have appreciable mechanical effect upon tissue sloughing in some apples. When cell separation resulted from vacuum infiltration, it appeared that nearly all middle lamellar materials had been removed or solubilized.

Weier and Stocking (119, p. 338) concluded that, when intercellular air has been completely replaced by liquid during processing, subsequent dehydration may occur without the repenetration of air into the tissue. They also mention that the change in appearance upon blanching may not be of primary importance, but it is an index of complete penetration of heat. Such penetration brings about at least two beneficial reactions: First, it inactivates certain enzymes; second, it softens cell walls and improves the texture of the cooked product. This softening also prevents the reformation of bubbles that would contain oxygen to react with the tissues.

Crafts (13, p. 184) in his work concluded that there were three general effects which account for the displacement of intercellular air from tissue during blanching: (1) Heating expands the air so that it escapes from the cut surfaces, (2) there is a certain amount of leakage of cell sap from the killed cells into the intercellular spaces, (3) heating softens the walls so that they bend and give under the compressional forces of surface tension. Thus when the heated tissue cools, sap fills the space from which the air had been expelled. When intercellular air has been completely replaced by liquid during processing, subsequent dehydration may occur without the penetration of air into the tissue. This is especially true if the cell walls are not too rigid. Intercellular air trapped in the tissues contains gaseous oxygen that is free to react with ascorbic acid during storage. Complete displacement of intercellular air during blanching and dehydration may be taken as an index of chemical and physical changes in the cell walls. These changes bring about marked improvement in texture of the cooked product.

Talburt, et al. (112, p. 16-19) suggested that in order to prevent a break down during sorting and processing of red raspberries which became "mushy" during canning, the elimination of size-grading operation mostly the shaker-washer, reducing the cook time, using still-cooking instead of agitating and the selection of less mature berries. They suggested (a) size grading the berries prior to washing and (b) reducing the time the berries are in water.

All the above processes gave a product with a better texture quality.

Meyer (79, p. 274) described the changes of intercellular air as follows: "The parechyma tissue of fruits and vegetables is composed of cells separated by tiny pockets and passages of air. When the fruit or vegetable undergoes processing, changes occur in the intercellular air. On boiling a fruit or vegetable, a discharge of intercellular air occurs and replacement of the spaces with the cooking water."

Guadagni (24, p. 404) used the "sirup filling" treatment in apple slices to prevent the browning of apple slices after freezing and thawing and also to improve flavor, texture, and drip characteristics. By this treatment, the tissue gasses were removed from the slices by the use of a vacuum and the empty places filled with the syrup which contains a small amount of antioxidant.
The most satisfactory quality product resulted from using solutions of sugar (syrup) between 40 to 60 percent of sucrose.

Hohl (36, p. 287) in a study on "preparation and pretreatment of fruits for freezing," pointed out that the best way to control the changes in color, flavor and texture, was by exclusion of air.

1. Vacuum packing was more effective for small fruits (berries).

2. Another technique to exclude air was to cover the fruit with syrup or dry sugar.

The time of harvest is an important factor because slightly immature peaches, strawberries and other fruits were preserved in better physical conditions.

Meyer (79, p. 225, 226, 265) stated that the substance chiefly responsible for changes in volume is water. When a plant wilts, water has been so extensively lost from the cells that they no longer have normal tugor but are soft and flabby. During processing solutes and water stream out of the vacuoles into the intercellular spaces or even out of the fruit or vegetable and the food becomes soft.

c. Changes in the Acidity and pH - Adams (1, p. 39) said that a knowledge of the total acidity of the syrup at various stages of processing is of value not only because it gives an indication of the rate of chemical interchange between fruit and syrup, but also because the palate appears to be sensitive to variation in this factor even when the pH is constant.

The rise in acidity of the syrup corresponds very closely to the fall in density, the stable state being reached rapidly in the case of most soft berries and more slowly in stone fruits and currants. In most samples of gooseberries, strawberries, raspberries and loganberries the acidity of the syrup was virtually constant one day after canning.

Sinclair (101, p. 161) described the buffer properties of organic acids in juices of citrus fruits as follows: "All chemical reactions of living cells take place in different systems. The function of a buffer system is to supply the cells with a mechanism for resisting large changes in pH of the reaction medium upon the addition of strong acids or bases. As citrus fruits contain considerable quantities of organic acids and mineral constituents, the buffer system of the orange is composed mostly of organic acids and the salts of weak acids and strong bases."

The same author referring to the relation of pH to the titratable acidity of orange juice stated that large changes in acid concentration can occur with only slight changes in pH. This characteristic of orange juice is exhibited to a greater or lesser degree by most acid fruits. At a given pH value, the juice may have various concentrations of total acids. One of the reasons for the variations is the dilution effect of water in the juice, where the change in pH is largely independent of increases in the water content of the fruit.

The variables that may affect the pH value are indicated by the following equation, which is approximate for calculating the pH of weak acids:

$$\mathrm{pH} = \mathrm{pKa} + \log \frac{\mathrm{salt}}{\mathrm{acid}}$$

where the term "salt" indicates that of the organic acid present. The variation of pKa (dissociation exponent) with concentration is very slight and may be assumed to be a constant. This leaves the factor, $\log \frac{\mathrm{salt}}{\mathrm{acid}}$, as the only one that may vary the pH. This is not a dilution effect; the dilution of orange juice with water may change the free-acid concentration considerably without changing the value $\log \frac{\mathrm{salt}}{\mathrm{acid}}$ because the salt and acid would be diluted in the same proportions. An increase in salt takes place as a result of increased amounts of cations available for combinations with the acid radical. The total cation content of the juice is derived from the ash constituents, but not all of these constituents are combined with the organic acids. Some are combined with such anions as the phosphates, sulfates, and a small amount of chlorides.

Leonard, et al. (60, p. 433-436) in their discussion of citric acid and pH of canned tomatoes conclude that the pH of the canned tomatoes, immediately after processing, was about the same as that of the fresh fruit.

Adams (1, p. 37) pointed out that the importance of pH values in connection with canned fruits may be judged from the fact that the hydrogen-ion is one of the principal factors affecting the corrosion of metals, is a regulating influence in biological changes, and is a strongly toxic agent to bacteria.

The author found in experiments on a large variety of berries that the pH values of the syrup with most fruits, was altering rapidly at the end of the exhaust and the early stages of the cooking process. The rates for plums and cherries were slower up to this point in the process than for most of the soft fruits, but later the pH rapidly approached a stable figure. By the end of the full cooking period, nearly all the syrups were very close to the constant pH value.

Sane, et al. (96, p. 279-282) in their work on the pH and total acidity of raw and canned pimientos, found that canning causes a decrease in pH.

Maier and Shiller (72, p. 529-534) concluded from their experiments that heating to inactivate enzymes had very little effect on the subsequent rate of decrease in pH. The reaction responsible for this change was, therefore, primarily nonenzymatic. In the absence of oxygen, the rate of pH decrease was somewhat slower than that of the control in air. The same authors in a previous paper (71, p. 322-328) wrote that the primary reaction system responsible for the decrease in pH is nonoxidative and nonenzymatic since neither inert atmosphere nor heat treatments prevented this change.

d. Effect of Heat During Processing on Sugars - Wiegand, (124, p. 19) studying the function of dextrose in canning fruits said that fruit having a high active acidity will cause the sugar to react in a manner very similar to that of dextrose because acid in the presence of heat will invert the sucrose to dextrose and levulose, thereby, influencing its osmotic pressure.

The fruit during cooking undergoes a considerable dehydration because of the high density of the surrounding syrup. The cells play the role of a semi-permeable membrane for interchange of solutions permitting the lower density fruit juice to pass into the syrup more rapidly than the sugar from the syrup to be reabsorbed into the fruit tissue.

Nicholas, et al. (84, p. 207) in their studies of calculating a criterion of no convection in syrup-packed products mentioned that the viscosity alone cannot account for the slower heating observed when food products packed in syrups are heated. They concluded that the slowest heating point is near the bottom of the jar which is a point of high sucrose concentration. The top of the jar is the point of lowest sucrose concentration and highest temperatures. Since there is a region of high sucrose at the bottom of the jar, there will be some retardation of convection currents. They point out that stratification takes place during heat processing, and retards the heat transfer by convection.

Mulvaney, et al. (80, p. 210) concluded that the sugar concentration gradient is not constant at any time in heated jars and the gradient in heated jars during the heating period cannot be deduced from the gradient at the corresponding time in the unheated jars.

Sizer (102, p. 61) studied "the kinetics of calalyzed sugar hydrolysis as a function of temperature." According to the Arrhenius equation, the chemical reactions increase exponentially with temperature: $\ell n \frac{k_2}{k_1} = \frac{m}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ where k_1 and k_2 are the rates of reaction. The m value represents the energy in calories required to activate one mole of the calalyst (inorganic or enzyme) for the reaction. In the case of HCl as calalyst the velocity has the rate given by the above equation and the m value is equal to 26, 000.

In a third paper, the same authors(84, p. 211) made experiments with model systems where built-in stratifications that restricted convection to selected regions of a jar were examined to determine the effect of stratification on the heating characteristics throughout the jar. They found that the slowest heating points were in the regions just under the boundary between the water and the syrup. In both systems studies (with and without plastic spears) the all-water part was the fastest heating, but the all-syrup part heated nearly as fast. The data suggest that the syrup alone is not responsible for the slow heating regions observed in some of the arrangements.

Braun, et al. (8, p. 47-49) in their investigation to sweeten foods by adding dry sugar to the empty can, followed by the addition of the food and water to complete the fill of the container resulted in swells and flat-sour spoilage, because the sugar does not completely dissolve during the heat sterilizing process. A decreasing concentration of sugar from the bottom to the top of the container was found. The data showed that the severity of a given heat treatment is less in cans packed with dry sugar than in similar cans in which the sugar was added in syrup form. High concentration of sugar in packing foods increased the thermal death time and decreased the sterilizing value of the process.

Magoon and Culpepper (70, p. 196) have shown a slight difference in rate of heating of cans filled with varying densities of sugar solutions and attribute the slower heating of the more dense solutions to the somewhat greater viscosities of these media.

Adams (1, p. 40) has done experiments on different types of berries and found changes in density of the syrup during processing. He also observed that soft and ripe fruits interchange their constituents with the syrup more rapidly than firm tough-skinned fruits. In cases where the syrup freely circulated round the fruit such as raspberries, which possess a large area in proportion to their weight, a stable density was reached rapidly. This process was slowed down somewhat in cases where the fruit had been packed rather tightly. On the other hand, fruits with firm skins which do not readily split, such as black currants, bilberries and cherries, may take a long time to reach a stable density. In the case of the berry fruits, he found that the syrups in nearly all cases reached a stable figure within two days of canning.

The same author described that during heating the sucrose of the syrup in the presence of acid is converted in part into invert sugar. In addition, the fruits contain natural sugars which have already been inverted to some extent. The inversion of the sugars takes place rapidly during the period in which the contents of the cans are at a high temperature, and is influenced to a large degree by the pH of the syrup. Both the natural pH of the fruits and the condition of processing vary so widely that it is impossible to give accurate figures representing the normal degree of inversion reached when the diffusion process is complete. A very high percentage of invert to total sugars in a can is usually a sign of excessive heating during processing or of a high temperature or a long period of storage.

Cotton, et al. (12, p. 3) described the chemical aspects of sugar as sweetner and flavor, the reactions of sucrose and invert sugar, and the physical properties of sugar as osmotic pressure, crystallization, solubility, thermodynamic properties, viscosity, stickiness, and conductivity. They report that sucrose in neutral or very slightly alkaline solutions is very resistant to decomposition by heat. It hydrolyses to dextrose and levulose under acid conditions, especially at elevated temperatures. Continued exposure to low pH and high temperature results in production of a few parts per million of hydroxymethylfurfural, as well as caramel, biacetyl, and methyl glyoxal. The first has reported bacteriostatic activity.

Sucrose possesses very appreciable antioxidant properties. This is important in color, flavor, and ascorbic acid retention. Lea (55, p. 72).

The solubility of oxygen in sucrose solutions is less than in water (Joslyn 41, p. 8-14), and the decrease in solubility is proportional to the concentration of sucrose. At a temperature of 20° C a sugar solution of 60° Brix exposed to the air contains only one-sixth as much oxygen as water alone.

Viscosity is a prime consideration in design of liquid handling systems for sugars. Viscosity affects texture of certain foods, such as preserves and candies. Junk, et al. (43, p. 506-518) give data for pure sucrose solutions and solutions inverted 20, 50 and 90 percent. Calculations from their data indicate that at 40° C a 71° Brix syrup, which is 90 percent inverted, has a viscosity roughly 43 percent of that of pure sucrose at 71° Brix.

e. Soluble Solid Changes During Processing - Sinclair (101, p. 131) in his studies on oranges stated that soluble sugars and organic acids are the main constituents of soluble solids. The changes and distribution of soluble solids in the juice of fruits is important because many metabolic changes are based on these, such as differences in osmotic pressure and susceptibility to freeze injury. He pointed out that during maturation of oranges, the concentration of acids decrease and the soluble solids increase.

Stanek (107, p. 126) hypothesized on the effect of mineral and amino components on the refractometric estimation of dissolved solids, that on dilution there occurred, in addition to contraction, other physical changes such as dissociation, formation of hydrates, etc., which affected the refractive index.

Pederson, et al. (86, p. 10) reported that the use of specific gravity as an indication of total solids, cannot be an accurate measure of the total sugar present. They found 14.5 percent solids content measured by specific gravity in juice of apple-raspberry juice, although the actual percentage of total sugars was 11.3.

McRoberts (77, p. 375) mentioned that during heating of fruit products for determination of soluble solids, an increase in soluble solids percentage appeared because of the inversion of sucrose since water is added to produce fructose and glucose according to chemical reaction $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H+} C_6H_{12}O_6 + C_6H_{12}O_6$

Adams (1, p. 40) showed that soft berry syrups reached a stable density within two days after canning. The changes in densities expressed in degrees Brix during processing are given by the following table:

	Degrees Brix of Syrup		
	End of Exhaust	First-Cook	End of Cook
Strawberries	42.3	36.8	34.5
Raspberries	41.8	37.6	35.4

He explains that the equilibrium is rapidly attained after storage because the syrup freely circulates round the fruit which has a large surface area in proportion to weight. In the case of cherries, black currants, etc., the rate is low because they have a firm skin which doesn't easily and quickly split.

Marshall, et al. (74, p. 116-118) showed that by soaking treatment on cherries the soluble solids content is decreased as the length of soaking time is increased. They presented the following results:

No soaking	10.8% soluble solids
6 hours soaking	10.0% soluble solids
12 hours soaking	9.5% soluble solids
48 hours soaking	8.9% soluble solids

A decrease of tartness and flavor also follows the loss of soluble solids.

f. Effect of Processing on Pigments

The color of a food is an important criterion of quality, e.g. if the color is natural or changed, suggesting the degree of deterioration or perhaps improvement of the food.

A delicate and bright color in fruits and vegetables is extremely important to the consumer. Since fruit products and fruit spreads are sold usually in glass containers, the color of the product is an important factor in influencing the consumer's choice. We can say people buy with their eyes instead of with their palates.

We do not taste color or the substances that are responsible for it, but we associate color with flavor, texture, nutritive value, and wholesomeness. A colored object may create an illusion, or yield a knowledge, or give a perception to consumers thorough psychological considerations. Color involves problems from areas of science and art as physics, phychology, philosophy, and aesthetics.

Subjective tests by potential consumers are still essential for determining acceptability, but a knowledge of the chemical constituents which determine color, texture, and flavor makes one able to follow changes more accurately during maturation, processing, and storage. The cause of any improvement or deterioration in quality can be more easily investigated. Recent advances in the physics and engineering of color measurements have adequately solved the problem of color measurement of foods, in terms of internationally accepted units.

Most of the pigments of fruits and vegetables occur in plastids which are bodies found in the protoplasm of the cell. The water soluble pigments (as anthocyanins) usually exist in solution in the cell sap and are not generally distributed through the cell.

Anthocyanins are present in fruits as glucosides, mainly in combination with sugars, usually glucose, rhamnose, galactose, or sometimes with other sugars. Because of glucoside structure they are readily water soluble. One of the most characteristic properties is their amphoteric nature, which is responsible for the change of their color according to pH of solution in which they are dissolved.

The residual colored substances left after removal of the sugars by hydrolysis are known as anthocyanidins; they all contain the same carbon skeleton that of a benzopyrilium salt, and vary only in the number of hydroxyl groups.

Three types of anthocyanidins have been identified in plant tissues, cyanidin chloride, delphinidin chloride and pelargonidine chloride according to Conant and Blatt (11, p. 614-616). In the oxonium salt form all the anthocyanidins and the corresponding anthocyans are reddish; these salts are remarkably stable and have extraordinary crystallizing properties. When heated with alkali, they pass into a quinonoid grouping; on further treatment with alkali the phenolic hydroxyl group forms a metallic salt which is bluish.

Sondheimer and Kertesz (104, p. 609) reported that the color of strawberries, raspberries, blueberries, grapes and in many other fruits and flowers is due to the anthocyanin pigments which range in color from orange to blue.

Joslyn (40, p. 308) has pointed out that during processing, changes in pigments take place because of decomposition or chemical reactions with constituents present in the can. Especially in anthocyanins there is a change in tint due to the formation of stannous salts.

Culpepper and Caldwell (14, p. 107), in the introduction of their work write that many of the anthocyanins form complex salts with metals, resulting in alteration in color. The color reaction with aluminum chloride is a specific reaction for anthocyanins and makes a distinction between them and flavones and tannins. They found the purple or violet discoloration of canned fruits resulted from the reaction of pigments of the fruit with the tin of the container and also in enameled cans during processing. In the case where fruits were placed in glass containers, the original color of the fruit was preserved except that it has less intensity because of the partial conversion into colorless form by heat. The degree of discoloration depends on the amount of the pigment and the acidity of the medium. When the acidity is high, the corrosion of cans is less because of the formation of the anthocyanin salt.

Pederson, et al. (87, p. 78-83) tried different temperatures of pasteurization of juices of fruits, and found in strawberry and raspberry juices that with pasteurization above 180° F, the undesirable flavor effect was less noticeable than the color effect. The same authors in their work in 1947 (86, p. 101) stated that color changes in all juices are due to changes in viscosity, hydrolysis of sugars and destruction of ascorbic acid.

Griswold (23, p. 35) reported on the factors influencing the quality of home-canned Montmorency cherries using photomicrographs of fresh and canned cherries. Fresh cherries showed two epidermal layers, one above the other, each one cell layer thick. The cells are filled with red pigment. The whole surface of the cherries is surrounded by a continuous waxy cuticle. The picture of the canned cherries is different; the red pigment is distributed throughout the tissues. He assumed that the distribution of anthocyanin is due to the changes in the permeability of the cell walls because of the heat and syrup which causes a change in osmotic pressure.

Color development in liquid sugars during processing is more rapid in inverted types than in sucrose and is considered a function of heat and pH. Davis and Prince (15, p. 39 and 59).

Kramer and El. Kattan (51, p. 400) studying the effect of application of heat on tomato juice color found the loss of the color is greater as the temperature is increased, but the color loss is a logarithmic function, where every increase in heating time results in a smaller increase of color loss. They found that the color loss proceeds according to equation: Color loss = $\frac{TS}{525}\left(\frac{RT-120}{40}\right)$ where TS is temperature summations above 140° F and RT is retort temperature. They pointed out that an extreme time of processing at lower temperatures results in a higher destruction of color.

MacKinney, et al. (69, p. 324) showed that any stage during the processing of strawberry preserves which resulted in an introduction of oxygen caused a loss of pigment and the relation between increase in browning and decrease in anthocyanin was linear.

Markakis, et al. (73, p. 117) in their studies on strawberry pigment degradation concluded that the use in all stages of processing of the lowest possible temperature or better by using a short-time high temperature treatment resulted in a more stable strawberry pigment. Considerable pigment destruction could be caused by heating at lower temperatures for a longer time.

Luh, et al. (65, p. 53) reported that a pink discoloration developed in canned pears after processing for 35 minutes at 212° F followed by a slow cooling rate. High acidity is also related to the pink formation because it is catalyzed by the presence of the hydronium ion and excessive heating which supplies the activation energy for the reaction. They concluded that the pink pigment was cyanidin.

Work on strawberry and boysenberry juices showed that the first effect of heating on color is to fade it, so to decrease the absorbency. An excessive heating turns the juice brown followed with an increase in absorption in the region of 400 to 460 mμ. The authors, Ponting, et al. (89, p. 471-478) say that the decrease in absorption was due to loss of the pigment (in W. L. 520 mμ) and the increase in another region (400 mμ) suggested a browning development. The ratio A_{520}/A_{420} in the case of boysenberry or A_{490}/A_{420} for strawberry gave the rate of destruction as it decreased when the heat damage increased.

g. Effect of pH, Sugars, etc. on Pigments - Sondheimer and Kertesz (103, p. 245-248) showed the difference in the optical density of strawberry juice when the pH was changed from 3.5 to 2.0. The changes in absorption are due to different rate of acidification which changes the equilibrium between the color base and the oxonium salt because of the amphoteric nature of anthocyanins. Based upon this characteristic behavior of anthocyanins, one can determine them quantitatively.

The same authors (104, p. 609) in their studies to reduce color loss in strawberry preserves, found that not only the concentration of anthocyanins have an effect on the absorption of the pigment, but also pH, certain heavy metal ions, protective colloids and co-pigments (the tannins, flavone glucosides, and possibly alkaloids). They found no effect of sucrose, pectic substances, and citric acid in normal concentrations on the pigments. The best conditions for preservation is to cool down immediately after cooking and to store at temperatures below 60^{o} F.

Kohman (49, p. 191-196) has given special attention to the problem of perforation of the can by fruits containing anthycyanins. He has shown that the acidity of the fruit is not the most important factor determining perforation, since different products with like acidity but unlike pigment content show large differences in the readiness with which they produce perforation. Kohman's results have lead him to the belief that the role of anthocyanin in perforation is that of a hydrogen acceptor - that is, the pigment takes up the hydrogen produced, so that perforation occurs without previous perceptible swelling of the can.

Tressler and Pederson (115, p. 87) in experiments on grape juice preservation found that oxidative changes happened when air was present in the cans or bottles.

Meschter (78, p. 574-579) on his studies of the effect of carbohydrates, etc. on strawberry products found that the effect of pH is important, when the acidity is high the stability of pigment is protected. He pointed out that in presence of iron or copper ion the ascorbic acid is oxidized to dehydroascorbic acid with the formation of hydrogen peroxide which is responsible for some of the color loss of strawberry products.

Sondheimer and Kertesz (105, p. 288-98) suggested the following scheme for the oxidation:

$$H_2O_2 + Fe^{++} \longrightarrow HO^{\cdot} + HO^{-} + Fe^{+++}$$

$$HO^{\cdot} + Fe^{++} \longrightarrow HO^{-} + Fe^{+++}$$

$$Fe^{+++} + \text{Ascorbic acid} \longrightarrow Fe^{++} + \text{dehydroascorbic acid}$$

$$HO^{\cdot} + \text{Anthocyanin} \longrightarrow \text{?} \longrightarrow \text{oxidation products}$$

Meschter (78, p. 576) has shown that the stability of pigments of strawberry syrup is at a maximum at a pH 1. 8, and that below this value the stability is less, because of a reaction between pigment and products of sugar degradation. Fulfural and hydroxymethylfulfural are the main intermediate products of the degradation of sugars responsible for pigment loss.

There are some pathways for pigment destruction in presence of oxygen. Lukton, et al. (67, p. 27-32) found an insoluble red-brown precipitate and a soluble brown material as a result of strawberry pigment breakdown from oxygen oxidation. They suggested a conversion or polymerization of the pseudobase by the oxygen and second, hydrolysis of pigment and formation of a red-brown precipitate. In nitrogen atmosphere, only minute amounts of red-brown precipitate were formed for equivalent pigment losses.

Habib and H. D. Brown (31, p. 482-89) concluded that if air was included in canned strawberries and raspberries the color values were lower. From chromatographic analysis, they found that the red color of anthocyanin pigments in strawberry and raspberry was attributed from four to eight compounds.

Marhakis, et al. (73, p. 121) studied the relation between oxygen, ascorbic acid pigment and found that pigment is less stable than vitamin C.

In the case of 5-hydroxymethyl-2-furaldehyde (HMF) they agreed with Meschter's results that the products of sugars during heating in acidic solutions "are harmful to the strawberry pigments," because hexoses form HMF upon heating with acids in solution. Since hexoses are present in strawberries, and added or formed from sucrose, the presence of the HMF is probable. When air was replaced by nitrogen a higher pigment retention resulted, which in the case of untreated strawberry juice stored at 50^{o} C for 160 hours was 30 percent, whereas in the same juice under air there was 3 percent retention.

Tinsley (113, p. 46) writes that glucuronic acid and the ketose fructose, are the more active in the rate of pigment degradation of strawberry at pH 3.4. He also concluded that there is an increase of pigment degradation at higher concentrations of glucose, fructose or sucrose at pH 3.40 and at 90^{o} C.

Meyer (79, p. 244-247) writes that the salts which are formed by the reaction of anthocyanins with ions have colors which depend on the type of anthocyanins and metal ion.

h. Conclusion on the Changes During Processing - Many chemical and histological changes happen during processing of fruits and vegetables, but little is known concerning the changes occurring in the chloroplasts. These are a complicated system containing lipoids, carbohydrates, proteins, and pigments. They play an important role in the color, flavor, texture, and keeping quality.

The cooking during processing brings a softening in the structure of raw materials and also changes in the matrix of cellulose and swelling or a partial hydrolysis of the starch granules.

The amount of air has a pronounced influence on color, texture and appearance of the finished products.

When we refer to histological changes we should consider not only on the cell wall arrangements but also in alternations of the intracellular substances.

3. Drained Weight Behavior in Canned Fruits

The drained weight of canned fruits is an important indication of the quality of the product.

Changes of drained weight give a consistent relationship between different factors which affect it, as the concentration and volume of the added syrup and/or pectin, the degree of maturity, growth conditions affecting the size of the fruit and its total solids content, spray treatments, the time and temperature of heat treatment and storage time.

The standards for grades of canned foods of the U. S. D. A. use the drained wieght determination as an index of the condition of the canned fruits and as an aid to processors in packing better and more uniform products.

Adams (1, p. 37) mentioned that during processing where high temperature and acidity exist, there is a reduction in drained weight because of extraction and hydrolysis of the fruit constituents resulting in the collapse of the cells.

Hirst and Adams (35, p. 38) indicated that the drained weights of canned strawberries, raspberries, blackberries, loganberries, and cherries were related to solubilization of pectin during processing. This was thought to be due to high temperature and acidity which caused hydrolysis and extraction of less readily soluble substances. Drained weights were lower in over-ripe and over-processed berries owing to breakdown of fruit structure and to osmotic action of the heavy syrup, which caused shrinkage and shriveling due to loss of water by the fruit to the syrup. Soft and ripe fruits interchange their constituents with the syrup more rapidly than firm, tough-skinned fruits.

Wiegand (124, p. 17) reported the effects of three syrup variations on drained weights of canned fruits (peaches, pears, apricots, cherries, prunes and berries), during storage up to 210 days. His results as given for pears showed an initial, rapid decrease in drained weights well below fill weights for all three syrup variations immediately after canning. An increase in drained weights followed which gradually leveled off above fill weights and remained nearly equal for the three syrup variations between 40 and 160 days.

Whittenberger (121, p. 299 - 306) worked out the factors which affect the drained weights of heat-processed red cherries. He found no relation between soluble solids of raw cherries and the drained weight of the processed fruit. The intercellular cement has an increased strength if the tissue was treated by physiological or "conditioning" treatments, by calcium ions or by bruising, but these treatments have the opposite result on the color, acidity, tenderness and flavor of the fruit. Microscopic studies showed that single whole cells could be separated easily from tissues of low drained weight fruits, but not from tissues of high drained weight.

In another paper (122, p. 29-35) he pointed out that unbruised red cherries soaked in water increased in weight and firmness and decreased in soluble-solids content and acidity. He concluded that little difference exists between bruised and unbruised cherries in weight gain and that bruising has a slight effect on the color and soluble solids content of the product.

Ross (95, p. 18-22) has found that different canned fruits showed an equilibrium between fruit and liquids (syrups-water) at a period of storage of three months.

Bedford and Robertson (6, p. 321-323) examined factors affecting the drained weight of canned red cherries. High rainfall especially 3-6 weeks before the time of harvesting resulted in a lower drained weight. Concentrations in syrup at 20 - 30 percent gave a higher drained weight than those in which fruits were packed in water or 40 - 60 percent syrups.

Weast (118, p. 366) showed experimental graphs for canned fruit changes in drained weights which occur after packing. The relationship of storage time to drained weight on a semi-log scale plot was linear. The time required after canning for the minimum drained weight is usually 12 - 24 hours and for cherries about three days. However, the slope of the line may differ with different concentrations of sugar in the cover syrup.

Leonard, et al. (59, p. 80-85) working on canned clingstone peaches tried to find the relation between fill of container and drained weight because this is important not only for the flavor and quality but also for the case yield per ton. After canning, the drained weight was only 89 percent of the fruit fill weight, but after 30 to 90 days, the retention was 99 to 101.5 percent, respectively.

The higher drained weights appeared in the case of water and when the fruit was packed with 40^{o} Brix syrup. In higher concentrations of syrups, 50^{o} Brix or above, the drained weight was lower than the fill weight. Generally, the final drained weight is inversely related to the concentration of sugar in the canning syrup.

Labelle and Meyer (53, p. 347-352) have worked on the factors which affect the drained weights of red tart cherries and they concluded that there is an opposition in treatments for firmness and drained weight with retention of color and flavor. Over-ripe fruit has lower drained weight. They suggested that cherries should be handled with a minimum of bruising and be chilled and soaked in cold water for 4-10 hours at 40^{o} - 50^{o} F.

Luh, et al. (64, p. 253-257) reported that the drained weight of canned apricots was affected by various factors as growing area, storage time, fill weight and the level of ripeness. The latter is the most important factor because slightly green fruits gave higher drained weight. They attributed this difference to the changes in pectic substances existing between the cell walls of the fruit tissue occurring during ripening of the fruit. Protopectin is converted to water-soluble pectin that readily diffuses into the syrup. This caused decrease in firmness of the fruit, facilitating the exchange of constituents between fruit and syrup. In addition, over-ripe fruit tends to break up during canning. This caused a lower drained weight because a larger part of the fibrous material went through the screen. An increase in drained weight appeared after 5-10 days followed by a slow decrease until an equilibrium was reached after 45 to 60 days.

Leonard, et al. (60, p. 433-436) reported that the drained weight of canned tomatoes was slightly decreased in the case where the tomatoes were treated with citric 0.1 percent or the sucrose added was 1 percent of the filled weight.

Buch, et al. (10, p. 526-531) demonstrated that aged red tart cherries were more rigid than those which were canned immediately after harvesting. They explain that during the aging period a portion of the pectin, mostly that located in some specific part of the cell wall and perhaps in the middle lamella, is demethylated to form pectic acid.

Sterling (109, p. 629-634) has reviewed drained weight phenomena at length. He showed that during the first two or three days after processing, drained weight of fruit packed in syrup drops markedly, reaching a turning point (T. P.), where an increase in drained weight takes place, at first rapidly and later very slowly till an equilibrium is reached. The time to reach equilibrium is less than six months.

4. Physical Measurement of Food Quality - The Shear-Press

Instruments for measuring quality factors as hardness, succulence, and stringiness, for various raw and processed foods have been developed.

One of the most important is the shear-press which is a multipurpose instrument. It is used in forecasting harvest dates for lima beans, and generally is a valuable means for grading and quality control.

All the types of texture testing instruments which measure the tenderness, hardness, or firmness, fibrousness, etc. in a number of different products are known as tenderometer, texturemeter, maturometer, penetrometer, fibrometer, or pressure tester.

These instruments give the kinesthetic characteristics of the food, which deal with the sense of feel, just as the characteristic of appearance has to do with the sense of sight.

The structural condition of fruits and vegetables is one of the most important factors in our satisfaction when we eat them.

These structural conditions must conform to what our experience has taught us about the quality of each product. A physical makeup that we desire most in one product might repel us in another. We like crispness, or juiciness when it is associated with the specific food we are eating such as an apple.

> Our problem, therefore, is to find physical instruments which will simulate and measure the sensations which the consumer experiences through her sense of feel, with the fingers and particularly in the mouth,

A. Kramer and B. A. Twigg write in their paper (52, p. 197). Shear-press is a combination instrument where first compression and then shearing forces are applied. It imitates the action of teeth which compress and then shear the food.

Kramer (50, p. 112-113) developed this instrument which at first utilized some principles of the tenderometer and texturemeter and later in 1956, he improved it for multi-purposes. He transformed the mechanical energy of shearing force into electrical energy, which could be applied to give a graph in a roll-type recorder. Each product has its own particular curve pattern.

Hills, *et al.* (34, p. 32-35) studied the effect of bruising of red cherries and they found that there was an increase in tenderometer readings if cherries were stored for 15 hours in air or in water at 65^{o} F compared with cherries which were processed immediately after picking.

Sidwell and Decker (99, p. 10-11) have reported that the development of shear-press with a new electric recording system gives accurate texture recordings. In the case of fruits, they write as follows:

> The curves that resulted from testing strawberries showed definite differences in varieties. Those which had tough skin and core tissue had curves with relatively sharp peaks; those with uniform texture showed a more even curve.

5. Changes in Canned Fruits During Storage

Introduction - Changes in cellular structure of fruits during processing result in separating, rupturing, shrinking, or in a combination of these changes in the cells with a softening of the fruit. Canned foods undergo significant chemical changes during normal ambient-temperature storage, resulting in losses in quantity and nutritive value.

Tressler, *et al.* (114, p. 20) gave quantitative data showing how important it was to maintain canned foods at low temperatures, especially in the case of long storage periods. Vitamin content, color, flavor and general acceptability and quality of canned foods was much better at low temperatures.

Kohman, and Sanborn, (48, p. 293) presented data regarding the effect of storage temperatures on the percentage loss from springers and perforations and the rate of loss of color in canned strawberries, blueberries, cherries, etc. They concluded that not only is the life of a can extended by storage at lower temperatures but what is of equal importance, the natural color of the fruit is preserved.

Murray (81, p. 16) in his study gathering together the most important information on all phases of canned food storage, indicates the beneficial effects of reduced temperatures. He writes that during storage, very complicated reactions bring about changes in canned foods, and the speed of these changes are accelerated by increasing the temperature. This acceleration follows the general rule where a chemical reaction is doubled when the temperature is increased about 18° F. Undesirable changes due to bacteriological factors sometimes happen, usually at higher temperatures. The most serious action is internal corrosion of the cans, mostly by acid fruits such as berries, which are inclined to produce hydrogen resulting in a swelled can.

a. Changes in Texture, Drained Weight, Tenderness

Whittenberger (121, p. 299-306) concluded that between two lots of cherries, the one with the greater original drained weight gained more weight during storage. He has pointed out that cells of canned fruits are considered as an open network "cellulose sponge" where solute concentrations throughout such products soon equalize. Concentration gradients could still exist between coagulated protoplasmic compounds inside cells and the surrounding liquid.

Huggart, et al. (37, p. 268-270) noticed that 70° F. temperature storage is the best for maintenance of the original quality in canned grapefruit sections, because at higher temperatures (e. g. 80°, or 90° F) they found some slight changes in firmness at a period of three months of storage.

Leonard, et al. (59, p. 80-85) demonstrated graphically the changes of drained weight and brix readings during storage of clingstone peaches. For the first days, the drained weight was lower than the fill weight. Between two to ten days the drained weight increased rapidly and then more slowly as storage time increased.

The same authors reported also that they found the same behavior for canned apricots, with the only difference that after seven to eight days, the rate of increase of drained weight was less.

Guadagni, et al. (27, p. 36-40) showed by tenderometer measurements that there was a rather rapid increase in firmness of frozen cherries, in a period of four to five weeks at a temperature of 20° F.

The same authors in another paper (26, p. 633-637) showed that the drained weight of red raspberries stored at 20° F temperature gradually decreased to an extent of about 10 percent.

Similar work (27, p. 36-40) on packs of frozen cherries didn't show any trend of increasing or decreasing drained weights at 10° to 30° F. Samples which were slowly frozen showed a 5 to 10 percent decrease in drained weights.

b. Changes in Titratable Acidity and pH

Adams (1, p. 39) reported changes in acidity of the syrup of canned strawberries, raspberries, etc. the first day after canning and gave the following table.

Acidity Expressed as Percent Citric Acid

Berry	1 hour cool	1 day's storage	5 day's storage
Gooseberries	0.70	1.15	1.15
Strawberries	0.29	0.33	0.41
Raspberries	0.22	0.60	0.63
Loganberries	0.85	1.48	1.62

Ross (95, p. 21) reported that changes of pH in canned cherries, peaches and pears during storage reach an equilibrium between fruit and syrup after a storage period of about three months.

Guadagni, et al. (26, p. 633-637) demonstrated that in a period of two weeks storage at 20° F frozen raspberries markedly decrease the total acid ratio, which is the ratio between the acidity of drained fruit and syrup. The level of this ratio after two weeks of storage was about 0.5 to 0.7 due to migration of acids from berries to syrup.

Luh, et al. (63, p. 380-384) have worked on the changes of tomato juice during storage and they showed that an increase in titratable acidity was accompanied by an undesirable metallic flavor and a hydrogen swelling. The acidity was about .50 percent after a period of storage of 50 days at 55°C. After 220 days at 35° C the acidity was 0.53 percent. The acidity of all samples at the beginning of the storage period was 0.475 percent. The mechanism of formation and nature of the acidic compounds is not known, perhaps they are produced by oxidation or degradation of sugars present in the juice.

Livingston and Tan (61, p. 525-526) analyzed a 43 year old strawberry preserve and they found that there was a continuous increase in total acidity. They presumed that the increase was due to the formation of acidic products from reactions such as oxidation, degradation of sugars, etc. They found no difference in the buffer system (pH).

Leonard, et al. (60, p. 433-436) investigated factors which affect the pH of canned tomatoes and found that canned tomatoes after storage for two to three months at room temperature showed a lower pH of about 0.2 to 0.3 units. They consider this change due to (a) the hydronium ion derived from the hydrolysis of calcium chloride (b) production of CO_2 from the reaction between sugars and amino acids and (c) the degradation of sugars resulting in the formation of organic acids.

Van den Berg (116, p. 434-437) measured changes in the pH of frozen vegetables and meats during storage at -10^{o} and -18^{o} C (14^{o} and 0^{o} F). He concluded that since the pH depends on several physico-chemical factors, as buffer capacity, and ionic composition, changes take place continually in frozen foods.

Precipitation of salts during storage because of the increase in concentration of soluble material in the liquid phase as a result of ice formation could cause a large change in pH. Salt precipitation could be affected by an ion exchange condition between proteins or other substances and the solution. He suggested because of the similarity in pH curves that the same process and salts are involved in the pH changes in vegetables, meats, and milk. The first pH decrease during storage is probably associated with the precipitation of alkaline calcium, magnesium and sodium phosphates. The subsequent large pH increase is due to the precipitation of sodium and potassium citrate and acid potassium phosphate. The buffer capacity of phosphates, carbonates, and citrates is of little significance because either the acid or the alkaline salt will precipitate during freezing.

c. Changes in Sugars and Density (Soluble Solids)

The discussion of functions which take place during processing of fruits with syrup explains that during the first days after processing fruits have a low drained weight due to the loss of water.

The time needed for sugars to move from the syrup to the complex matrix of the fruit is short or long, depending upon processing conditions and the composition of the syrup.

The magnitude of movement of sugars into the fruit is a function which covers a period of time. The relationship between sugar penetration and the molecular size of the sugar species present in the syrup is important. These three phenomena are discussed by many investigators and the results of their work will be cited here.

Adams (1, p. 40) explains that the water of the fruit passes from the more dilute solution inside the fruit to the more concentrated solution outside the fruit as a result of osmotic action. The following table shows the changes of density of syrups from the end of cooling until five days of storage.

Densities Expressed in Degrees Brix

	End of Cool	1 hr. Cool	1 day's Storage	5 day's Storage
Gooseberries	36.9	34.6	26.6	26.3
Strawberries	34.5	30.3	27.6	26.9
Raspberries	35.4	33.0	28.9	28.3
Loganberries	33.6	31.4	26.3	25.7
Cherries (sweet)	33.1	32.0	28.1	24.8

The inversion of sucrose to invert sugars goes on slowly during storage. The temperature and pH are the main factors for this change. The results of this change are tabulated below:

Invertion Expressed as Percent of Total Sugars

	pH	4 months Storage	6 months Storage	8 months Storage
Gooseberries	2.72	61.8	67.3	--
Raspberries	3.35	24.5	24.7	26.1
Loganberries	2.88	45.5	49.6	--
Blueberries	2.95	36.3	43.0	46.0
Cherries	4.00	27.9	27.9	28.0

Wiegand (124, p. 16) reported certain variations in syrup effects that were interpreted on the basis of a higher rate of absorption of dextrose than of sucrose by the fruit due to its higher osmotic pressure and higher mobility because of the lower molecular weight (smaller particles), although dextrose is a simple sugar with a lower saturation point and solubility than sucrose. Dextrose with a higher osmotic pressure on a w/w basis stimulates osmosis resulting in a higher diffusivity which facilitates its molecules to move into the fruit sooner preventing shrinkage and loss of volume thus maintaining plumpness.

Two more factors are also important for a rapid attainment of equilibrium between syrup and the liquid of the fruit, namely the acidity (pH) and the type of fruit.

Pederson, et al. (86, p. 10) determined total and reducing sugars of different kinds of juices (apples, apple-raspberries, etc.) after several months of storage and for different temperatures. Significant changes were found due to different temperatures of storage; the amount of hydrolysed sucrose was proportional to the temperature of storage. There is a trend for an opposite effect between sweetness and acidity, by increasing the acidity the sweetness is lowered. The increase of acidity may have a relation to the change of viscosity.

Joslyn (41, p. 8-14) demonstrated that 30 - 31° F temperatures for 24 to 72 hours were the optimum conditions to obtain a syrup penetration in berries. The following table shows the loss of water and the absorbance of 50° B syrup by fruits:

Fruit	Treatment	Water lost %	Sugar Absorbed %
Strawberries	Whole	39.45	2.75
Strawberries	Whole, frozen at once	42.50	3.2
Strawberries	Whole, stored for 24 hrs. at 32° F	40.00	6.7
Red Raspberries	Whole	22.20	5.25

The same results were given by Wiegand (123, p. 16).

Livingston, *et al.* (62, p. 116-120), concluded that the main storage change in processed applesauce was a breakdown of the carbohydrate content, the inversion of sucrose and a considerable development of 5-hydroxymethyl-2-furaldehyde. They did not observe significant changes in vacuum, pH, and viscosity at room temperatures. There was a slight increase in acidity. With increased storage temperature, a loss in jar vacuum, a marked increase in darkening and a breakdown of the pectin fraction, accompanied by a reduction in viscosity.

Guadagni, et al. (26, p. 633- 657) demonstrated that the fruit/ syrup soluble solids ratio of frozen red raspberries during storage tended to reach one at temperature above 25° F by a gradual increase of solids content of the berries while the syrup solids decreased. There is a very slow change in the ratio at 20° F temperature.

The same authors (27, p. 36-40) on packs of frozen cherries found the same correlation in soluble solids between fruit/syrup. A period of eight to ten days is required to reach at equilibrium between fruit and syrup at 30° F.

d. Diffusion of Sugars into the Fruit by Such Function as Sorption, Osmosis, Sponge or Elastic Membrane Cell Walls, and an Explanation of Drained Weight Phenomena

An illustration of the modifications which take place during processing and storage of canned fruits in reaching equilibrium between the syrup and the fruit, can be given by running through the theories which explain the basic physical and chemical phenomena involved.

Friedman and Carpenter (18, p. 1745) worked on the diffusion velocity and molecular weight of glucose. The results showed that there is a linear correlation between diffusion and the square root of the concentration.

McBain and Liu (75, p. 59) write that,

> Diffusion is one of the simplest and most fundamental properties of substances in solution and yet its characteristics are seldom adduced even in discussing such closely allied phenomena as electrical conductivity or its dependence upon concentration.

They generalized the Nernst and Einstein equations in a combined form. The Nernst equation, is applied to the diffusion of electrolytes: $D = \frac{2RT}{\frac{1}{U} + \frac{1}{V}}$ where U and V are the ionic mobilities. The Einstein equation is applied to uncharged colloidal particles and large spherical molecules: $D = \frac{RT}{N6\pi\eta r}$ where r is the radius of the particle, η is the viscosity of the medium. The denominator gives the magnitude of the resistance to movement of each of the particles calculated by Stokes Law, $f = 6\pi\eta r$, where f is the frictional resistance of the molecules, Weiser (119, p. 189).

The new equation given by them facilitates the solution of problems since dimensions and solvation of molecules and colloidal particles in solution, the differences found between the gross viscosity of a system and that which determines its diffusion, and the effect of the simultaneous diffusion of various substances upon each other are given by the modified equation. For example, it was shown that different substances do not diffuse independently, but that one may construct a liquid diffusion pump whose action is analogous to that of the ordinary gaseous diffusion vacuum pump.

The relation of these factors is given by the equation:

$$D = \frac{iRT}{\text{Sum of resistances}} = \frac{iRT}{\Sigma(1/V_m)}$$

where iRT is the actual osmotic term instead of RT term used by Nernst and Einstein. The term RT, represents the driving force of the diffusion process and $\frac{1}{V}$ the resistance. The factor i is van't Hoff's empirical ratio between osmotic effect observed and that expected for an ideal non-electrolyte. The denominator expresses the sum of all the resistances to motion of the particular species as ions, molecules and particles, where V is the mobility of the particle (ion, molecule, colloidal particle) characterized by the symbol m.

In the case of 0.05 N and 1.00 N solutions of sucrose, they found that the viscosity of these two solutions as determined in capillary flow viscometer is, namely, 1.047 and 3.080, respectively, times that of water, whereas the diffusion coefficients differ only by 18 percent in spite of the fact that Einstein's equation predicates that diffusion is inversely proportional to the viscosity.

Gladden and Pole (22, p. 3902) found that the diffusion coefficients in glucose and sucrose solutions decrease with increasing concentration, and that the activation energy for diffusion for both sugars increases approximately linear with the mole fraction of the solute.

In the case of sucrose, the activation energy rises at a more rapid rate. Because the activation energy for diffusion rises above the heat of vaporization of water, the mechanism of diffusion involves the simultaneous breaking of several hydrogen bonds, as many as three in the case of the most concentrated glucose solutions.

Gillman (21, p. 84-92) found that the rate of diffusion and temperature in a sucrose solution moving through a membrane gave a straight line obtained by plotting log D against 1/T. The value of the diffusion coefficient for sucrose did not depend on the length of the diffusion period, the absolute concentration level or the influence of solvent counterflow. The above are influenced by the assumption that Fick's law is true with D constant, and second that an infinitely sharp boundary was formed at zero time.

Van Hook (117, p. 370) has indicated that the diffusion coefficients of aqueous sucrose solutions diminish linearly from concentrations above one molar to at least the saturation concentration. The Stokes-Einstein implication of an inverse diffusivity-viscosity relation is entirely inadequate to explain the results obtained from this work. They assumed that some other factor is operating which has a more pronounced effect upon viscosity than upon diffusion. A hydrogen bonded cluster of sucrose molecules might offer tremendous fluid resistance to movement through a medium, and yet lose or exchange its individual members quite freely in diffusion.

The high initial osmotic pressures in cover syrups would no doubt cause a rapid translocation of water from fruit to syrup immediately after canning. It seems logical to assume that a translocation of sugar molecules from syrup to fruit would also occur, depending on the permeability of the fruit matrix. The diffusion rates of individual sugar molecules would be dependent upon their respective concentration gradients and diffusion coefficients, according to Fick's first law of diffusion which is given by the equation: Weiser (120, p. 188-191) $- D \frac{dn}{dx} = vn$, where D = diffusion constant, the minus sign signifying that the solute diffuses in the direction of decreasing concentration, v = velocity of a molecule, n is the number of gram molecules of solute per unit volume.

On combining the Stokes and Ficks laws, we obtain the equation $D = \frac{RT}{N} \cdot \frac{1}{6 \pi \eta r}$ which expresses the diffusion constant in terms of the viscosity of the medium and the radius of the particles which are large compared to those of the medium.

Some of the diffusion studies reported above have been conducted in model systems of two or three components, water and one or two sugars. Unfortunately, because of the many components present in canned fruits, these theoretical findings cannot be directly applied to the problem of sugar penetration.

On the other hand, many factors appear to affect the penetration of sugars into a canned fruit product: type of fruit, processing conditions and composition of the syrup, although some of these factors have been studied, uncertainties still exist regarding the relationship between sugar penetration and the molecular size of the sugar species present in the syrup. The following literature review will concern studies on different kinds of canned fruits.

Ross (95, p. 18-22) has indicated that translocation of sugars from syrup to fruit, in the case of cherries, pear halves and peach halves and slices, is mostly an osmotic phenomenon where a rapid movement of water and hydrogen ions and relatively restricted movement of sugars within complex fruit matrix takes place.

In this theory, the membranes of the cell are selective: they will permit certain molecules to pass more freely than others. Thus, water will move through much more readily than dextrose which, in turn, will move through more readily than sucrose.

The rapid translocation of water of fruits to syrup, following the initial osmotic pressure gradient, causes the initial shrinkage in drained weights of the fruits. At the same time, usually about three days after canning, the sugars of the syrup move in the fruits resulting in a rapid reduction of the osmotic pressure gradient until a retardation of water translocation happens when there is an isosmotic condition between fruit and syrup.

True equilibrium conditions are reached after a period of storage of about three months with a further increase of drained weight of fruit. A small increase in fruit drained weight may be expected after a longer storage period. The different types of fruit used gave different drained weight recoveries because the rate of translocation of sugars and water depends on the type of fruit pack and type of cover syrup.

Leonard, et al. (59, p. 80-85) reported factors which influence drained weight of canned clingstone peaches. The semi-permeable membrane of the peach cells is destroyed after canning and the exchange of the solvent and solute molecules between syrup and fruit is facilitated. The rate, direction and extent of diffusion of the substances in the whole can follow the laws of thermodynamics and the time required to reach equilibrium was controlled by the concentration gradient, mobility of the moving molecules and elastic properties of the tissue (cell walls).

The brix of syrup decreased while that of the fruit increased for a period of about 30 days when an equalization was realized. The sucrose concentration had an effect on the drained weight. In the case where fruits were canned in 50° Brix or higher concentrations, the drained weight was lower than the fill weight.

Hughes, Jr., *et al.* (38, p. 111-115) studied the penetration of maltosaccharides into canned clingstone peaches and the distribution of radioactive sugars was followed using the method of autoradiography. According to this study, sugar penetration into the fruit occurs "in mass." However, higher concentrations of sugar were found in the vascular bundles than in the neighboring parenchymatous tissues.

Sterling (109, p. 629-634) has reviewed drained weight phenomenon extensively, and proposed several hypotheses to explain various consistent relationships. The role of polysaccharide molecules of the cell wall was considered important. On the current hypotheses of drained weight behavior, the author writes

> When there are differences in sugar concentration (*i.e.*, differences in water activity) between the living cell and its environment, movement of water will occur in the direction from regions of higher, to those of lower, water activity. In hypertonic solutions, cells will therefore tend to lose volume as water leaves the cell. In hypotonic solutions, they will tend to gain volume because of water entry.

The osmotic hypothesis in relation of sugar, acid and water movement, which is mostly applied to living cells, could explain drained weight changes.

He writes that:

> Osmosis may be defined as the movement of a solvent, through a membrane permeable to it alone or to it more than to the suspended solute, from a region of greater solvent activity to one of less solvent activity.

The direction of water movement is determined by the differences of water activity while membrane permeability regulates what kind of particles except water could pass through it. The canning process is lethal for cells and the selective permeability of the living cells is lost, therefore, osmotic phenomena can no longer be involved and the fruit tissue appears to have sufficiently large "pores" to permit diffusion of sugars and acids.

Gallop in a recent work (20, p. 25) writes the following about the drained weights changes:

> Drained weights vary widely, often without ready explanation. Canned strawberries usually show a recovery of 65 - 70 percent of fill-in weight as drained weight, with the figures rising for other fruits, up to about 100 percent for clingstone peaches. Frozen fruits also vary widely in drained weights. Such a wide range of drained weight recoveries has not been highly correlated with any simple index, such as initial fruit to syrup Brix ratio. While the weight change has been almost wholely attributed to osmotic effects, cell volumes, cell wall elasticity and cell wall strength must contribute to the final drained weight when solute equilibrium prevails throughout the product.

The "cellulose sponge" theory, which Whittenberger (121, p. 299-306) tends to regard, has a limited significance because it does not explain the increase in weight beyond the turning point and the role of sugars in obtaining an equilibrium in drained weights.

Cell wall firmness, which is a factor explaining in part diffusion problems, defines the elastic properties of cell walls. Occurrence of cell wall lysis during maturation showed that breakdown of the wall must be attributed to degradation of noncellulosic, probably pectic, materials. Sterling (109, p. 631) pointed out:

> While a pectic gel is generally weaker than a cellulosic gel, the cellulose-reinforced pectic gel of the cell wall does have considerable rigidity and strength, although in cooked plant materials, failure under stress usually occurs in the middle lamella; in uncooked tissues, failure often occurs across cell walls rather than along the middle lamella between them.
>
> During fruit shrinkage in canning syrup, the cell walls are deformed. If the pectic materials in a wall exist as a rigid gel, that wall will be better able to reestablish its original form upon release of the stress than one in which the pectic substances are degraded. The importance of cell wall firmness (high relaxation time) lies in the potentiality of establishment of cell shape.

In the paper on the effect of the cell wall on drained weights, Sterling (109, p. 629-634) assumes that there are two possible actions of hydrophilic materials in the drained weight recovery. First, they facilitate water sorption resulting in a re-establishment of original cell volumes in the absence of turgor. Secondly, they may confine water in the fruit when sugars are still present in greater concentration outside the fruit.

These two hypotheses do not explain the turning point and the author concludes that:

> It is difficult to picture a mechanism by which the unaltered hydrophilic materials within the cell could increase the weight of the fruit to a value higher than the fresh weight. If the polysaccharides of the cell walls are 'swollen' by cooking, then there is indeed a possibility for ultimate weight increase in excess of the filling weight.
>
> The solutes of the fruit and of the syrup can attain a fairly close approximation to complete equilibrium in a reasonable period of time. Hence, except for denatured protoplasmic proteins within the cell, fruit and syrup should not be regarded as separate entities after canning (at least, when peeled fruit is considered). Rather, a distinction should be made between cell wall substances and the solution which bathes them.

In another experiment by Sterling (110, p. 157-160) peach tissues were cooked or canned in syrups which contained radioactive sugars and radioactivity was found to be highly concentrated in the cell walls of the fruit. It was concluded that the sugars were absorbed against a concentration gradient, via hydrogen-bonding. These bonds would occur between hydroxyl groups on the sugar molecules and hydroxyl groups on polysaccharide molecules (cellulose, pectic materials, hemicelluloses) in the cell wall.

A sugar-adsorbing role for the cell wall could help explain the rapid entry of sugar molecules into the fruit tissue. It could also explain the production of a surplus concentration of sugar within the cell wall, with the consequent lowering of water activity in that structure.

Pectic materials would have an important role in this adsorption because of their hydrogen-bonding capacity, much larger per unit molecular weight than is available in the more highly crystalline cellulose.

Sterling (109, p. 629-634) proposed the theory that a final equilibrium of drained weights after a period of storage will be approached when the rate of sugar movement is very low, because of the saturation of the free hydroxyl groups. The rate of water uptake in the cell walls will also decrease. Then another diffusion equilibrium will be established with other organic and inorganic compounds in the fruit and syrup. Finally, the sugar concentration should be higher in the fruit than in the surrounding syrup, because there is also an intracellular equilibrium between sugar absorbed on the cell wall and that dissolved in the cell sap. The initial concentration of the syrup has a decided effect on the final drained weight because of the degree of the cell wall dehydration, resulting in a polymer-polymer hydrogen bonding, instead of polymer-water hydrogen bonding, when cell shrinkage occurs.

e. Changes of Pigments During Storage

Concord grape juice pasteurized and bottled changed little during storage. Tressler and Pederson (115, p. 88-99) reported, in contrast with partially filled bottles which showed a rapidly deterioration because of the oxygen of the contained air. The rate of deterioration was proportional to the storage temperature. The changes noted were clouding, the bright purple-red color turning to brown, a slow deposition of a brown sediment and some changes in aroma and flavor.

Pederson, et al. (87, p. 78-83) observed that the color of raspberry, strawberry, and currant juices was difficult to preserve in its original state although the best methods of deaeration and pasteurization were applied. The changes during storage at room temperature or above were due to small quantities of remaining air. The change in color was followed by an "oily" flavor development.

Beattie, et al. (5, p. 395-403) concluded that the rate of destruction of ascorbic acid in strawberry, raspberry, and currant juices was more rapid at higher storage temperatures. Occurring at about the same rate was the destruction of red color. Temperature of pasteurization had little effect upon changes during storage. The presence of air had a marked effect on ascorbic acid destruction and some effect on color. The results of these experiments showed the reactions which happened between color and ascorbic acid were opposite since the pigments were reduced and the ascrobic acid oxidized.

Joslyn (40, p. 308-314) demonstrated that changes in tint or hue happen during storage as a result of reaction between fruit, added substances and the walls of the can. Changes may also occur due to catalysis by enzymes or metallic impurities or autocalalysis. The several factors which are involved during storage usually occur in consecutive stages rather than simultaneously.

Pederson, et al. (86, p. 81) have indicated that changes which occur in juices during storage are complex in nature including hydrolysis of sucrose and loss of ascorbic acid. Though enzymes are apparently inactivated, and the effects of oxygen, light, and metals are reduced to a minimum, serious deteriorative changes nevertheless occur. Perhaps the most objective and sensitive change is in the color, which rapidly decreases, and a brown color and precipitate develop.

Studies on strawberry pigment deterioration have been analyzed by Sondheimer and Kertesz (103, p. 246; 105, p. 288; 106, p. 477). They demonstrated the effect of ascorbic acid on strawberry pigments (anthocyanin) and observed that there is a marked tendency to brown at unfavorable storage temperatures. At temperatures above 0^{o} C, two main types of nonenzymatic color reactions occur: the red anthocyanin color is lost and secondary brown pigments develop.

The same authors (104, p. 612) pointed out that at storage temperatures around 65^{o} to 70^{o} F the color loss in fruit spreads is greatly accelerated.

Nebesky, et al. (82, p. 261-274) investigated various factors which affect color stability of fruit juices during storage. Factors studied were time and temperature of storage and the relationship of oxygen, light, sugar, pH, and antioxidants. All fruit juices showed changes during storage but they varied with the specific fruit. Fruit juices with a higher color underwent a more marked change. The stability of the color of blueberry, strawberry and raspberry juices decreased in descending order. Visual observation indicated changes of juice color from a bright, clear red to a light red which turned dull red after three months storage and further darkened after six months of storage.

The most important factors accelerating deterioration were heat and oxygen. Addition of 1-ascorbic acid to the strawberry and raspberry juices had as a result a progressive bleaching. This effect could be avoided by using antioxidants. Increasing pH values served to retain color value during storage.

Lee, et al. (57, p. 16) found the same results as the previous authors. Different kinds of fruits gave a characteristic storage behavior in susceptibility to change or deterioration. The lower the temperature of storage, the better the color retention, when anthocyanins were responsible for the color. A gradual clarification would happen in the case of color loss (lower optical densities). The degree of stability diminished from black raspberry juice to red raspberry, cherry and strawberry.

Pratt, et al. (92, p. 367-372) demonstrated the effect of ascorbic acid and riboflavin on the loss of color in anthocyanin pigments of strawberry juice. One of the results was that as the length of storage was increased, there was a corresponding increase in the amount of brown color. The other conclusion was that the greatest loss of the two vitamins appeared during storage of the samples in which anthocyanin pigments were present. The breakdown of ascorbic acid and the color pigments of strawberry juice was measured by spectro photometric and polarographic methods.

Livingston and Tan (61, p. 525) have written in the introduction of their paper on strawberry preserves that :

> Several months of storage at room temperature are usually sufficient to produce a definite off color, and the associated ultraviolet absorption caused by the presence of furfuraldehyde and other carbonyl products of carbohydrate breakdown.

Kertesz and Sondheimer (45, p. 106) demonstrated that: (1) strawberry preserves keep better at storage temperatures below 60^{o} F because at a temperature around 65^{o} F. there is break in the straight line which related pigment concentration to time and (2) that the browning reaction, due to non-anthocyanin pigments, usually occurred when the red color already had been partially destroyed.

Decereau, et al. (16, p. 125) studied the effect of storage at 100^{o} F on strawberry jelly and found that the retention of anthocyanin pigment was 26 percent after 19 days of storage, and after a period of 6 months, pigments destruction was 100 percent. The results of this study were like those of Kertesz and Sondheimer (45, p. 107).

Guadagni (26, p. 633-637) reported that the time-temperature tolerance of frozen red raspberries for the same degree of color and flavor change varied exponentially with temperature over the 10 to 30^{o} F range, and the time required for an equivalent change was increased two to three fold for each 5^{o} F reduction in temperature.

Guadagni, et al. (27, p. 36-40) have discussed the same subject of time-temperature tolerance of red cherries. Discoloration or browning of cherries exposed to the headspace atmosphere was rapid during storage at 20^{o} F. The loss of red pigment gave a discoloration to the fruit, which was followed by a browning resulting from an oxidation of tannin-like phenolic compounds. Cherries, exposed to the headspace atmosphere became discolored rather rapidly and thereafter essentially no increase in number of brown cherries occurred. This relationship in a hermetic container varied between 15 - 18 percent of the total cherries in each container, since oxidation would be limited to the amount of oxygen sealed in the can and the degree of syrup coverage.

Measurements between controls and stored samples gave differences in Hunter color and color difference meter "a" values which are a measure of relative redness. It was shown graphically that even though the number of brown cherries remains fairly constant, the intensity or degree of browning in these cherries continued to increase, because the change in "a" value or relative redness continued to increase.

Measurements of color changes in strawberry pie fillings by Kitson (47, p. 75) showed that the color changed from bright red to dull brown upon storage at high temperatures. Strawberry pie fillings stored at 40° F showed slight browning after six months while those held at 70° F were discolored a similar amount in a month. The rate of change increased as the storage temperature increased.

Luh (66, p. 173-176) in his work on chemical and color changes during storage of canned tomato ketchup, presumed that fructose is probably the constituent that causes the browning reaction and that the the pH affects the rate of darkening.

The results of the last previous authors are summarized by Meyer (79, p. 248) as follows:

> Prolonged storage of fruits with red or red-violet pigments is accompanied by bleaching of some pigment and the development of a red-brown and finally a brown color. Storage temperature is most important in the rate at which the change in color occurs. It has been found that strawberry spread stored at 34° F showed little change in color, although it was fairly rapid at 65° - 70° F and much faster at 100° F. Much the same results have been obtained with currants, raspberries, and strawberries.

f. <u>Translocation of Sugars, Acids and Pigments Through the Berries as a Kinetic Energy of Distribution by Concentration Gradient</u>

Adams (1, p. 38) demonstrated that the added syrup in cans is neutral or slightly alkaline. The fruit juices gradually go from the fruit to syrup during processing where the first stages of distribution of soluble constituents takes place with completion during storage. At the same time a fall in density of syrup is followed by a corresponding rise in acidity.

Ross (95, p. 19) showed the type and direction of changes which occurred in syrup cutouts during storage. The curves of the graphs indicate that a nearly constant level of Brix of the syrup was attained after a rapid decrease during the first week of storage. The brix of the fruits changed in similar manner but in opposite direction, becoming nearly constant and equal to syrup cutouts, after a rapid increase during the first week's storage. It was pointed out, Adams (1, p. 40), Ross (95, p. 22) that the rate of the translocation was dependent on syrup type, type of fruit pack, time and temperature.

Bedford and Robertson (6, p. 321-323) demonstrated the relation of put-in weight to drained weight of canned red cherries in various packing media. Cherries packed with 20 to 30 percent syrup had higher drained weights than those packed either in water or in 40 to 60 percent syrups. The relationship between the syrup concentration and juice cut-outs for the various put-in weights of cherries showed that the juice cut-out varied directly with the soluble solids content of the fruits, the syrup concentration, and the put-in weight of cherries. Cherries packed with heavy syrups had lower concentrations of sugar in the syrups after canning than at the time of filling, while those packed in 15 percent or lower syrups had cut-outs higher than that of the original liquid. The average soluble solids content of the fresh cherries was 15.2 percent. With a put-in weight of 14 ounces of cherries, the juice cut-out increased about 4 percent for every 10 percent increase in the packing syrup concentration.

Leonard, _et al._ (59, p. 80-85) pointed out similar results from previous investigations on drained weight. Fruit size must be considered, because a large amount of syrup adheres between the fruits on the screen when the drained weight is determined. The concentration and quantity of the cover syrup have a pronounced effect, because a higher concentration gradient between the syrup and the fruit creates a greater movement of fruit fluid into the syrup. During storage, soluble solids diffuse from the syrup into the fruit, causing the weight of the fruit to increase until equilibrium between the constituents is reached. The type of fruit has an effect on the rate of translocation of soluble solids and fluids between the syrup and the fruit. Cherries reach their minimum drained weight three days after canning Bedford (6, p. 321), Whittenberger (121, p. 302). This indicates that cherries because of their epidermal structure (skin) show a resistance to the movement of fruit fluid into the syrup.

Hughes (38, p. 111-115) reported the rate of penetration of malto saccharides into processed clingstone peaches using C^{14} labeled sugars. It was shown that the syrup volume was higher 1 1/2 days after canning and then was reduced continuously. The figures were as follows: at zero time, volume was 75 ml, at 1 1/2 days, about 91 ml and at 60 days, about 81 ml. This was explained by the fluid movement from the peach into the syrup during the first one to two days.

The conclusion on the rate of penetration is the same as before mentioned. The higher the concentration gradient of sugars outside of the fruit, the more rapid the initial movement of the sugar into the flesh, although an opposite movement of the fluid of the fruits exists at the same time. There is a relation between the degree of polymerization and the rate of penetration, because the diffusional coefficient and concentration gradients are decreased with increasing molecular size.

Philip (88, p. 289) studied osmotic and diffusion phenomena in living individual cells and tissues. Diffusion and osmotic phenomena in whole pieces of tissue have often been assumed to follow a course quite similar to that in a single cell. The results showed that the half-time for equilibration of an individual cell is very sensitive of cell position and the half-time of tissues will vary as the square of the ratio of their dimensions and that large internal gradients may exist within the tissue. The term "half-time" means that the equilibrium concentration within the cell is half accomplished, when the cell is immersed in solution.

Sterling (109, p. 629-634) writes about the subsequent increase in drained weight:

> The equilibrium of water activity at the turning point is quite transitory. As more and more sugar is taken up by the cell walls of the fruit, there is an abrupt reversal of the principal direction of water movement. The normally existing concentration gradient for the syrup sugars is probably enhanced by the continual adsorption of those sugars on cell wall polysaccharides.

> Thus, the concentration gradient is kept at a high level. Water movement will then follow sugar movement closely, as the gradient of water activity changes correspondingly. As the dehydrating cell walls straighten, the cell volume is increased, and augmentation of the drained weight takes place.

Products which have been packed with a high percentage of syrup show a higher viscosity which is a source of the difficulty of heating these products, Nicholas, et al. (85, p. 488). But the same authors (84, p. 210) concluded that viscosity alone could not explain the observed slower rate of heating. The explanation of this difference was a problem studied by different investigators (Adams (1), Bedford (6), Leonard (59), Ross (95), as to how the liquid and soluble solids exchange take place between product and covering liquid. It is found that equilibrium takes place over a period of time that is long compared with the heat processing time. After adding syrup to the product, the water leaving the product rises to the top of the container with the result that within minutes appreciable differences in syrup concentration are established between the top and bottom of the container. This phenomenon of stratification has been studied by Mulvaney, et al. (80, p. 204). The maximum difference in soluble solids content of the syrup and product at between the top and bottom of the jar for processed sweet fresh cucumbers occurred in the syrup after one day and amounted to about 21 percent and the corresponding difference in the product occurred at about two days and was about 17 percent. The highest difference between product and surrounding syrup was at the moment the syrup was added.

After processing, a period of six to eight days was required for the soluble solids in the product and syrup to reach equilibrium. During this period, water was still leaving the product at the bottom, rising to the top because of the density of the surrounding syrup and there diluting the syrup from 50 percent (original) to 15 percent soluble solids. The product showed maximum loss of water at the bottom of the jar, resulting in maximum shrinkage. The difference between top and bottom of the jar in soluble solids concentration after a storage of about seven months at 74° F temperature, was found to be about 0.5 percent for the syrup and the corresponding difference for the product about 0.1 percent. There was still a difference between product and syrup soluble solids of about 1 percent.

The changes in pH between top and bottom after processing time and storage in both the syrup and product showed that the largest difference was immediately after processing and it was almost at an equilization point at the eighth day. The acetic acid (2.8 percent) which was added with the syrup, showed the maximum difference after processing (top 1.33 percent and bottom 2.82 percent). Equilization of acetic acid concentration between top and bottom occurred about 64 days after processing.

In the discussion of their results, the authors gave the following explanation in relation to the movement of the water from the bottom to the top of the jars:

> A possible explanation why the water molecules leaving the product do not all mix with the syrup is that the water molecules do not have sufficient energy to break or add to existing hydrogen bonds of water molecules and sucrose molecules that tend to attract the sucrose molecules into a dense, viscous mass. The process of water molecules diffusing into the syrup and/or adding to these bonds occur slowly. As a result of this slow rate of diffusion, the water rises to the surface buoyed up by the surrounding heavier syrup before it mixes into the syrup.

Guadagni and Nimmo (25, p. 604-608) have reported the effect of time and temperature on color distribution of frozen raspberries. It was observed that two weeks at 30° F caused a relative large transfer of pigment from fruit to syrup and generally that the syrup of samples stored at 10° to 25° F was more intensely colored than that of control samples kept at -20° F. The temperature during storage had a pronounced effect on syrup color. At 10° F there was a marked increase in syrup color, which was four times greater after three months than that which occurred at 0° F in one year.

At temperature of 20° F the berries became softer and the liquid dissolves larger amounts of soluble pigments and other constituents, which lower the freezing point of the juice. The unfrozen juice is drawn into the syrup by diffusion. As the temperature is elevated the rate of juice transfer to the syrup is more rapid. It is concluded that as the color intensity of the syrup increased, the amount of color in the berries decreased until an equilibrium between the two phases (fruit-syrup) was established, which is dependent upon the time-temperature relationship.

In the case of over-mature and broken berries, the color blends into the syrup very easily because free juice exuding from broken overripe berries immediately colored the syrup to an extent depending on the degree of breakage and color intensity of the berries.

Guadagni, et al. (27, p. 36-40) reached the same conclusion for frozen pitted cherries. A transfer of color from cherry skins to surrounding syrup occurs at 10° F and above. The effect of storage at 20° F on color distribution between cherries and surrounding syrup, showed an equilibrium (the same intensity) after 36 days of storage.

Guadagni, et al. (30, p. 467-470) postulated a simple kinetic theory for the distribution of color and acid between raspberries and syrup. Previous work of the same author on raspberries and cherries showed that the rate of diffusion of color from berries to surrounding syrup was one of the best criteria for estimating temperature history for frozen berries. It was found experimentally that the diffusion of pigments and acids followed a first order process with rate constants which appeared to follow the Arrhenium equation in the range of 10° to

30^{o} F temperature from which the magnitude of the activation energy (E) of an adsorption process is calculated: $d\ln \frac{V}{dT} = \frac{E}{RT^2}$ where V is the velocity corresponding to the respective temperatures.

An equation which explains the experimental data developed by the authors on the assumption that a reversible process takes place during the distribution of color ($A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$) was $\ln \frac{R+1}{R - Re} = k(a+t)$ where $R = \frac{A}{B}$ ratio of color (berries/syrup), where A = color in berries and B = color in syrup at time $T = a + t$, $K = K_1 + K_2$ at temperature T, Re = $\frac{K_2}{K_1} = 1$ at equilibrium, a = effective time between introduction of syrup to berries and initial color ratio measurement, and t = time at a known steady temperature after the initial measurement. The experimental data gave the following values for constant k at different storage temperatures: 30^{o} F, k = 0.204; 25^{o} F, k = 0.112; 20^{o} F, k = 0.046; 15^{o} F, k = 0.0088; and 10^{o} F, k = 0.0036.

This theory is applied also to similar measurements for total acid and ascorbic acid ratios. The only apparent difference lies in the fact that the equilibrium values for the three measurements differ. Thus, the value Re in equation should be 0.7 for total acid ratios, and 0.5 for ascorbic acid ratios. Accurate determination of activation energies cannot be made from the experimental data, but a value in kilocalories over this temperature range was of the order of magnitude of 60 for color diffusion and 37 for acid diffusion.

Guadagni, et al. (28, p. 148-150) reported results according to their theory on the effect of temperature in larger than retail packages of frozen boysenberries. Color distribution between berries and syrup followed the same equation where the value Re (equilibrium color ratio) was 1.4 based on a limited number of samples. The straight lines obtained from the experimental data showed that the diffusion of color followed a first-order process. The data showed that the rates of ascorbic acid oxidation in IQF (individually quick frozen) berries were approximately twice as high as in syruped fruit at 10° to 20° F but at 30° F the difference was much smaller. They assumed that:

> These results are probably due to the fact that most of the syrup at the lower temperatures was still frozen and hence exerted its maximum effect in preventing oxidation of the berries.

There was a small difference if ascorbic acid changes were expressed as increases in dehydroascorbic acid and diketogulonic acid (DHA + DKA) with time between syruped and IQF berries. The rate was about 6:10 mg/100 gr (DHA + DKA) for syruped and IQF berries respectively.

Conclusion

Diffusion phenomena, as a process involving mass transfer operations, may be observed in many types of food technology problems.

Description of a diffusion process requires the observation of concentrations and concentration gradients or some functions of these variables, in addition to other variables such as distance, time, temperature, magnitude of particles and viscosity of medium.

Diffusion may be thought of as a process which leads to the homogeneity of a certain component within a single phase. This idea implies two factors, the concentration gradient and the diffusion coefficient or diffusivity. Fick's first law gives the relation, which states that the particles of each different substance in a solution will diffuse from a region of high concentration to a region of less concentration. Diffusion will continue until every component reaches an equal concentration throughout the solution.

McElroy (76, p. 20-21) writes:

> The relative concentration of each substance in solution is critical in determining the direction of diffusion of that substance. Since no two molecules can occupy the same space at the same time, an increase in the concentration of any one substance necessarily displaces an equivalent amount of all other components in the solution.

"Diffusion processes are related to chemical kinetics on the one hand, and to sorption and solution equilibria on the other," Barrer (7, p. 3-11) writes in the preface of his book. The study of diffusion touches on a number of physico-chemical problems. The flow by diffusion can be divided into two states, the stationary and non-stationary. From the non-stationary state derives the "permeability constant" which is the quantity transferred/unit time/unit area of unit thickness under a standard concentration or pressure difference. "Diffusion constant" (D) which touches our problems derives from the stationary state, which is related to the Fick's law $P = -D \frac{dc}{dx}$, where the term $\frac{dc}{dx}$ is the concentration gradient.

Rideal (7, p. 1-2) in the introduction of the book of the previous author writes:

> Migration across a surface or through a solid medium may thus involve movement across an energy barrier from one position of minimum potential energy to another. At sufficiently high temperatures in the higher energy levels, activated surface migration naturally merges into free migration, with a consequent change in the temperature dependence of the diffusion.
>
> The mechanism of the transfer of material across phase boundaries likewise presents a number of novel and interesting problems. Here we have to consider the abnormal distribution of diffusing material at the phase boundary.

Powell, et al. (91, p. 430-435) discussed factors affecting flow of liquids as thermal conductivity and viscosity. In every system the rate of reaction depends upon the initial state of the reactants where they approach each other to make an "activated complex," which further decomposes to yield the final products or equilibrium. The course of this process could be described as three stages of different energy levels, where the initial system has to gain enough activation energy to pass over the energy barrier before it can reach the final state. The velocity of the process is given by the relation of the concentration of activated complexes and the rate with which they are crossing the top of the barrier.

Arnold (2, p. 3937) postulated that one could assume the classical kinetic theory to be applied for liquid systems where the resistance of diffusion is due wholly to binary collisions and the volume occupied by the molecules is the same for all systems. Intercellular forces introduce a factor which experimentally has been found to be independent of the nature of the diffusing substance and directly proportioned to the square root of the solvent viscosity.

Powell, et al. (91, p. 430-435) demonstrated that when a shearing force is applied across two layers of molecules, flow takes place when a single molecule passes others around it and drops into a hole (equilibrium position). He had introduced a relation of viscosity to shearing forces expressing: "Fluidity or reciprocal viscosity, is defined as the difference in velocity per unit shear. The viscosity should vary expontentially with the reciprocal of temperature." It has been found experimentally that the composition of the solvent gives the factor of flow, due to the readiness with which it contributes holes for the substance. The diffusion model is considered the same as that for viscous flow, a single molecule jumping from one lattice position to another through the liquid. The mechanism which determines this rate of diffusion of large molecules through a liquid composed of small molecules is given by the diffusion of the smaller molecules around the oncoming larger ones, by the same mechanism which these small molecules use in diffusing around other small molecules.

6. Small Fruit

Introduction - The type of fruits used in this study are called small fruits. From the pomologist's point, they are classified as aggregate fruits. Raspberry, blackberry, and strawberry fit this classification. The term "berry" forms a part of the name of a number of the small fruits. However, strawberries, raspberries, and blackberries are not true berries from the botanical standpoint. Examples of true berries are blueberries, cranberries, gooseberries, and grapes.

Acreages in small fruits in U. S. A., 1954, are listed by

Shoemaker (97, p. 1): Strawberries, 250,000 acres; raspberries, blackberries, and related types, 100,000 acres; blueberries, 3,000 acres for the cultivated highbush type and at least 50,000 acres for the wild types.

The proximate composition of the constituents of 100 gm of edible portion of the fruits of our study is as follows: Data from the book, "Nutritional Data", (33, p. 78-81). * Data: Meyer (79, p. 276)

Name	Water gm	Protein gm	Fat gm	Ash gm	Total Carbo-hydrates gm	Acidity* gm	Crude Fiber gm	Vita-min C mg
Strawberries	89.9	.8	.5	.5	8.3	1.12	1.4	60
Raspberries, Red	84.1	1.2	.4	.5	13.8	1.34	4.7	24
Blackberries	84.8	1.2	1.0	.5	12.5	1.08	4.2	21
Blueberries	83.4	.6	.6	.3	15.1	1.66	1.2	16

a. <u>Strawberries</u> - The strawberries which were used for this study were of the Northwest variety. It is cultivated in western areas being introduced in 1949. The fruit is large at the beginning of the season and becomes medium in size toward the end of the season. It is suitable for canning and freezing. For the best quality they should be ripe when picked.

Strawberries, like most other berries, do not usually improve in quality after picking. The sugar content does not increase, and acidity tends to remain at a constant level. It is essential, therefore, that the fruit be fully ripe at the time of picking.

Austin, et al. (3, p. 382-386) demonstrated that there is an influence of temperature and light upon the post-harvest development of fruit color. Fruit is considered as ripe when fully colored. They found that a full color appeared when fruits were subjected to a temperature of 75 - 85° F in complete darkness for about 48 hours. Soluble solids content of berries ripened in the dark, compared favorable with that of field-ripened fruits.

Sondheimer and Kertesz (103, p. 245) pointed out that strawberry pigments differ from those of raspberries, cranberries, and grapes because they are unable to form colored complexes with the common heavy metals with the exception of lead acetate. The red anthocyanin of strawberry preserves is gradually lost during storage and a secondary brown coloration slowly develops. These two reactions characterize the undesirable color changes which occur during processing as well as storage. The rate of loss of red pigment is much more rapid than the flavor changes.

Strawberries are the most important of the small fruit crops in Oregon and next to pears the most important of all the fruit crops in the State.

b. Red Raspberries

The red raspberry has been an important horticultural crop in Oregon for many years, being grown both in home gardens and in commercial plantings. The Willamette variety used for canning, which has its origin in Oregon was introduced in 1942. It is now the leading variety in Oregon. It has been popular with growers because of its large size, firm berries, ease of picking and productivity for processing. Color and firmness are particularly well retained by canned and frozen berries.

Red raspberries soften quickly in warm weather and should be removed from the field as soon as possible after picking. They must be picked every other day in warm weather or at most every three or four days in cooler weather.

c. Marion Blackberries

Marion Blackberries is a new variety that shows promises in Oregon's small fruit industry. It comes from a breeding development at Oregon State University and the name was given because this blackberry is extensively cultivated in the Marion County area.

Marion berries have a typical, round, blackberry shape, medium-large, somewhat longer than wide, with an attractive bright-black color and they show an average firmness. Their flavor is superior to other varieties which are grown in Oregon (Boysen, Evergreen, etc.). Experiments showed that Marion berries are satisfactory for canning.

Karrer and Pieper (44, p. 519) found that the pigment which was extracted from the forest blackberry was identical with that obtained from the garden variety. It consists of a monoglucoside of a cyanidin, either identical to or an isomer of chrysanthenin or asterin found in asters and chrysanthemums.

d. Blueberries

The variety of canned blueberries was the Jersey. It is a vigorous variety resistant to stem canker, producing large berries late in the season. There was a production of about 566,000 cases of canned blueberries in the United States in 1959.

The mature fruits of the highbush blueberry (as Jersey, Rubel, etc. varieties) rapidly change in color from green to red and then to dark blue. Once the epidermis of the berries becomes completely blue in color, it is impossible to observe if the berries have ripened adequately for harvesting. All blue-colored fruit is picked, therefore, variable degrees of ripeness may be included in the harvest.

Bailey, et al. (4, p. 194) made the following statement regarding the harvesting of blueberries:

> They must be neither too green nor too ripe. The stem end of ripe berries has a dark, rich, blue color. A reddish tinge there indicates immaturity. Underripe fruit is sour and lacks blueberry flavor. Picking should be done every six or seven days. If done more often than this, too many underripe berries are picked.

The fruit should be left on the bush until fully mature since the blueberry does not increase markedly in sugar content after harvest. Shutak, et al. (98, p. 181) showed that berries ripened on the bush averaged 3. 6 percent higher insoluble solids than berries ripened off the bush.

Nelson (83, p. 1300-1302) in his work on non-volatile acids of fruits found that the predominating acid of the blueberry is citric, with a little 1-malic acid.

It is characteristic of blueberries that the aroma, flavor and color are intensified by heating.

While blueberries are easily canned, the berries become soft and often burst. They may vary from a highly attractive, free-flowing product to one that is clumped into a firm mass. Severely clumped berries are less desirable, are more difficult to use and separation often results in torn skins and unattractive pulp.

Powers, *et al.* (90, p. 99-102) determined the causes of clumping in canned blueberries. They concluded that factors which influence the occurrence and degree of clumping were the variety of blueberry, agitation of cans during cooling and the severity of processing. Chemical and histological observations showed that clumping could be reduced by cooling with agitation which apparently interferes with the binding together of berries by surface wax or cutin. An extensive cuticular wax covers the outside surface of the fruit which can be distinguished into waxy cuticle which is the outmost portion of the skin and under this is a second continuous wax-like layer. By rinsing with chloroform for a few minutes, part of the waxy materials can be removed. The time, temperature, and agitation during storage are important factors because berries showed a tendency to clump in higher cooking temperatures, longer time of processing and in still cooking. The results showed that between 10 varieties which have been studied, Jersey was one of the most successfully processed and after non-agitating processing cooling with less clumping.

It is interesting that canned blueberries produce a high degree of corrosion and perforation during storage for a long time. Studies carried out by Leach (56, p. 623-625) long since brought out the fact that canned blueberries, having an acidity approximating one-twentieth normal, dissolved and carried into solution several times as much tin in a given time as strawberries or raspberries having twice the titratable acidity. Leach also tested various concentrations of malic, citric and tartaric acids for their ability to dissolve tin from tin plate, finding that the pure tenth-normal acids dissolved only about one-tenth as much tin as did blueberries of one-half the acidity in equivalent time. The action of the pure acid ceased after about three months, no more tin being dissolved after nine months additional exposure. No such stoppage of action occurred in blueberries, which were nine times as efficient in dissolving the metal as canned tomatoes and twenty times as efficient as the pure acids.

The explanation of this action is given by the fact that anthocyanin continuously removes metal from combination with the acid and thus prevents an equilibrium between free acid and tin salt which occurs in pure acid solutions. In the presence of large amounts of anthocyanin, salts of tin with the acids of the fruits can have only momentary existence since they are immediately decomposed with transfer of the tin to combination with the anthocyanin.

EXPERIMENTAL PROCEDURES

This work was undertaken to study the effect of time and temperature of processing and storage on the diffusion rate of sugars, pH, acids and pigment in four types of canned berries.

Canned fruits which are covered with syrup undergo a number of chemical and physical changes during processing and storage. These changes which are related to the type of fruit have a direct effect on the homogeneity of the product which affects consumers' preference.

The most important changes to consider are those of pH, acids, pigment, soluble solids and drained weight together with various organoleptic qualities, as flavor, color, and texture.

Design of Experiment

Experimental packs of strawberry, raspberry, blackberry and blueberry were prepared in No. 10 cans to show the diffusion of sugars, acids, pigments and pH changes, in heated and unheated cans.

For each fruit, three cans for each treatment were packed. All figures are the average values for three cans for four berry variations, namely, 1. unprocessed (without cooking), 2. processed and examined promptly after cooling ($\sim$ 95° F), 3. processed and stored for one month and 4. processed and stored for six months storage at 78° F.

Samples of syrup were removed with 50 ml pipettes at five vertical positions, both at the center and at the side of the cans. The syrups were analyzed for brix, acidity, pH and pigment concentration. Cans were drained by inverting the can with the lids severed but left in position, on an 8 mesh, 10" drained weight screen, puncturing the can bottom, and allowing the can to drain for five minutes. 100 g samples of drained solids were taken at the top, middle and bottom layers, for shear-press readings.

Materials

1. Fruits. The Northwest strawberry, the Willamette raspberry, the Marion blackberry and the Jersey blueberry were used for this study. The fruits had all the characteristics of fruit commercially used for canning. They were harvested from the University Farm and precooled overnight at 35° F in one of the cooling rooms of the department. Each flat of berries was mixed and washed, in a McLauchlan vibratory washer, and sorted on an Allen vibrating table and drained on 8-mesh stainless steel trays before hand filling into cans. Fruits very small or very large were removed during sorting

to obtain an average size.

2. Containers. Berry fruit enamel cans 603 x 700 (No. 10) were used in this study, similar to commercial applications.

Methods

1. Preparation of Packs. For strawberries, raspberries and blackberries coded cans were filled at random to standard weight: fruit/can = 4.75 lb., 60° Brix syrup/can = 2.125 lb. with approximately equal portions of fruit from each tray. In the blueberry packs 4.50 lbs. of fruit/can and 2.125 lbs. of syrup, 40° Brix were used. The cans of fruit were held at 25 inches vacuum for one minute in a manually-operated vacuum closing machine, and the vacuum was released by filling with 60° Brix syrup at 170° F. (40° Brix syrup for blueberries). The cans were steam-flow closed at 20 inches vacuum.

2. Heat Processing. The cans were immersed upright for 30 minutes in a stationary cook bath at a temperature of 212° F (boiling water), with precautions being taken to minimize movement of the cans; they were then cooled to a center temperature to 100° F by immersion in running cold water.

The cans were handled carefully throughout the study to minimize agitation of the product. Cans for the storage treatment were stored at a constant temperature of 78° F in a dark room.

3. Methods of Analysis. The following methods were used in this work:

Can Vacuum. Vacuum readings were taken, with a checked U. S. gauge puncture gauge, after the cans had cooled to room temperature (approximately 25° C), and the same time opened for analysis.

Can Gross Headspace. Headspace was measured directly with two small stainless steel rulers, as the distance between the top of the can double seam, and the top of the product.

Drained Weights. The determination was carried out according to the standard procedures described in the Almanac of the Canning Industries, edited by E. E. Judge, 1960 ed. (p. 148-149)

Shear Press Measurements. The texture of the berries was determined by the use of a modified Kramer Shear Press using 100 gm. of berries placed in the sample holder and applied force-response curves which were obtained on an x-y Recorder, using a thousand pound ring with a transducer value of 0.0025. The maximum force was measured.

Soluble Solids. The soluble solids concentrations were measured using a Bausch and Lomb, Abbe-type refractometer, and values were expressed as ° Brix at 25° C.

pH. The pH measurements of syrups were made with a

Beckman Zeromatic pH meter. The diluted syrup in the beakers was stirred by a magnetic stirrer.

Total Acidity. A five (5) ml sample was titrated in 50 ml of distilled water with 0.1 N NaOH to reach a pH value of 8.2, as indicated by a Beckman pH Meter. Results were reported as percent anhydrous citric acid.

Pigment Concentration. The effect of pH on the absorption of strawberry and raspberry pigments reported by Sondheimer-Kertesz (103, p. 245); Guadagni-Nimmo (25, p. 604-608). That is, the absorption is decreased by raising the pH up to a value of 5-6. Since we are interested in the relative distribution of color rather than the total amount at any given time, all measurements were made at pH 3.4± 0.05 and the color index was based on the absorption obtained at this pH alone. There was no particular reason for selecting a pH value of 3.4 except that the natural pH of berries is near this figure.

Detailed Procedure for Color Measurement. All samples for analysis were at room temperature. Two ml of raspberry syrup and 5 ml for the rest of the berries were diluted to 50 ml with buffer adjusted to pH 3.4. The buffer was prepared by mixing 0.1 N HCl and sodium citrate solution in the ratio 5.5 volumes HCl to 4.5 volumes citrate solution. The citrate solution was prepared by dissolving 21.008 grams of monohydrated citric acid in 200 ml of carbonate free

0.1 N sodium hydroxide solution and diluting the mixture to one liter. The solution was filtered through Whatman No. 4 filter paper. The buffered solutions were kept for one hour at room temperature before the measurement of the absorbancy. The absorbancy of the clear solutions was then determined in a Beckman, Model B, Spectrophotometer. The cells used were a Beckman 1 cm absorption cell.

Wave lengths of 497 mμ were used for strawberries, raspberries and blackberries and 519 mμ for blueberries, since the maximum absorption of the spectrum was in this region.

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental data will be discussed for the four fruits at the same time, in seven parts, respectively, covering the diffusion phenoma for sugars, acidity, pH, and pigments and the second part, the drained weights, shear press changes and headspace-vacuum.

1. Sugars.

The soluble-solids concentration gradient formed immediately after packing the fruit is shown by the graphs in Figures 1, 2, 3, and 4. The rate of distribution of sugars between top-bottom was almost the same for all the fruits except blueberries, which gave a distribution pattern for sugars in the can of a somewhat different form.

The explanation of this phenomenon has been reported by Bedford (6, p. 321) Leaonard (59, p. 80) Ross (95, p. 20) as an exchange taking place between product-liquid and covering syrup, which resulted in stratification of sugars as they adjusted in successive multiple layers. This concept of rapid movement of the water from the fruit (in this case soft fruits), Adams (1), is considered as a function of osmotic phenomena, Sterling (31) Jost (40) between syrup and fruit (cell walls).

We could assume also that the system is a dynamic one, because a hydrostatic pressure exists between the fruit matrix full of water containing a number of dissolved substances (organic-minerals) and syrup where the concentration of sucrose is much higher.

The differences between top-bottom are more noticeably large in the products processed and immediately analyzed, Figures 1, 2, 3, and 4. This explains what Adams (1) Reeve (93) Simpson (100) Maier (70, 71) Gallop (20) have proposed, that processing causes histological changes resulting in an outflow of water and other cell materials during cooking and immediately thereafter.

The temperature and time of processing affect the characteristic cell permeability by a loss of selectivity due to physical destruction of the cell, Sterling (108).

The effect of cooking on the fruit, resulting in a differential concentration throughout the can, is shown by the change in concentration of syrup between the unprocessed product and the processed ones. There is also a differential from top to bottom in the unprocessed product which is due to a low rate of exchange by diffusion-osmosis between fruit and syrup and a specific gravity separation of the syrups.

This top-bottom difference is more notable in the case of blackberries and blueberries, Figures 4 and 2, which is a matter of the type of the fruit from the structural point of view and also because of the higher percentage of natural sugars, which show about 5° Brix more than the other berries. Also the blueberry packs syrup was 40° B. The Brix curve for unprocessed blueberries is high and the zero storage is also high. The osmotic pressure between fruit and syrup is less with more sugars inside the cells and less outside resulting in a lower rate of diffusivity. Consequently, the concentration gradient is more uniformally proportioned from top to bottom of the can.

The above concepts are more probable for blueberries and seem to be associated with the high degree of tissue cohesiveness, which originates from the strength and heat stability of the intercellular pectins. This indicated that the skin of the blueberries offerred greater resistance to the movement of fruit fluid and syrup. Soft and ripe fruits interchange their constituents with the syrup more rapidly than firm, tough-skinned fruits, Adams (1).

A poor appearance and clumping at the top of the cans indicates a maximum water loss, which produces a shrinkage of the product.

Where the fruit is in the syrup, the rate of shrinkage depends on the density of the juice within the cell because a higher density of juice results in less pressure difference and there is less juice movement from fruit to syrup.

The high concentration gradient of sugar from the outside of the fruit to its interior causes a diffusivity pressure difference across the membrane of the fruit cells and results in adsorptive accumulation of sugars into the flesh of the fruit. This fact is observed at the top and bottom positions of the strawberry curves where the rate of movement of sugar and water gave a sigmoid curve after one month's storage, Figure 1. A probable explanation is that a semiequilibrium condition exists at this time at the top and bottom points, suggesting an en masse transfer rather than a diffusional transfer.

Hydrolysis of sucrose, occurring during processing and storage, Adams (1) Wiegand (124), disturbs the existing conditions because the products of hydrolysis with a smaller molecular size can migrate faster and have a higher diffusivity (easier absorbance), by the fruit tissue. Sterling-Chichester (110), studying adsorption of glucose by cooked peach tissue concluded that the cell walls of such tissue attract glucose. As a result, a gradient of decreasing concentration toward the center of the cell is established through the movement of glucose molecules toward the cell walls. This fact could explain the existing condition after one month's storage when, as the curves show, Figure 1, there is a tendency of the concentration of the syrup at the ends of the can (top-bottom) to stay unchanged with a small movement from a higher concentration to a lower concentration.

Another explanation is that the rate of hydrolysis should be higher around the wall of the can because the temperature of cooking is higher for a longer time in these areas (top-bottom) of the can. The over-all picture of the changes in the can gave the conception of a tendency towards disappearance of sugars from the bottom with a simultaneous movement towards the center of the can. After a six month's period, an almost equal concentration existed in every place in the can, Figure 1.

A true equilibrium condition, as a result of final equalization of the concentration of sugars in the whole can, depends mainly on the translocations of water and sugars in opposite vertical directions which reach a phase of equal concentration activity, Mulvaney, et al. (80), Ross (95), after a period of about six months as is shown by the curves in Figures 1, 2, 3 and 4.

The Brix readings at equilibrium was found to be about 26 degrees after a storage period of six months for the three fruits and something lower in the case of blueberries because the syrup used was 40^{o} Brix. (Table 1). Leonard, et al. (59) showed graphically the influence of sucrose concentration on the equilibrium Brix; which may be applied in the case of berries. As they pointed out, these results could be used to predict the amount of sucrose needed to obtain a certain desired final equilibrium Brix.

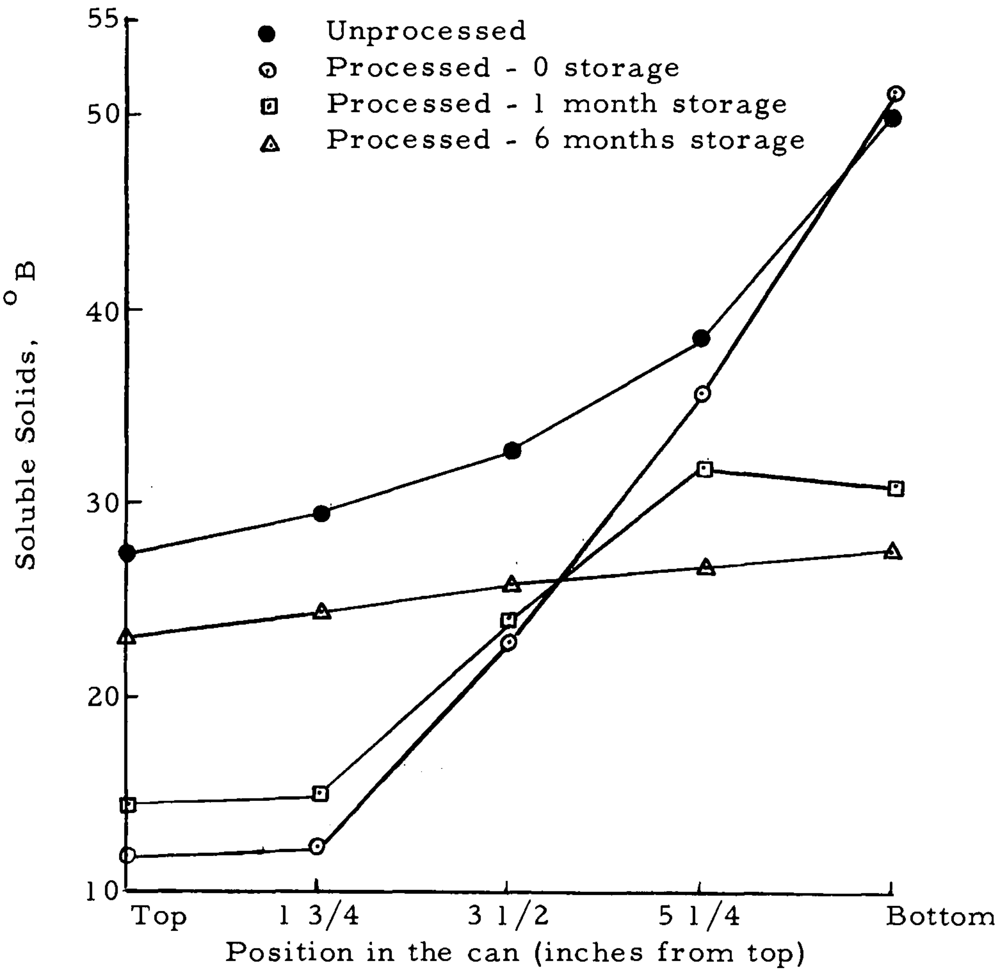


Figure 1. Diffusion of Soluble Solids in Canned Strawberries(center)

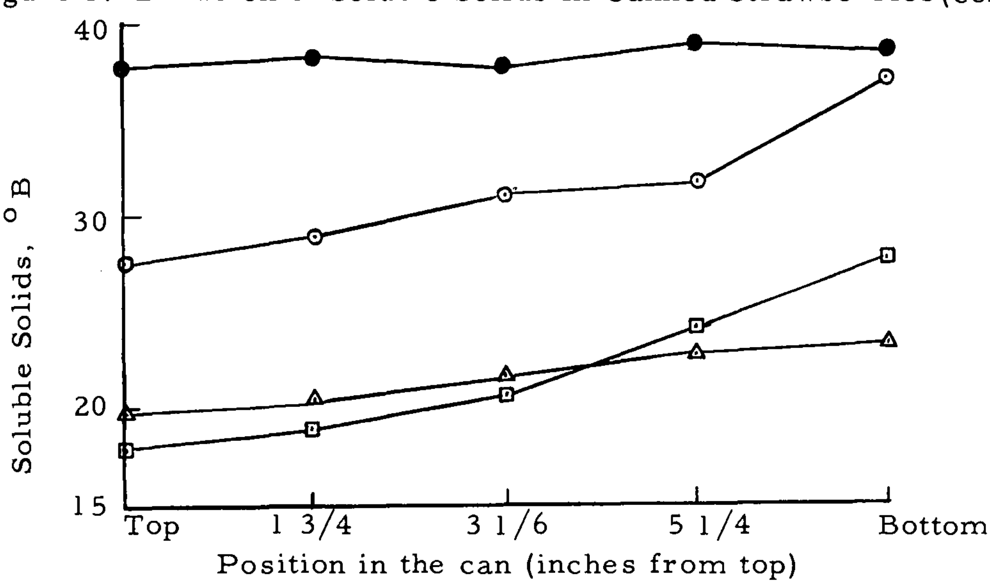
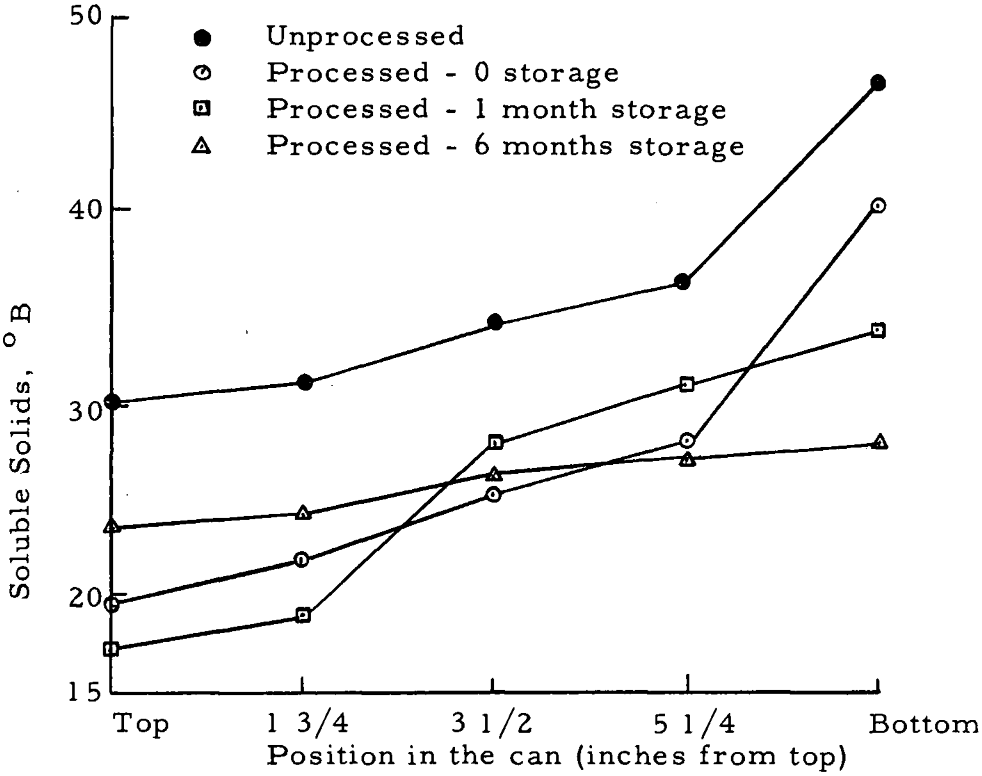


Figure 2. Diffusion of Soluble Solids in Canned Blueberries(center)



Figures 3. Diffusion of Soluble Solids in Canned Raspberries (center)

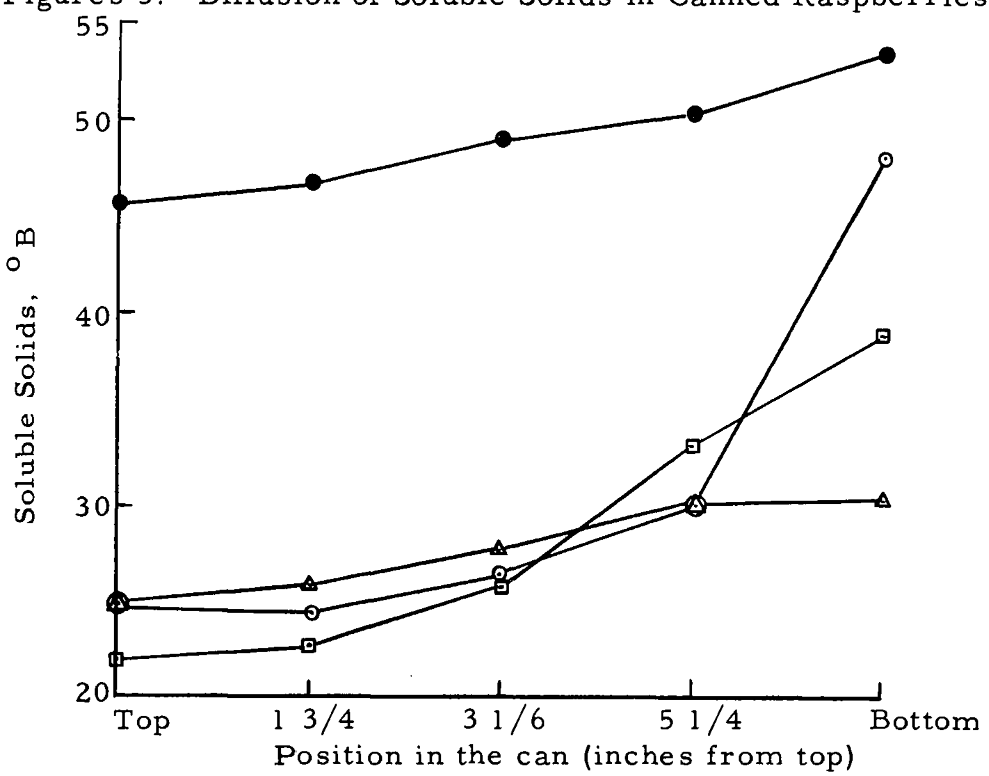


Figure 4. Diffusion of Soluble Solids in Canned Blackberries (center)

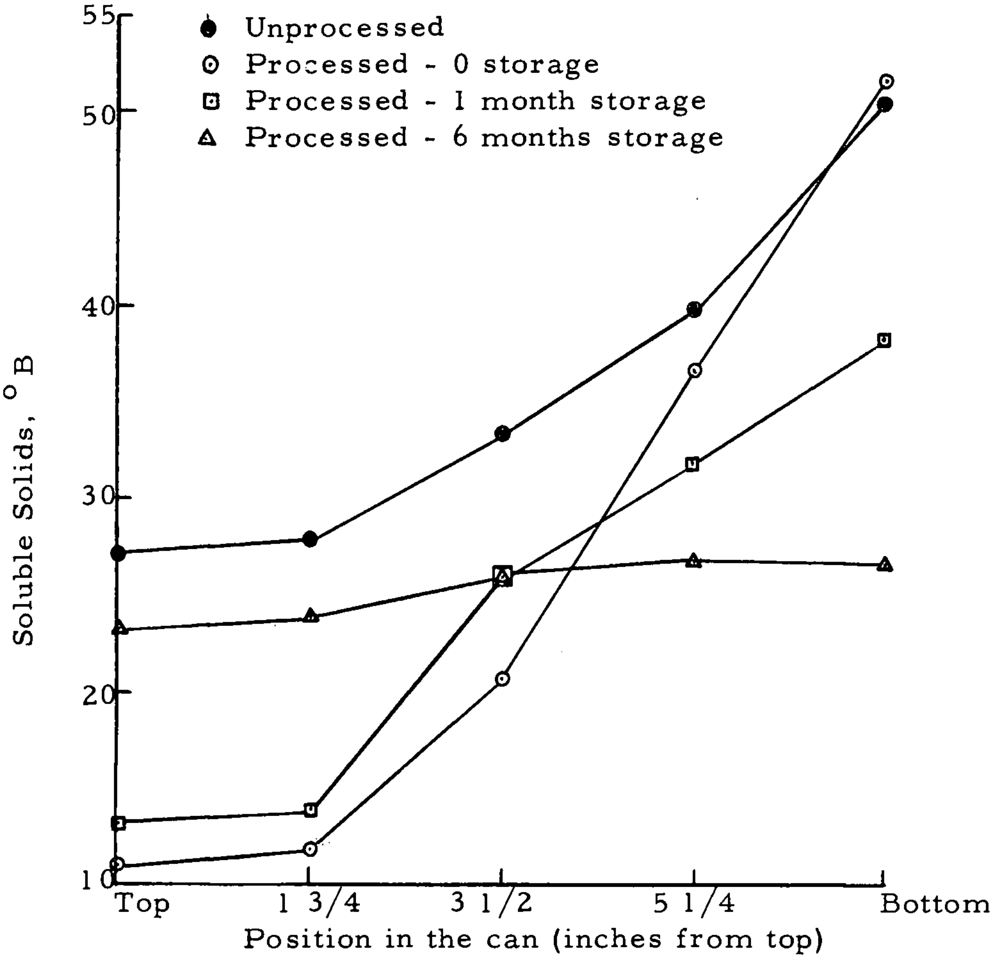


Figure 5. Diffusion of Soluble Solids in Canned Strawberries (side)

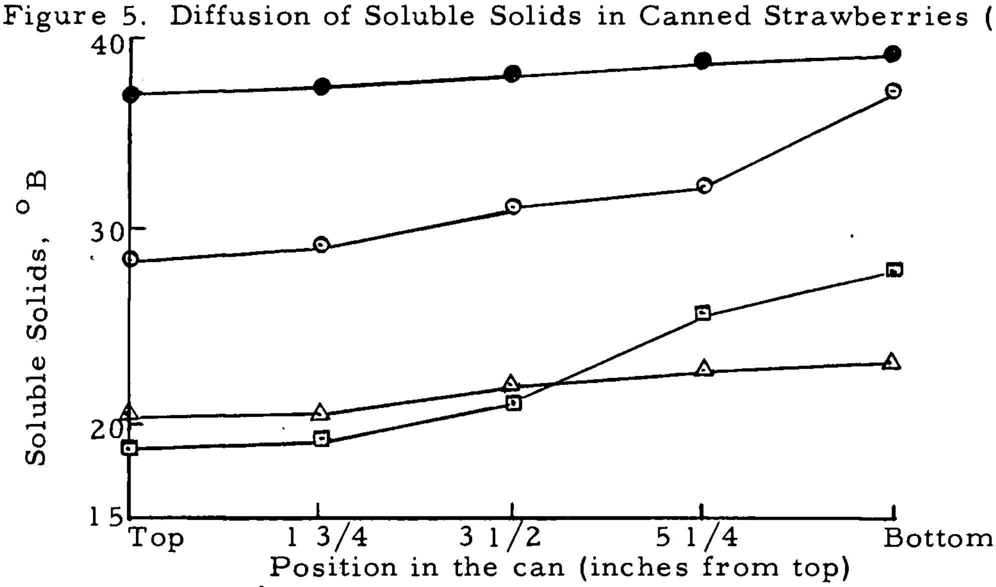


Figure 6. Diffusion of Soluble Solids in Canned Blueberries (side)

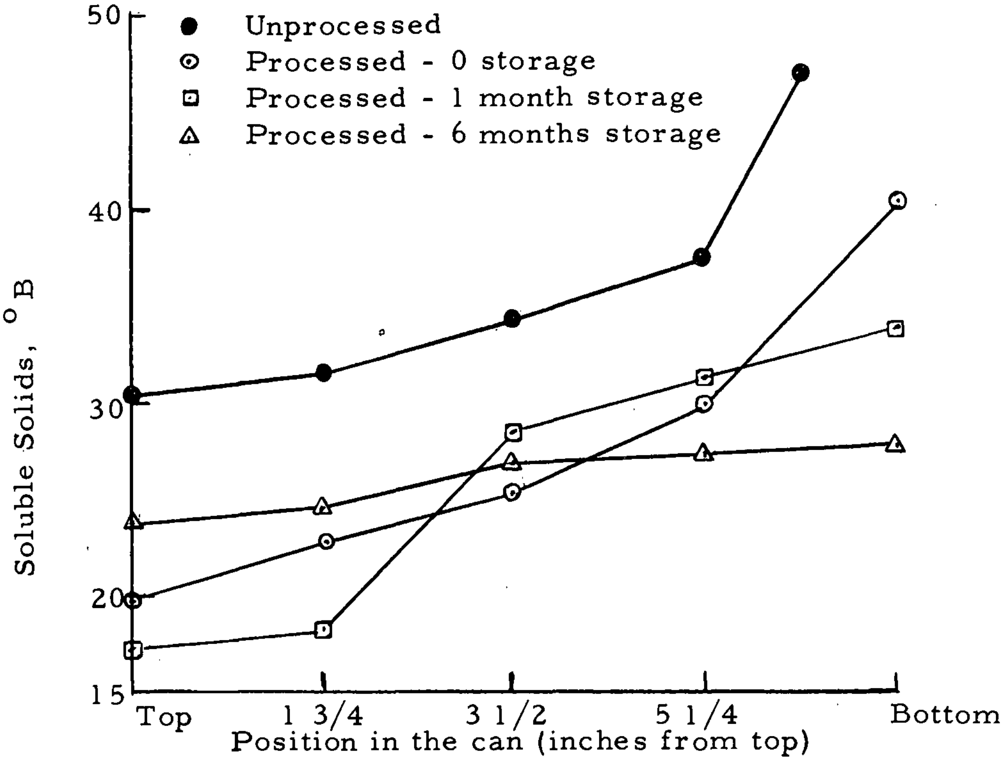


Figure 7. Diffusion of Soluble Solids in Canned Raspberries (side)

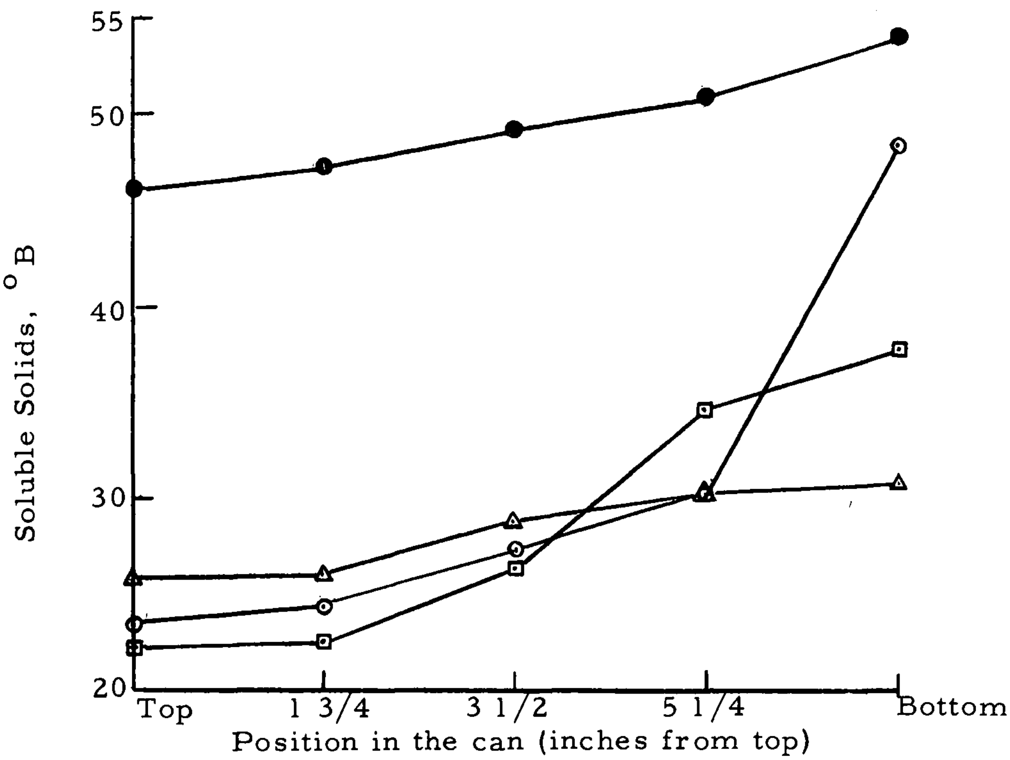


Figure 8. Diffusion of Soluble Solids in Canned Blackberries (side)

TABLE 1

MEAN CHANGES IN SYRUP SOLUBLE SOLIDS (° B), ACIDITY, pH, PIGMENTS AND VACUUM DURING PACKING, PROCESSING AND STORAGE

Type of Berries	Days	°Brix	Citric Acid %	pH	Pigments Optical Density*	Vacuum Inches
Strawberries	Unprocessed	40.03	.49	3.42	.224	4.00
	0	34.00	.48	3.35	.289	4.33
	30	29.57	.52	3.37	.254	4.33
	180	26.10	.56	3.44	.147	4.93
Red Raspberries	Unprocessed	36.70	.67	3.22	.180	3.50
	0	30.53	.94	3.13	.178	4.83
	30	26.27	1.19	3.13	.260	4.83
	180	26.53	1.28	3.08	.159	4.83
Blackberries	Unprocessed	49.80	.27	3.29	.239	2.43
	0	33.33	.58	3.17	.316	2.67
	30	30.47	1.28	3.13	.355	4.33
	180	29.20	1.25	3.08	.658	4.50
Blueberries	Unprocessed	38.50	.04	4.10	.000	2.50
	0	31.83	.21	3.21	.192	2.33
	30	23.33	.57	3.24	.490	3.33
	180	22.43	.56	3.16	.500	5.00

* 1 cm Beckman cell. Wave-length 497 mμ for strawberries, raspberries and blackberries and 519 mμ for blueberries.

A comparison between center and side of the cans showed similar rates of diffusion, Figures (1-8), except in the cases of strawberries where in the bottom side points showed a higher soluble solids concentration.

2. Acids

A comparison between the four unprocessed fruit packs, Figures 9, 10, 11 and 12 shows that the rate of distribution is not the same but depends on the type of fruit, and the original percentage of acidity of the raw fruit. Strawberries and raspberries showed the same stratification pattern between top-bottom, with big differences in acidity at the two ends of the can.

The blackberry packs (Figure 11) gave a rate of diffusion much lower than the raspberries (Figure 10) and had much more acid to diffuse than the strawberries (Figure 9). The blueberry packs showed no change in the unprocessed can and the total acidity was low. Little diffusion of acids took place from the fruit to syrup during the packing period, due to the characteristic texture of the fruit (tough and waxy skin).

The previous observations are in agreement with Adams (1, p. 39) results: "The rise in acidity of the syrup corresponds very closely to the fall in density, the stable state being reached rapidly in the case of most soft berries."

The picture of the curves between unprocessed and processed fruits gave an idea of type of fruit from a structured point of view. A particular discussion for each fruit gives some difference among them.

1. Strawberries. There was a difference in acidity which tended to be minimized with time (Figure 9). It is assumed that the water migration from fruit to syrup and then its subsequent translocation through the can was almost realized during the packing period. The fruit acids are dissolved in water and follow the water movement which is in the opposite direction and concentration gradient to the sugars.

2. Raspberries and Blackberries. The acidity differences between processed and unprocessed cans were large especially in the case of raspberries (Figures 10 and 11). This is evidence that the diffusion of water and acids from the fruit to syrup takes place in two steps, that is, during packing and at a higher rate during cooking. The slope of the concentration position curves were almost the same with no common point as there was in the case of strawberries, except for blackberries where the bottom positions showed similar concentrations. At the 1 3/4 inch surface just below the top a slight increase in the acidity appeared. This abnormality could be explained from the fact that the rate of translocation in the top area is lower and

the time from packing-processing to analysis was not enough for the expected movement. The translocation of sugars in this area is also slower giving an explanation of the relationship of acid-water to sugar movement.

3. Blueberries. In the case of blueberry packs, the effect of cooking was clear because the acids diffused from the fruit and distributed throughout the can according to the general trend of translocation (Figure 12).

The third step of interchange which takes place between fruit and syrup followed by a final equilibrium of the constituents happens during the storage period. The picture of this stage has almost the same trend as the previous two. For each particular fruit, the following conditions existed:

1. Strawberries. An almost complete equilization of acids appeared after six months storage, passing through the expected changes as the blending of sugars with water and acids took place. A percentage difference of 14 percent existed between top-bottom after 6 months storage.

2. Blueberries. After 6 months storage, the blueberries reached about the same equilibrium as the strawberries, but achieved equilibrium at different time periods. The equilization was nearly completed since the percentage difference is about 8 percent, top to

bottom. It is important to notice that a large rise in acidity of the syrup happened during the first month of storage resulting in an increase of about 90 percent from the time of packing. It is assumed that the diffusion coefficient for acids is low and so a longer period of time is needed for the exchange equilibrium between sugars and water-acids.

3. Blackberries. The packs of these berries have shown an extreme pattern in the diffusion and translocation of acids. During processing a rise in acidity of the syrup occurred (around 100 percent) which after a month's storage again increased more than 100 percent. It is almost the same behavior as in blueberries with the only difference being that more of the acids had been taken out of the fruit during processing. We could assume that blackberries as softer fruits than blueberries would give this type of movement.

4. Raspberries. These berries are of the soft type, as it is proved from the rapid rate of exchange of the constituents during processing and storage. Although equilization of sugars is almost complete, the acids are far from equilibrium after six months storage. This happened also in blackberries. Because of the destruction of the fruit matrix, the characteristic permeability of the cells of the fruit tissue no longer exists. The fruit is filled by sugars which establish an equilibrium during storage, while the acids have more

difficulty in moving into the fruit. This behavior could be explained from the fact that in the syrup, there are two types of dissolved substances; that is nonelectrolytes as sugars and electrolytes such as acids, mineral salts, and pigments. The rate of translocation of electrolytes depends on the size of the molecule and the existence of the ionic charge on the particle which interacts with the electrostatic field of oppositely charged molecules. In the case of acids, a lag in their movement appeared because they have to go through this field, where temporary bonds are taking place between different types of opposite charged ions or associations with water molecules or other molecules which have dipole characteristics.

The experiments showed that little difference existed in the rate of translocation of acids from bottom to top between the center and side of the cans (Figure 9 and 16). A small concentration difference existed in the strawberry packs, where during packing and processing a smaller concentration appeared at the side which changed during storage and actually was about equal after six months storage.

3. pH

The active acidity of the syrup is expressed by the pH value, which gives the intensity of the acidity which is more important than the total acidity for canned foods. Berries are classified in the first

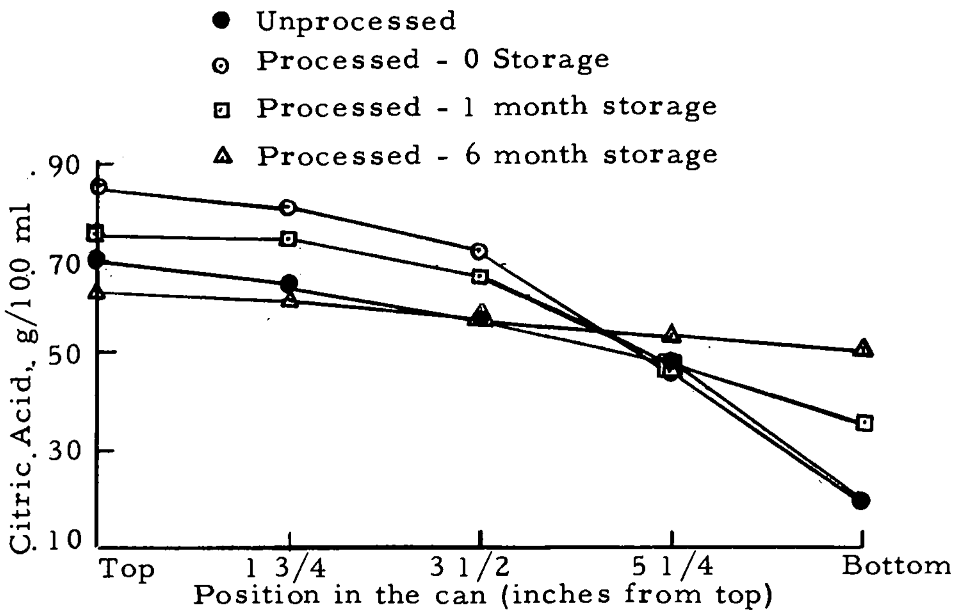
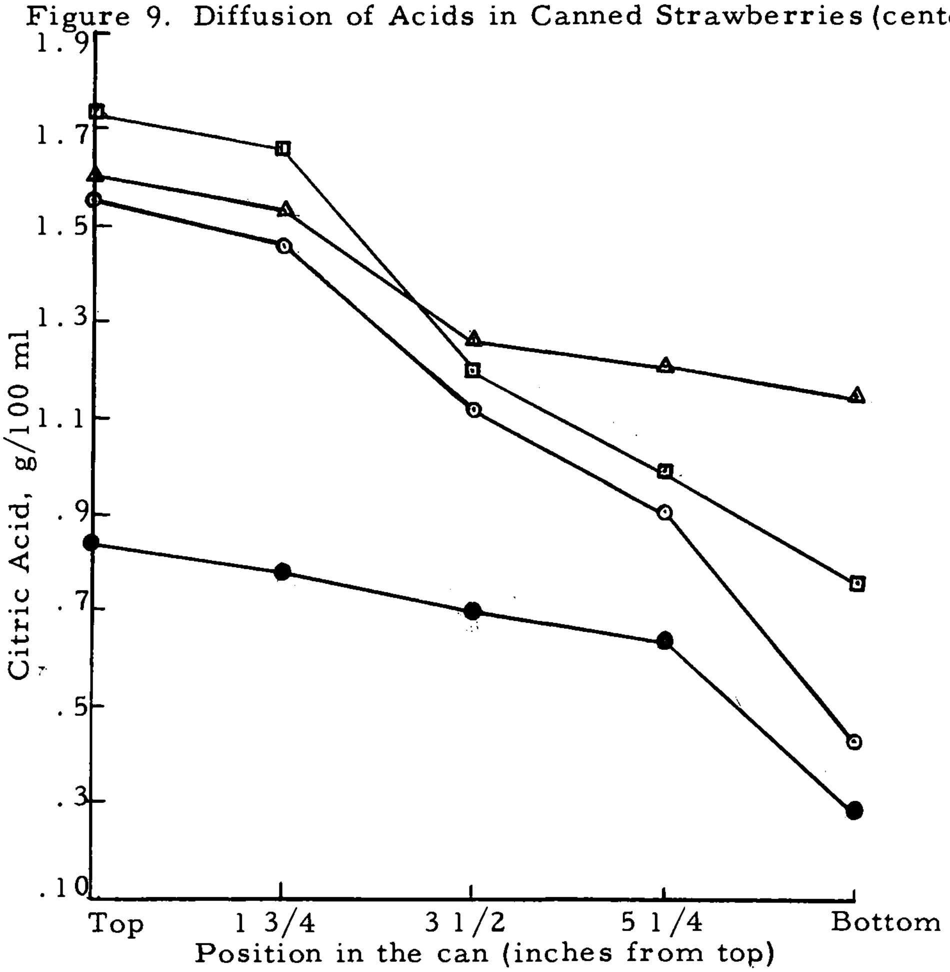


Figure 9. Diffusion of Acids in Canned Strawberries (center)



Figures 10. Diffusion of Acids in Canned Raspberries(center)

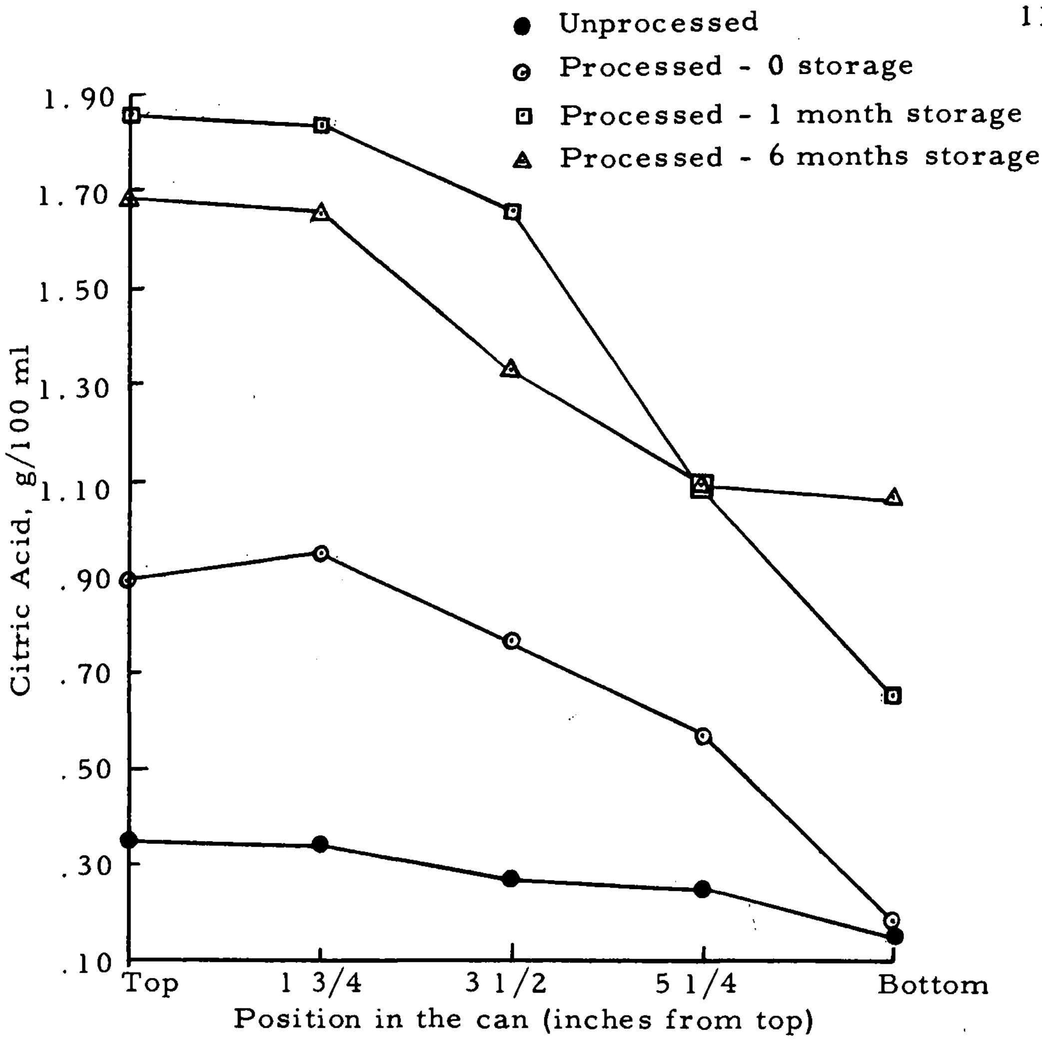


Figure 11. Diffusion of Acids in Canned Blackberries (center).

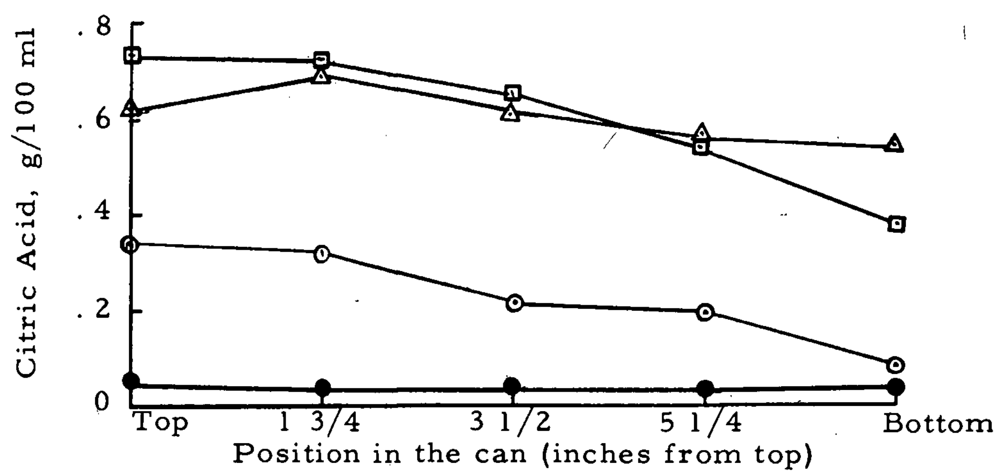


Figure 12. Diffusion of Acids in Canned Blueberries (center).

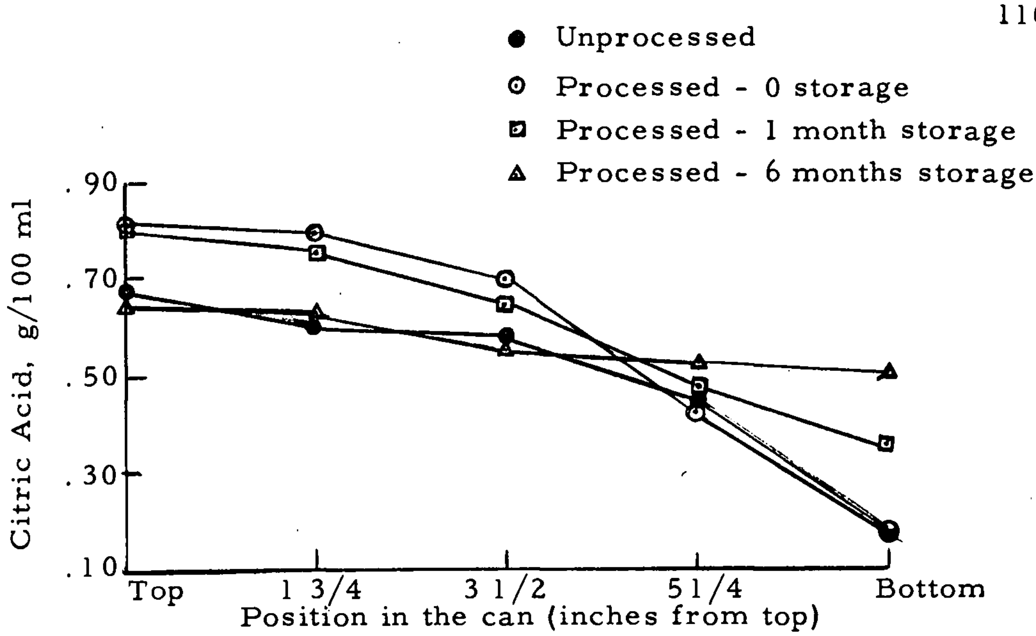


Figure 13. Diffusion of Acids in Canned Strawberries (side).

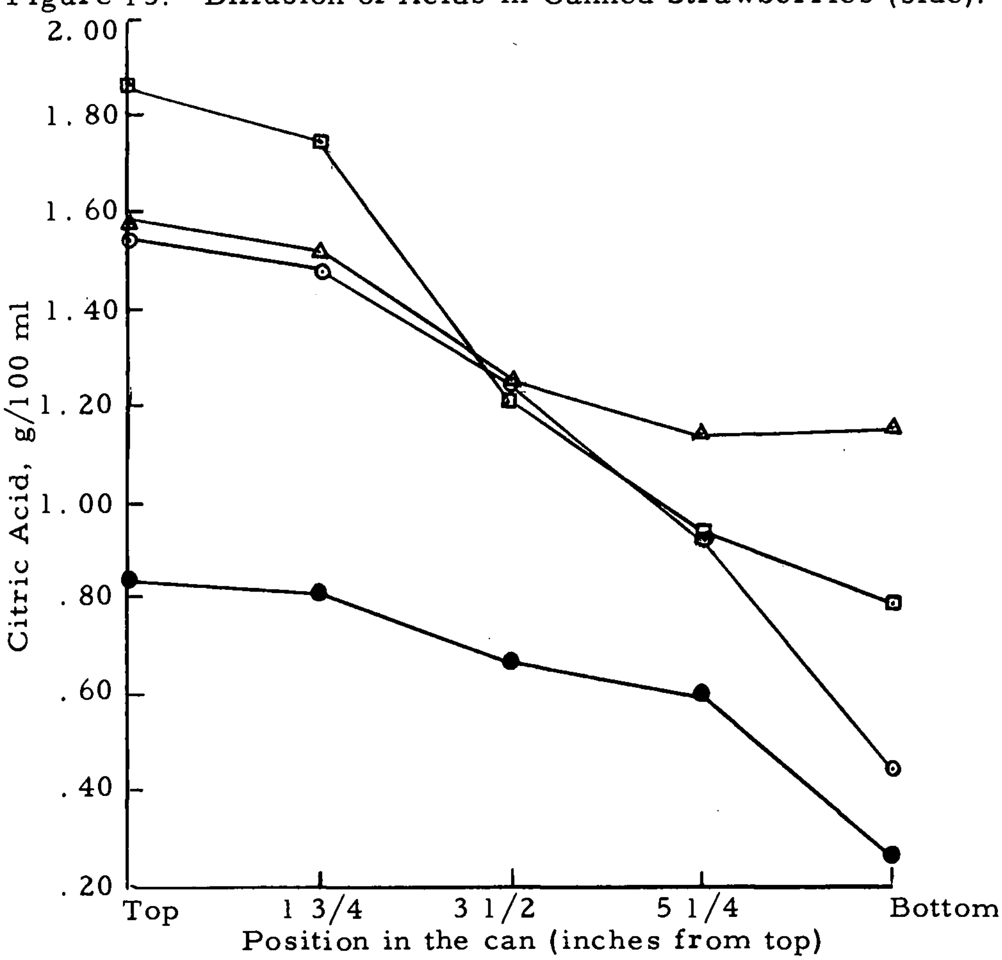


Figure 14. Diffusion of Acids in Canned Raspberries (side).

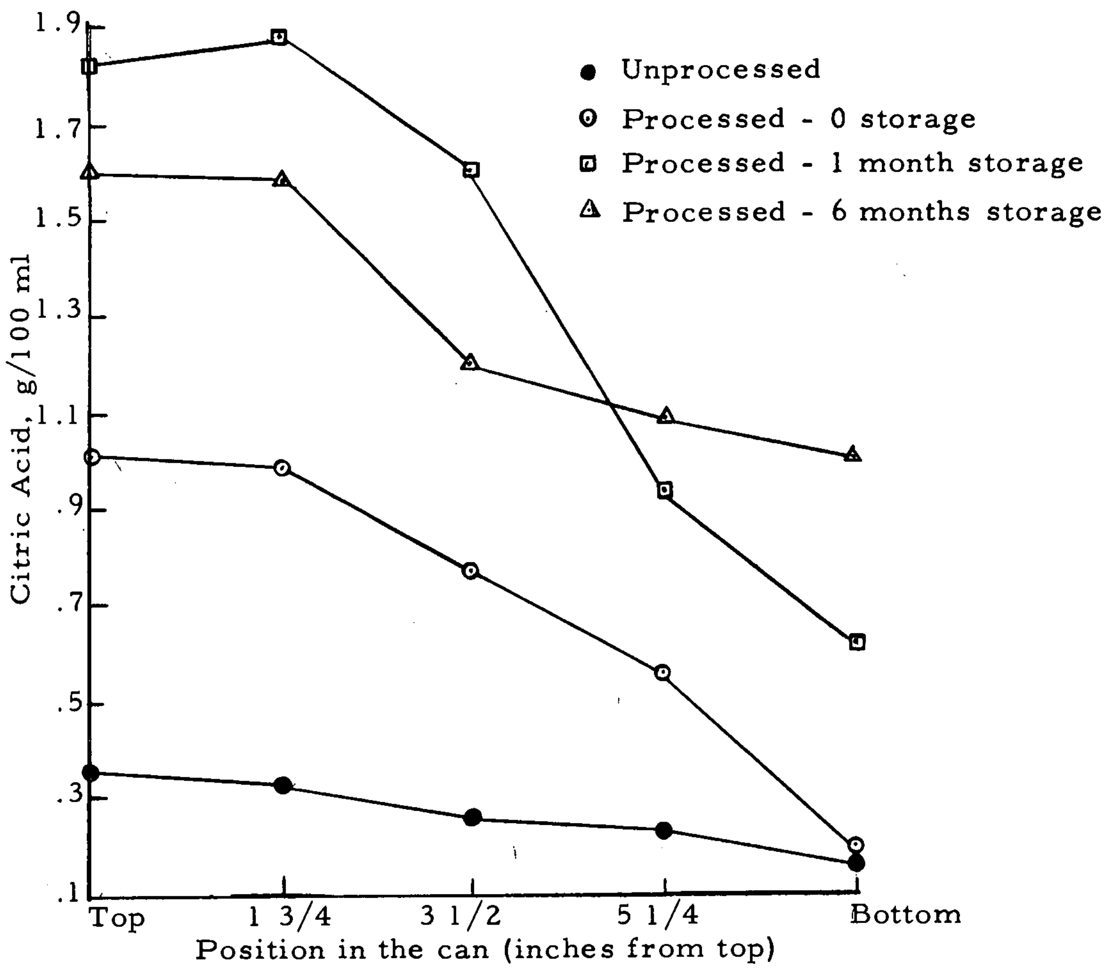


Figure 15. Diffusion of Acids in Canned Blackberries (side)

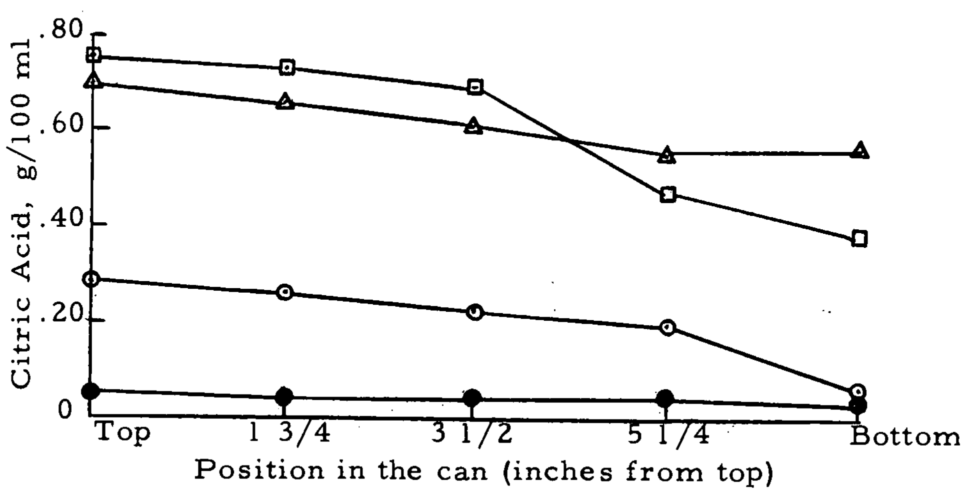


Figure 16. Diffusion of Acids in Canned Blueberries (side)

class from the point of can corrosiveness. They belong to the high acid (low pH) food class. The use of cans with tin plate enameled according to specifications for this type of fruit is necessary, Adams (1), Brighton (9), Hartwell (32, p. 336).

A comparative study of the four berry products after packing (Figures 17, 18, 19 and 20) shows that the rate of distribution of pH in the whole can depends on the rate of diffusion of acids from fruit to syrup. The pH value of the syrup was neutral or slightly alkaline. The type of the fruit and the degree of tightness of the product affect this rate. That is, the first step is the loss of water and acids from the fruit cells and then the water solutions are translocated in the can on the basis of density.

The amount of acids contained in the fruits must be taken into account and mainly the type of acids which each fruit contain, because they give the intensity in the acidity according to their degree of ionization.

In previous chapters we have discussed the distribution rate of acids which is characteristic for each fruit, which pH values follow also. As the acidity of the syrup becomes higher, the pH value is lower. The graphical representation of these two quantities against position in the can show the opposite direction of movement between total acidity and pH. The pH changes do not follow exactly the changes in the acidity. Some apparent irregularities appeared as in the case of strawberries, Figure 17, where the pH at the positions 1 3/4 in. and 3 1/2 in. below the top in the unprocessed cans showed a lower pH value than at the top of the can although the total acidity was actually less in these two areas. The same relationship appeared in raspberries, Figure 18, and blackberries, Figure 19, for the position 1 3/4 in. below the top. In blackberries the difference in acidity was small with a large pH difference between the can bottom and the point above it. This is more obvious in the blueberry packs, where, although the acidity doesn't have any large change from top to bottom, the pH values are very different.

The above observations could be explained by the fact that in areas where pH values were low, water was found in larger amount. Because the acids are more dissolved in water which facilitates, to an extent, their degree of dissociation, an increase in the intensity of the acidity and a lower pH resulted in this area. The existence of more fruit juice in some areas could be related to berry breakage in local areas and also to translocation of juices within the can on the basis of density.

In the case of blueberries, Figure 20, the higher pH value at the bottom should be expected because the amount of juice and water is much lower in this area.

In the case of strawberries and raspberries, several different functions could have happened during the packing-processing period. The fruit, because of its low density compared to 60^{o} Brix syrup, floats to the top of the can where it is closely packed. Below this fruit area, stratified syrup layers are found ranging from a low concentration syrup immediately below the fruit to a high density syrup at the can bottom. Because at the middle and upper part of the can there is more water and a greater concentration of acids, the pH values are lower. The lower pH values occur in the middle region although the acidity at the top is higher.

Strawberries and raspberries have about 90 percent and 97 percent citric acid and 10 percent and 3 percent malic acid, respectively, Nelson (83). The rate of diffusivity between the hydrogen ions, the malic ions and the citric ions is different, the magnitude depending upon the degree of their adsorption to water molecules to form water-cation or water-anion associations. Because the citric acid molecules are larger and the water association should be stronger with three positions of ionization, they will have the lower diffusion coefficient, which governs the rate of translocation from the can top to can bottom. Malic acid should have a higher coefficient and the hydrogen ions the highest.

The above situations brings the hypothesis that in the positions of 1 3/4 in. and 3 1/2 in. below the top of the can there are hydrogen ions, malic anions and citric anions in concentrations proportional to their diffusion coefficients. An electrostatic potential would be established between the fruit mass and the liquid layers lying immediately below the fruit which could have a major role in the nature and extent of can corrosion.

This hypothesis appeared true from the fact that this irregularity is more distinct in the case of strawberries when the amount of malic acid is higher.

The changes which take place during storage have two characteristic points; first, all berries except strawberries show pH values which tend to continuously decrease (Table 1)

Blueberry packs, Figure 20, showed a higher rate of change than other berries. Strawberries have a different behavior. There is a reduction in pH after processing, and increase after a month's storage period and after six month's storage the pH level was at its high point in four out of five locations. It is possible that a redistribution of constituents between fruit and syrup occurred which resulted in an increase of pH values of the fruit. The work of Adams (1), Ross (95) Guadagni, et al. (25) showed similar results.

Blueberries show the opposite trend since equalization of syrup-fruit pH values tend towards a minimum.

The second characteristic is the trend of pH values to be almost equal in the syrup throughout the can after 6 month's storage. An almost true equal equilibrium existed in strawberry, Figure 17, and blueberry, Figure 20, packs after six month's storage. Raspberries, Figure 18, and blackberries, Figure 19, are less homogenous in pH because of their soft texture which blocks a diffusion between fruit-syrup. A lower pH value appears 1 3/4 in. below the top, although the acidity is higher at the top. It is possible that the type of acids at the top give a less active acidity (lower disassociation constant). Part of these acids may be produced from degradation of reducing sugars or by other mechanisms, Leonard (60), Luh (63), during processing and later storage, which would be accelerated by the presence of the headspace air and the higher total acidity.

Samples from the center and side of the cans gave no notable difference in the rate of the diffusion of their constituents and their translocation during packing, cooking, and storage, Figure 17 - 24. An obvious difference existed in the case of strawberries, Figure 17 and 21 where the samples from the side of the can showed higher pH values in the processed products than the unprocessed ones. It may be due to the higher temperature around the outer surface of the can for a longer time which accelerated the diffusivity and the degree of blending of the syrup and juice resulting in a slightly lower acidity and a higher pH.

4. Pigments

Anthocyanins are the characteristic pigments of berry fruits. They are dissolved in water and are affected by sugars, pH, ascorbic acid, temperature, oxygen, Meschter (78), Markakis (73), Nebesky (82), because of their chemical formulation.

The transfer of pigments from berries to syrup and their distribution throughout the can are affected by the above factors and time which is important in defining the rate of these functions.

Absorption curves, Figures 25, 26 and 27 for the unprocessed four berry packs show that a relative large transfer of pigment takes place from fruit to syrup during the packing period. The rate of diffusion and translocation of pigments into the syrup is almost identical for strawberries, blackberries and raspberries.

This is not true for blueberry syrup which gave no absorbance for unprocessed fruit. The rate of pigment diffusion before processing is zero because of the fruit structure.

The changes of pigment concnetrations from top to bottom expressed as an optical density, follow the same pattern as acids because both of those substances are present in the water phase (juice) which is running in an opposite way to sugars (bottom to top, initially).

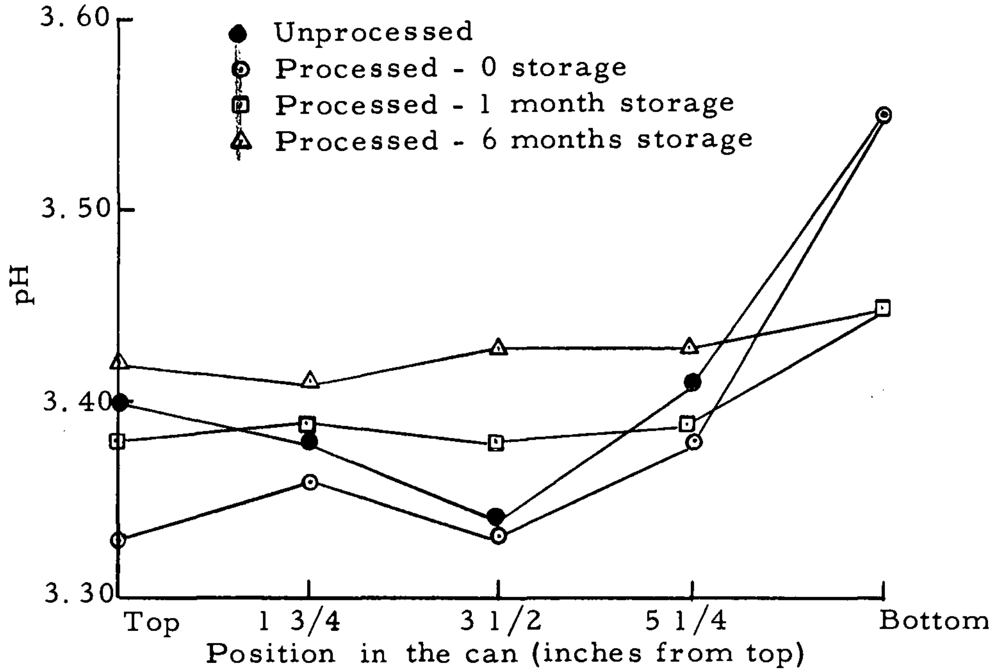


Figure 17. Changes in pH in Canned Strawberries (center).

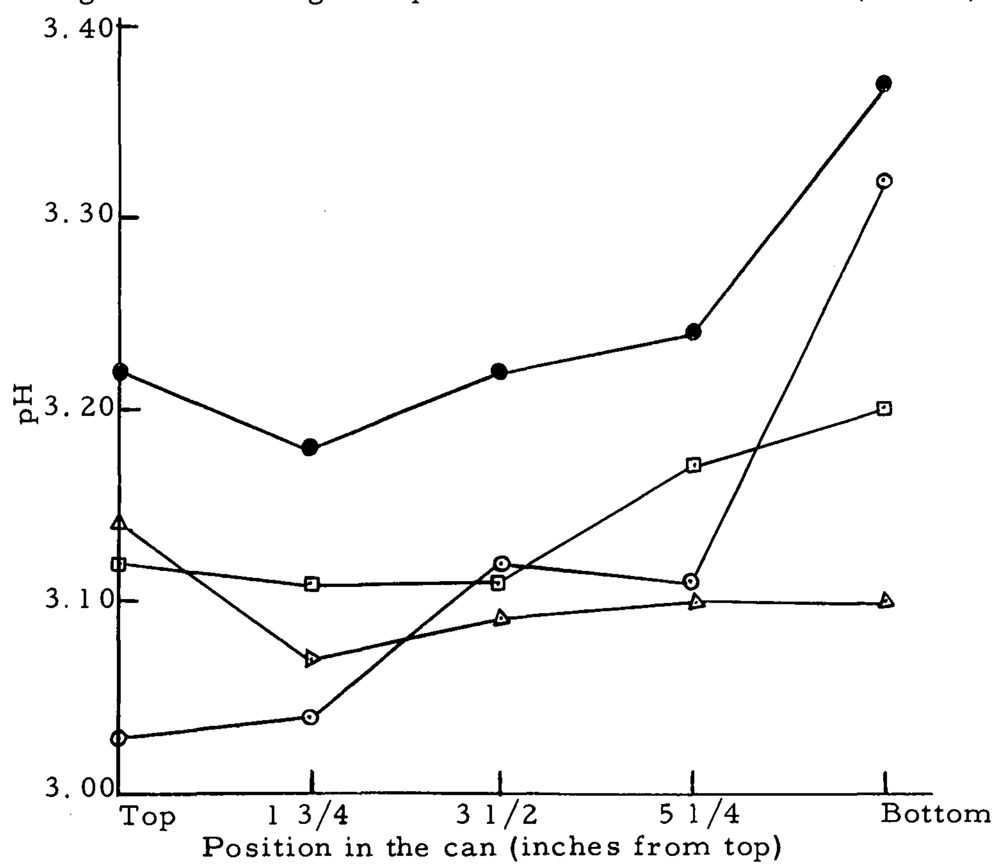


Figure 18. Changes in pH in Canned Raspberries (center)

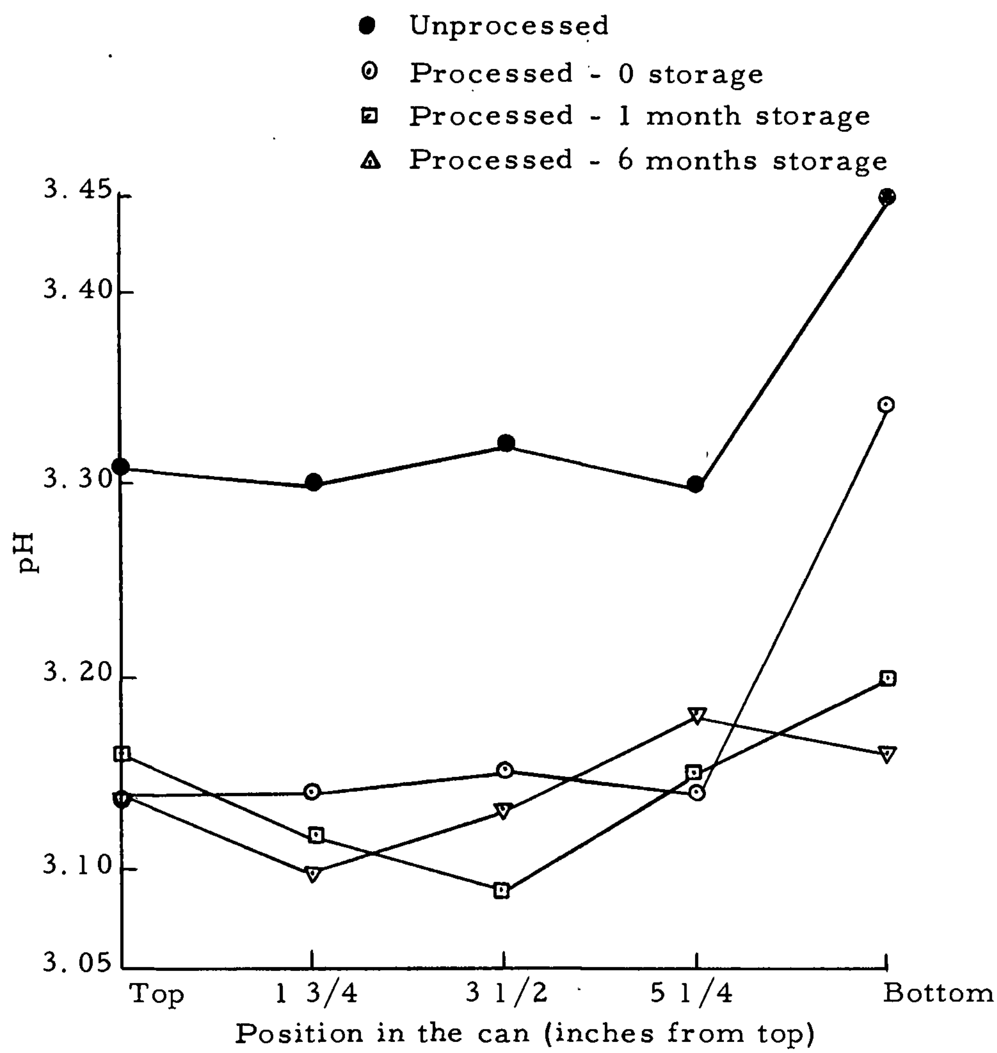


Figure 19. Changes in pH in Canned Blackberries (center)

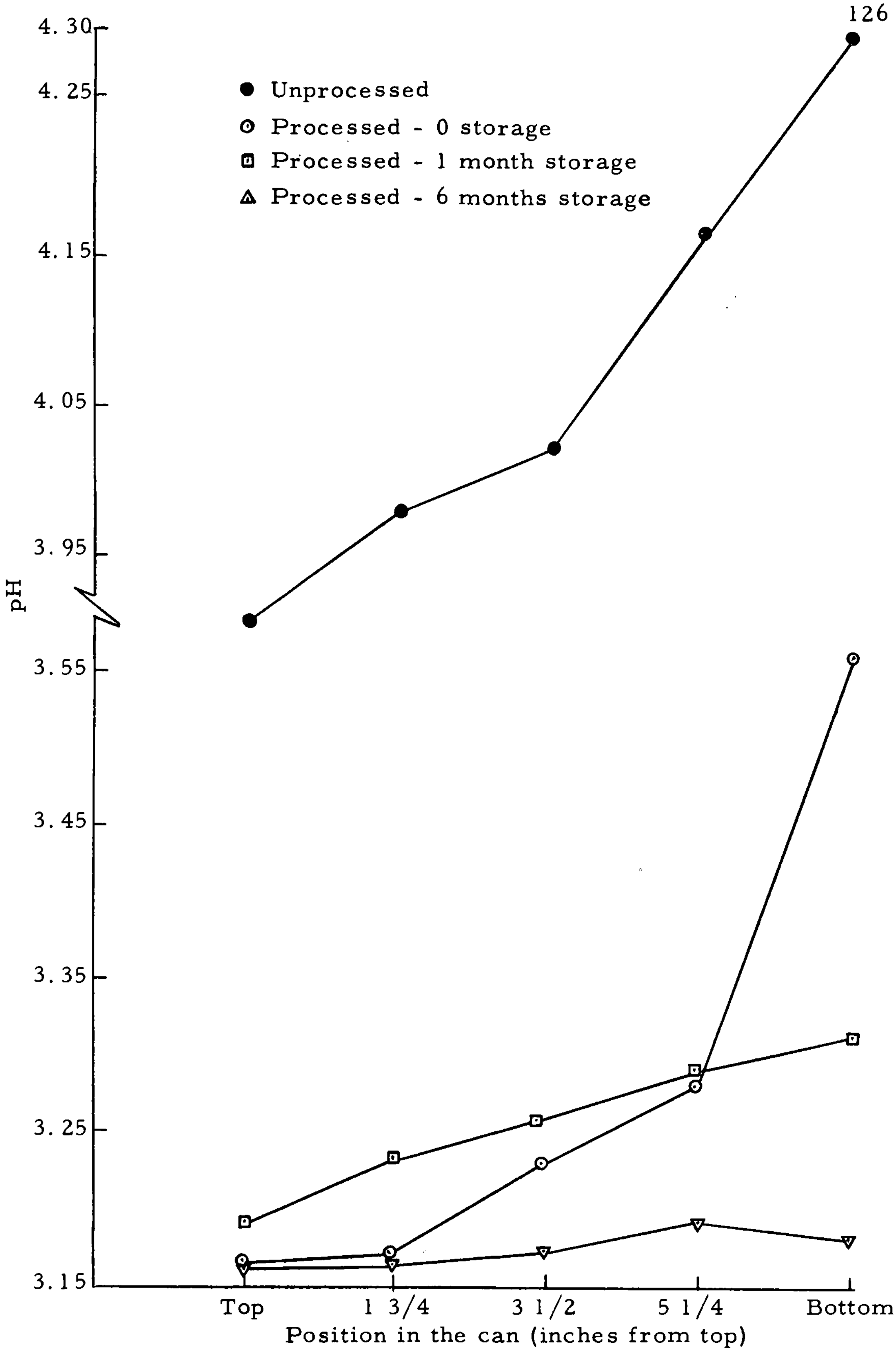


Figure 20. Changes in pH in Canned Blueberries (center).

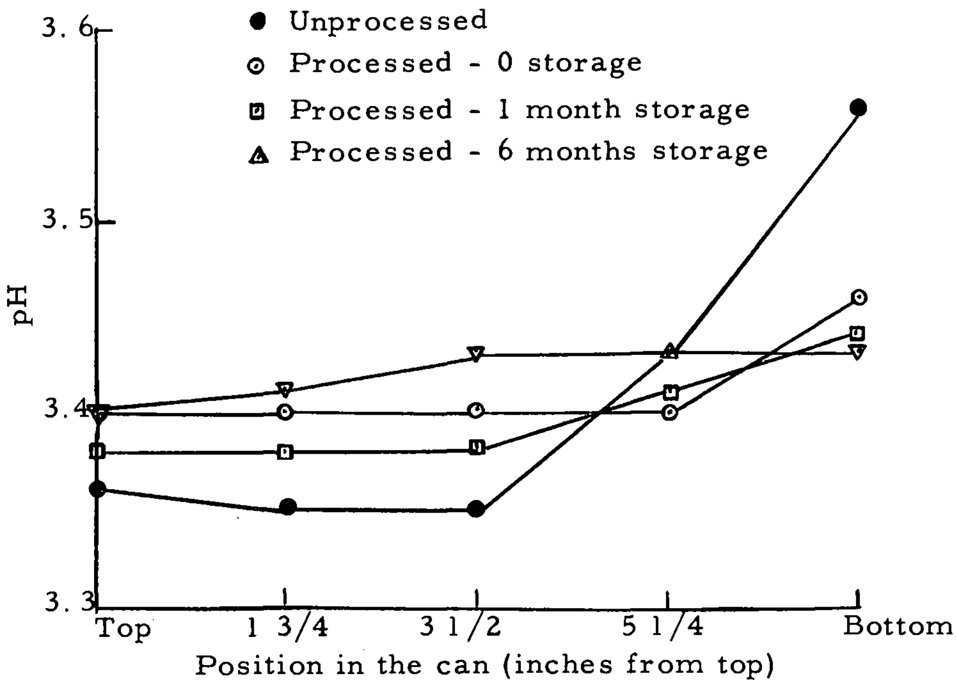


Figure 21. Changes in pH in Canned Strawberries (side).

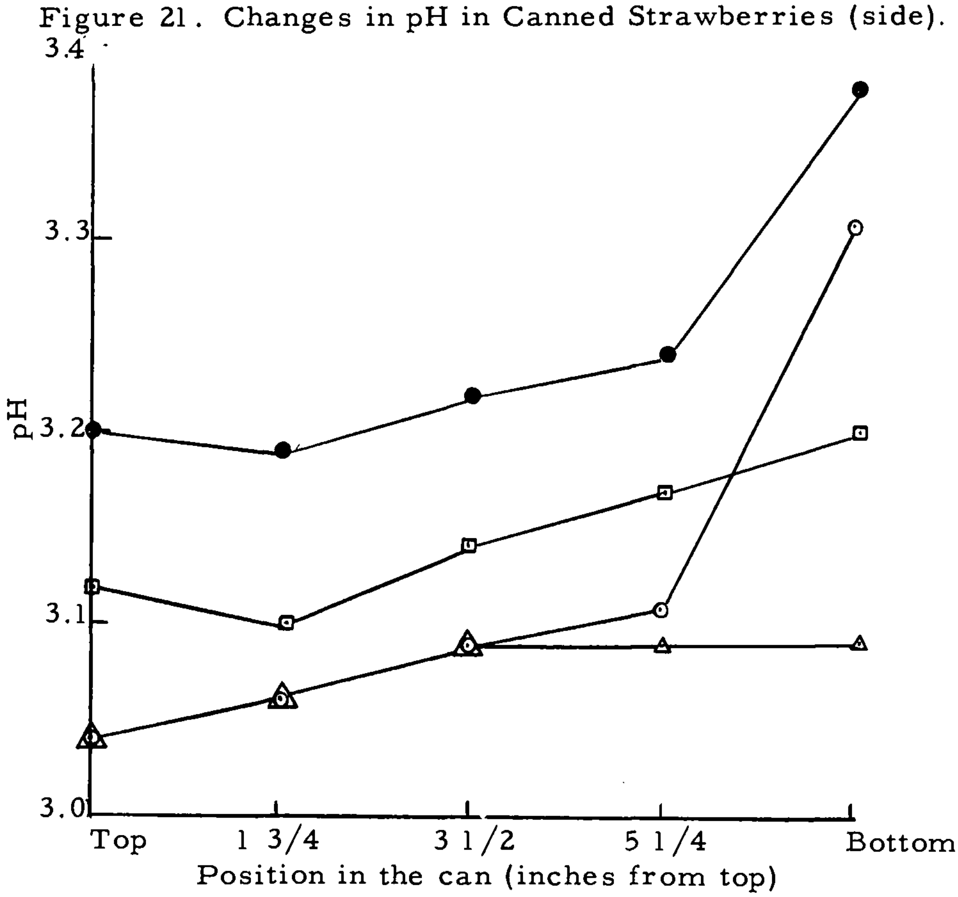


Figure 22. Changes in pH in Canned Raspberries (side)

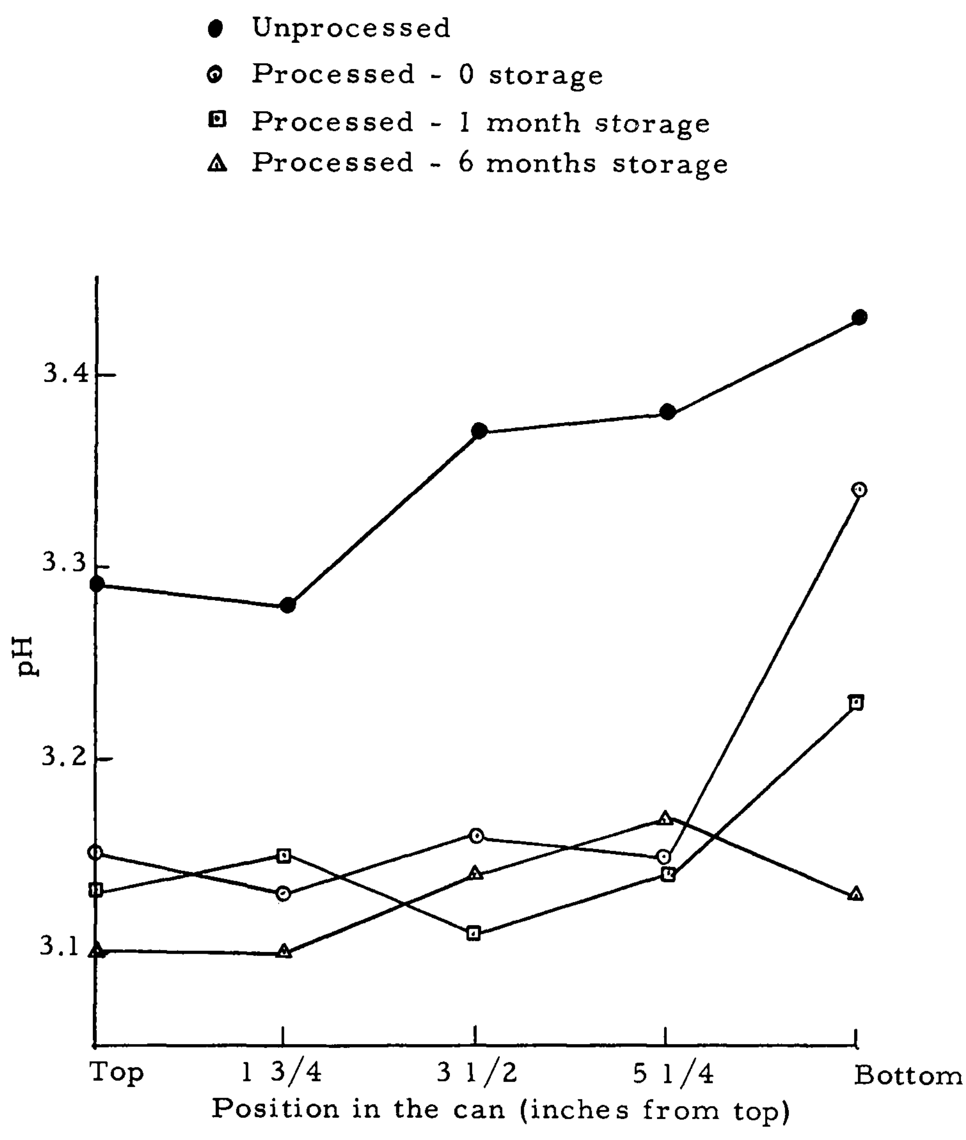


Figure 23. Changes in pH in Canned Blackberries (side)

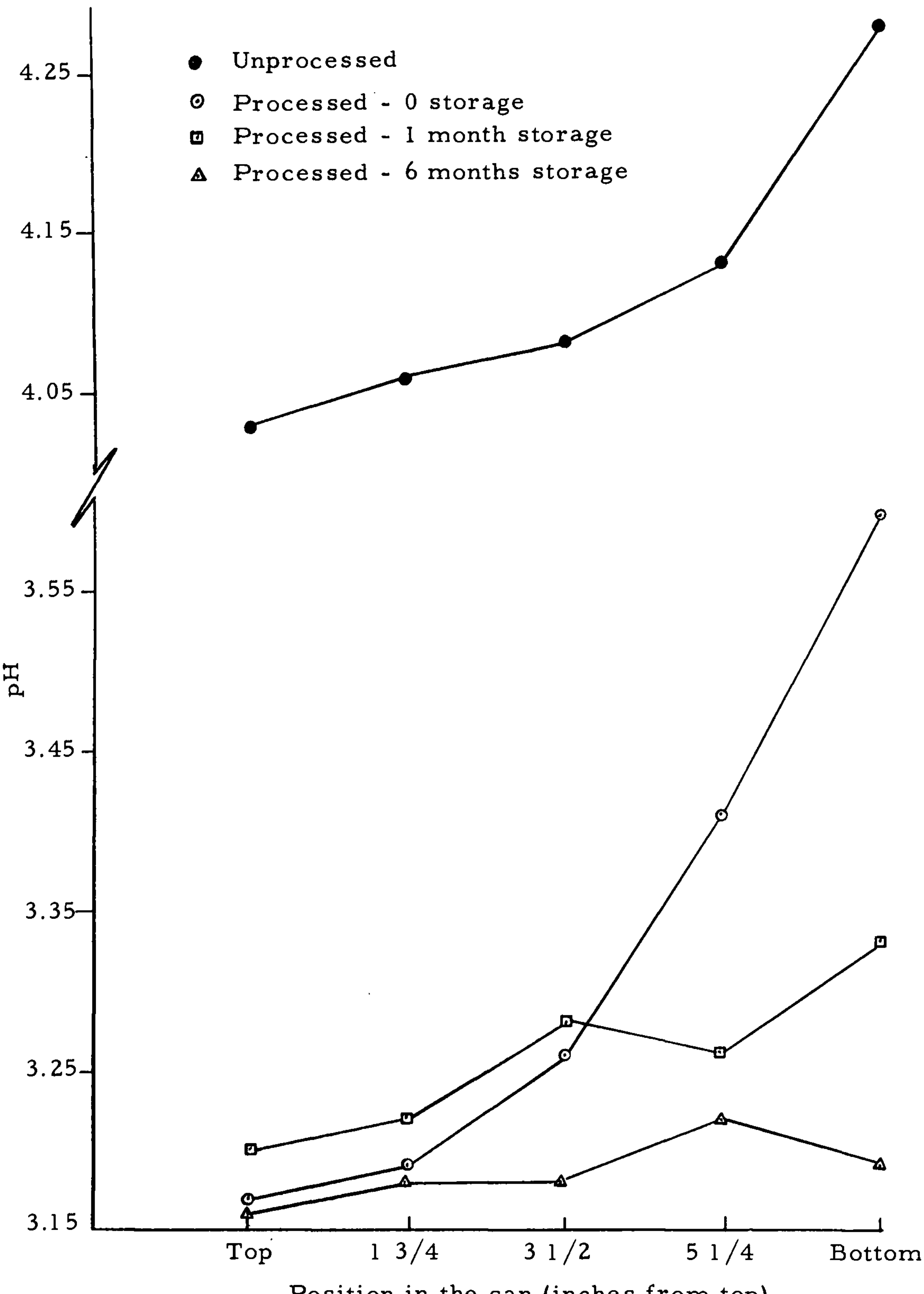


Figure 24. Changes in pH in Canned Blueberries (side)

The movement of pigments from fruit to syrup was more significant at the time of processing as is shown from the corresponding curves, (Figures 25, 26, 27 and 28). The fact that temperature affects the rate of diffusion and the color of syrup varies markedly has been shown by Guadagni, et al. (30). The constant, K, of the equation which they developed for the color distribution, increases with temperature and was characteristic for each fruit.

Blueberries gave color to the syrup during the processing time, as a result of effect of heat on the skin and cell walls of the fruit, Figure 28.

The effect of heating on pigment is to cause it to fade. During storage, the optical density is changed because the buffered pigment solutions undergo degradation and an insoluble or soluble brown color may develop. The susceptibility to deterioration varies with the fruit; Ponting, et al. (89), Lukton, et al. (67), Markakis, et al. (73), Nebesky, et al. (82).

According to the above conclusions of the investigators mentioned, a rough relationship for the rates of translocation and the trends of an equalization equilibrium during storage could be assumed.

Except for blackberry, Figure 27, the movements of pigment in the product of the other fruits, Figure 25, 26 and 28, moved towards homogeneity after six months storage by passing through a high optical density period during the first month. It is assumed that at this time most of the pigments have been extracted out of the fruit. It appeared that at the first or second position below the top the density was higher.

The explanation could be based on the assumption that a harmful effect of headspace oxygen on pigment stability is mainly in strawberry products. This affect is accelerated by the presence of ascorbic acid, which in the case of strawberry there is a larger amount. Sondheimer-Kertesz (106), Markakis, et al. (73).

By comparing curves of Figures 17, 18, 19 and 20, and 25, 26, 27 and 28, it may be seen that the changes of pH and pigments follow the same patterns which confirm the observations that in the upper-middle of the can there is a lower pH value which in the can would give a higher optical density to the pigments of the syrup. Sondheimer-Kertesz (103), Guadagni-Nimmo (25).

Blackberries, Figure 27, showed a different behavior, continuous increase of optical density of the pigment appeared from the packing period to six month's storage. Three possible explanations could be given that, first, the fruit has a special structure which does not permit the rapid extraction of the pigment from the fruit. This same picture was given in the case of acids.

Secondly, the pigment concentration is higher, Guadagni, *et al.* (29) and the amount of pigment which blends into the syrup depends on the original amount of pigment of the berries. It is known that raspberries and blackberries have a longer high quality life than strawberries which means less degradation of pigment.

A third hypothesis is that a soluble brown color could develop which gave a darker color in the juice resulting in a higher degee of absorbance.

Lukton, *et al.* (67) observed during the opening of cans after six months storage a dull reddish brown color at the top.

Strawberries, Figure 25, and raspberries, Figure 26, show a lower average optical density after six months storage. A gradual clarification of the juice because of the formation of a chalcone could occur which further is degraded to a brown insoluble polyphoenolic compound. As the length of the storage was increased there was a corresponding increase in the amount of brown color present. Lee, *et al.* (59), Sodheimer-Kertesz (104), Markakis, *et al.* (73), Pratt, *et al.* (92).

The strawberry syrup is more susceptible to losses because of the presence of larger amounts of ascorbic acid, Markakis, *et al.* (73), Pratt, *et al.* (92).

Blueberries having one-fourth the ascorbic acid content of strawberries show a better retention of pigment as expected. This is seen from the curves (Figures 25, 28) which at the period of six months storage show a higher pigment optical density. A different form was observed in the curves of blueberries after six months storage in that they show a higher optical density at the three lower points of the can.

This may be related to the fact that there is a specific gravity separation of the berries in the pack. Most of the fruit floats and within this floating mass there could be a density gradient based on the specific gravity of the fruit. In addition, a small percentage of the berries are sinkers. If the fruit with the higher density also contained the highest pigment concentration, this fact could account for the higher pigment concentration in the middle regions of the can.

Center side positions of the cans for the four fruits and for each of the treatments gave almost identical results, Figure 25 - 32. The distribution of pigment in the syrup at each level of the packs had about the same optical density.

5. Drained Weights

The drained weight changes observed in the four berries during the different treatments used were generally similar to those noted previously (literature review) by other investigators, (1, 109,

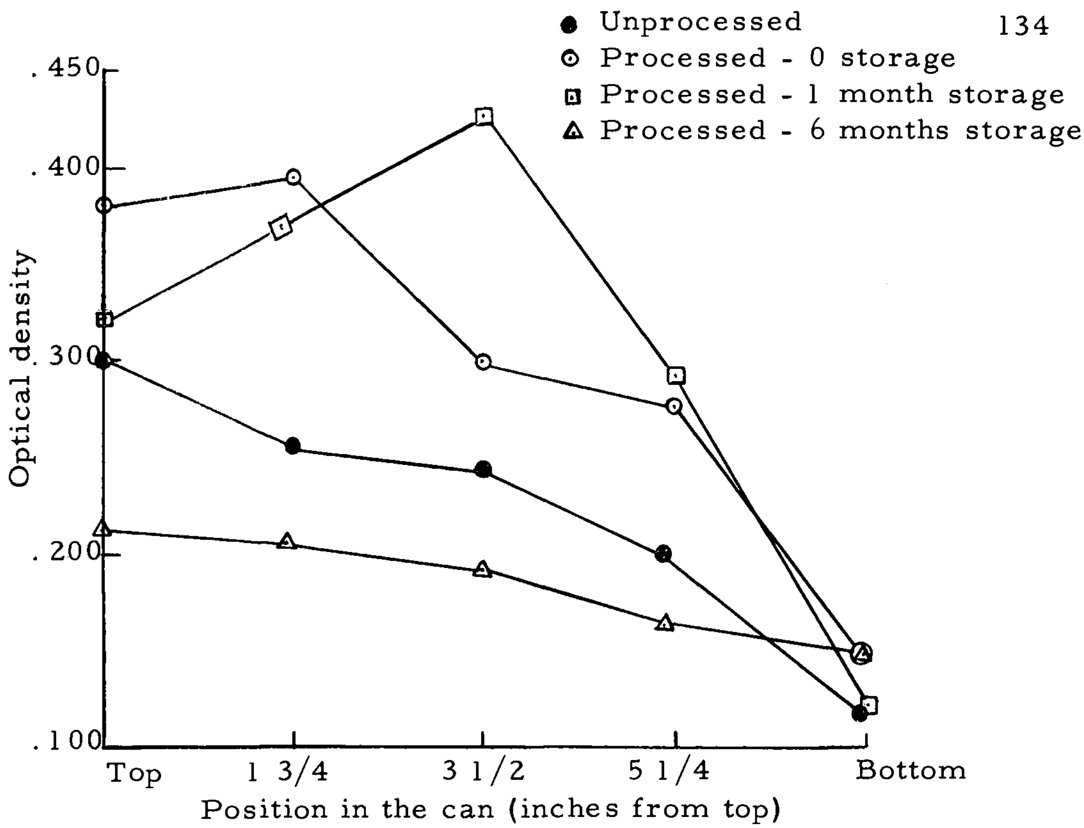


Figure 25. Diffusion of Pigments in Canned Strawberries(center)

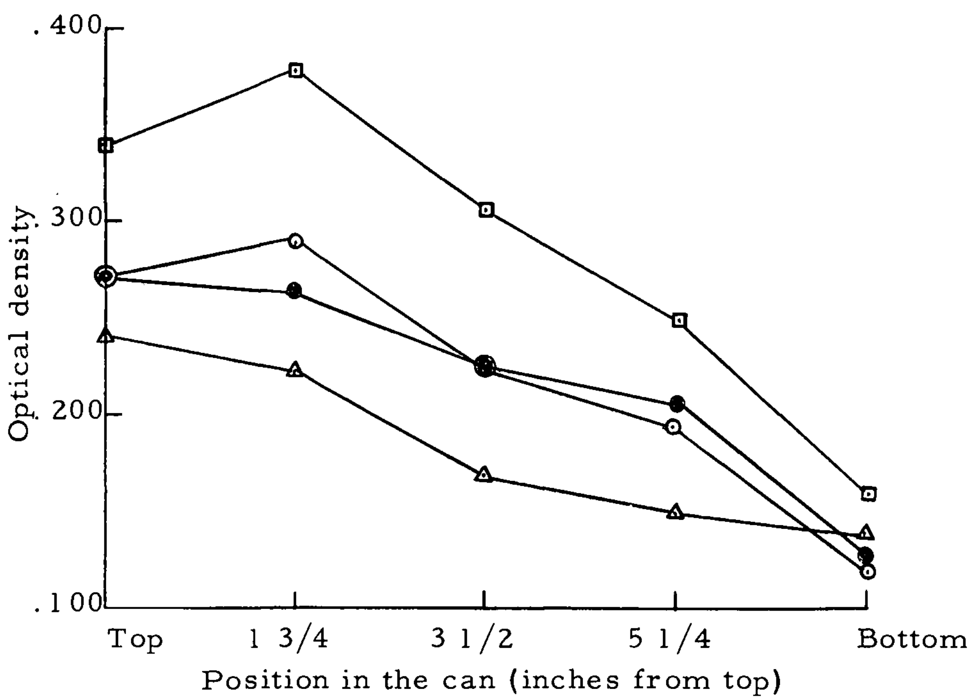


Figure 26. Diffusion of Pigments in Canned Raspberries(center)

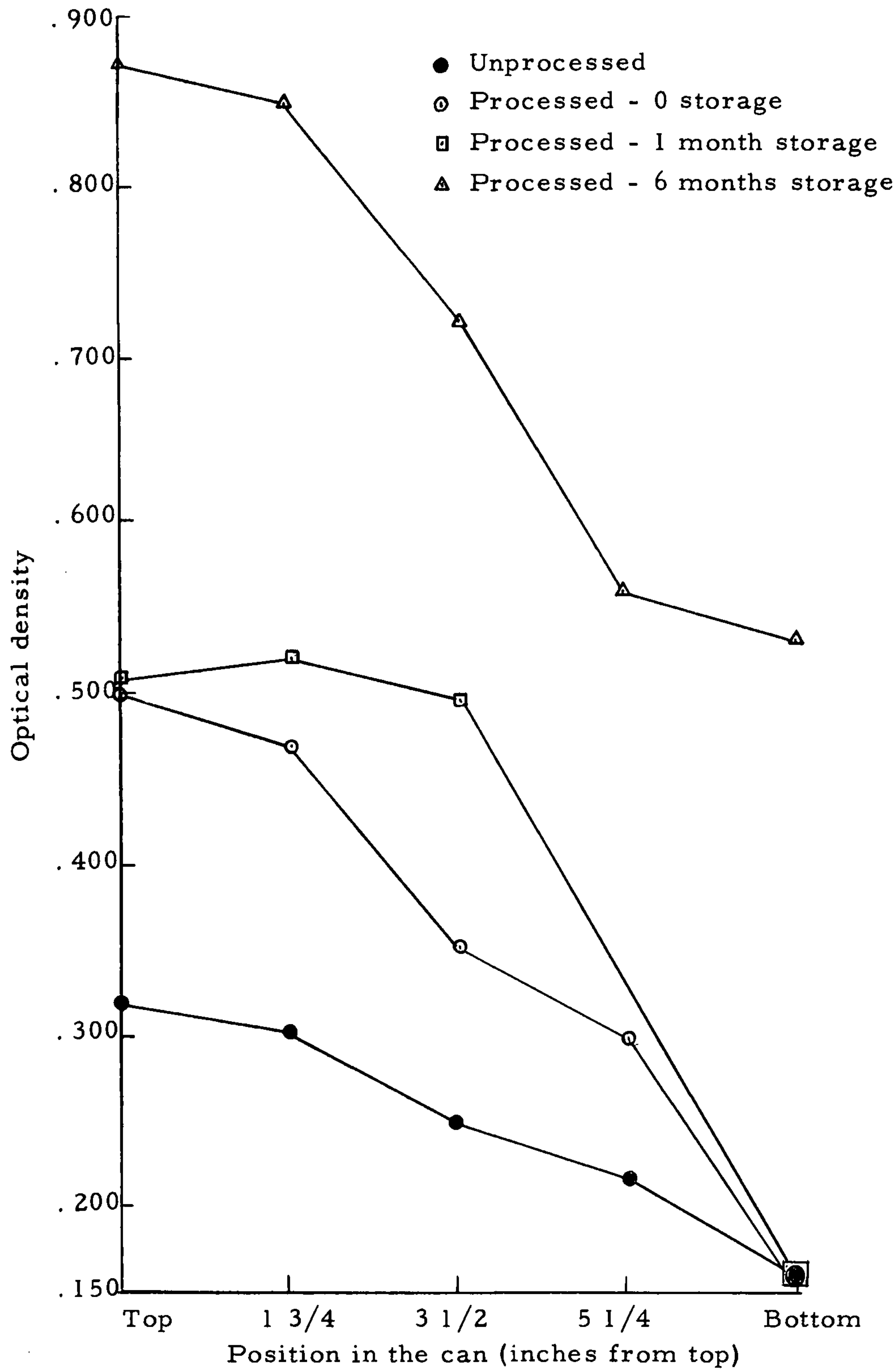


Figure 27. Diffusion of Pigments in Canned Blackberries (center)

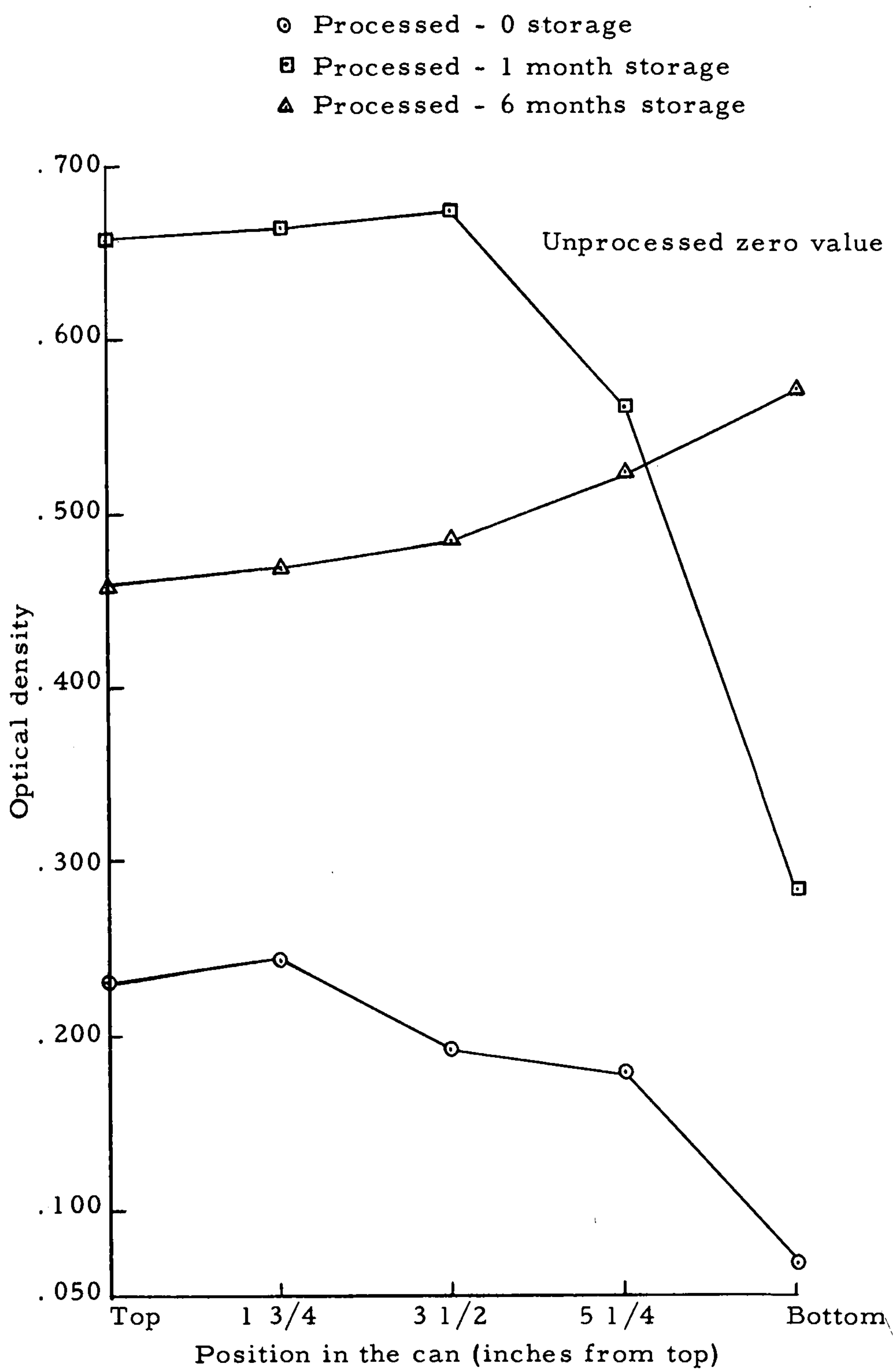


Figure 28. Diffusion of Pigments in Canned Blueberries (center)

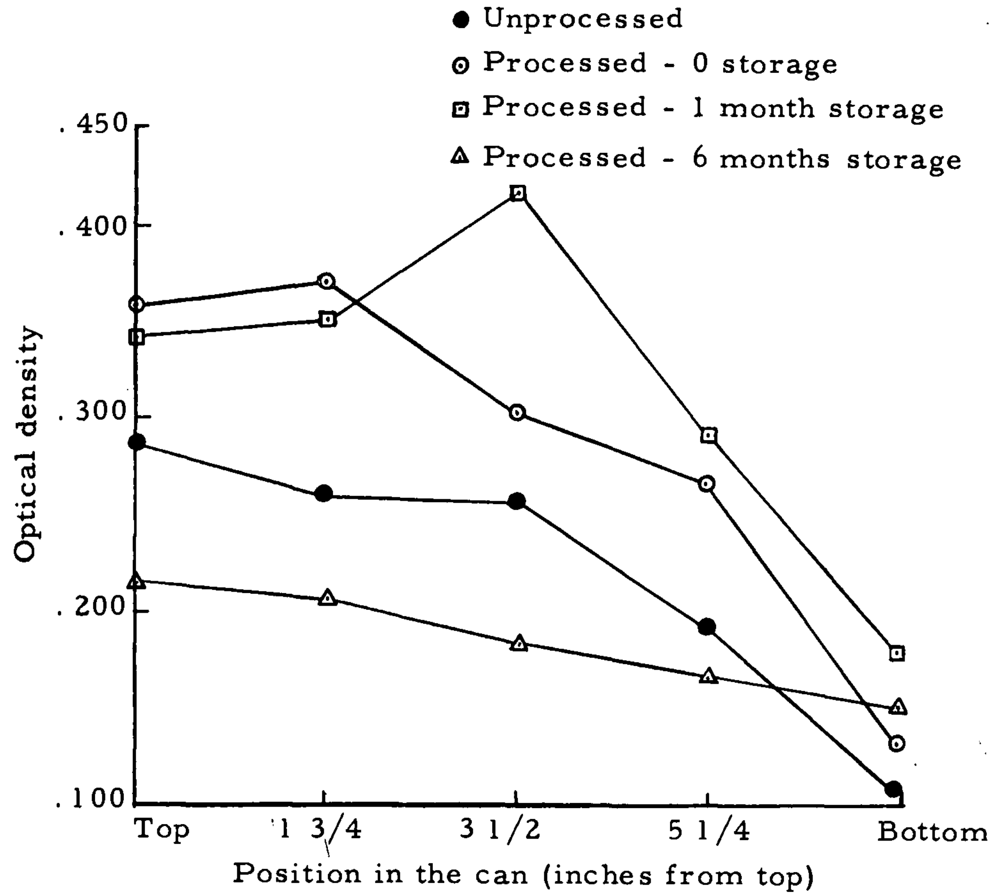


Figure 29. Diffusion of Pigments in Canned Strawberries (side)

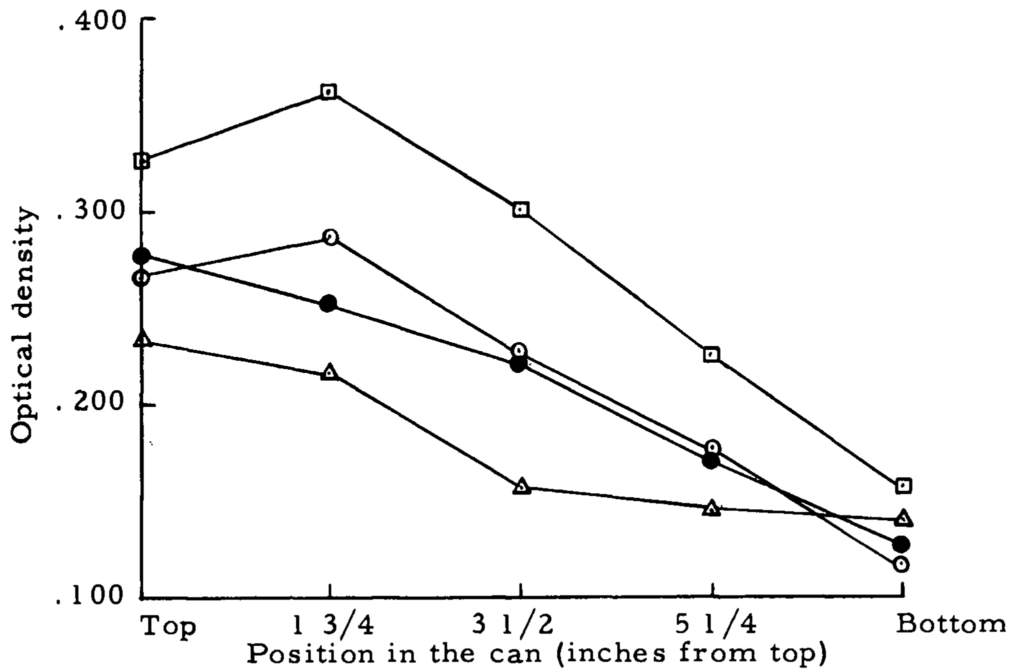


Figure 30. Diffusion of Pigments in Canned Raspberries (side)

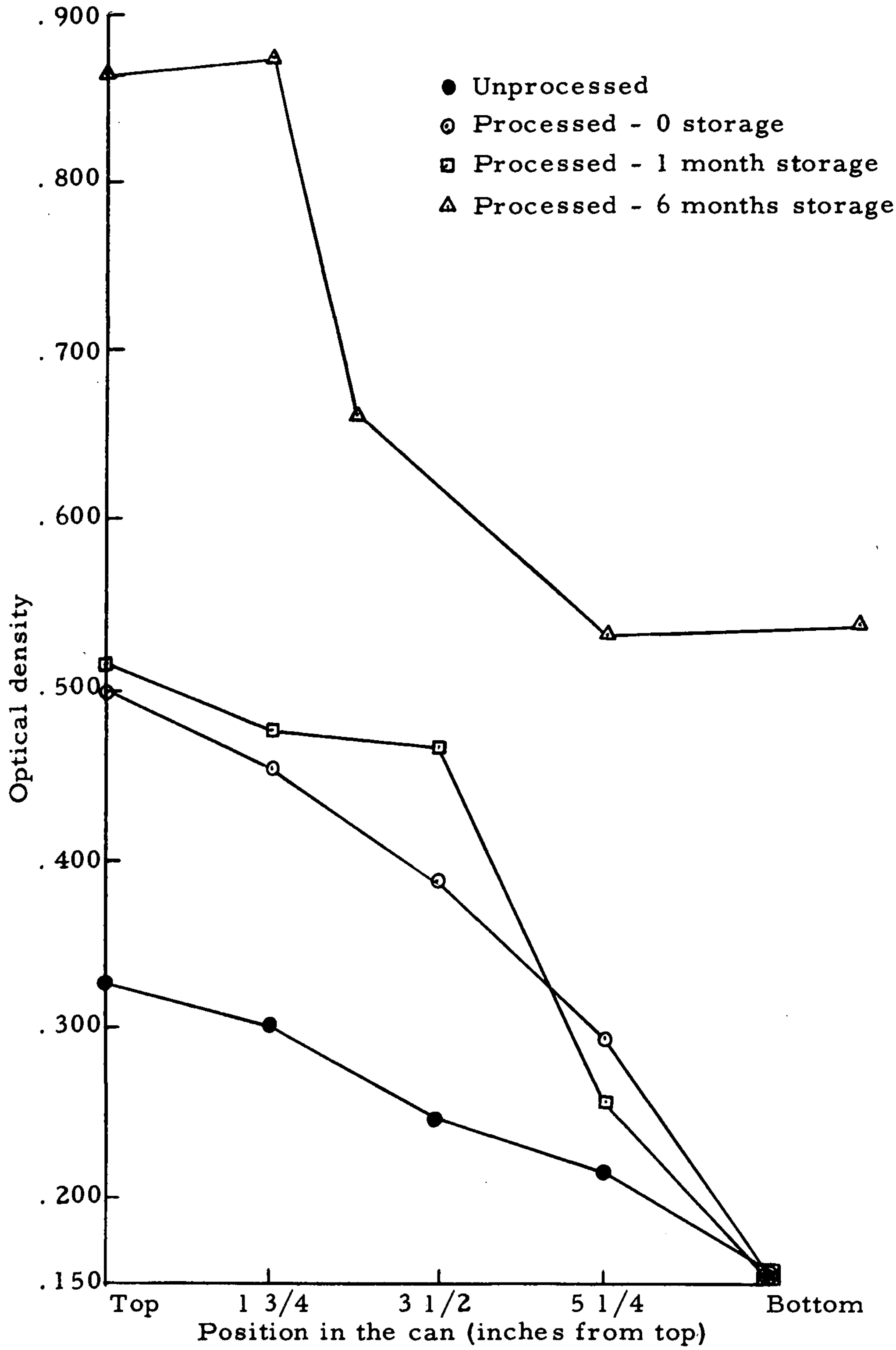


Figure 31. Diffusion of Pigments in Canned Blackberries (side)

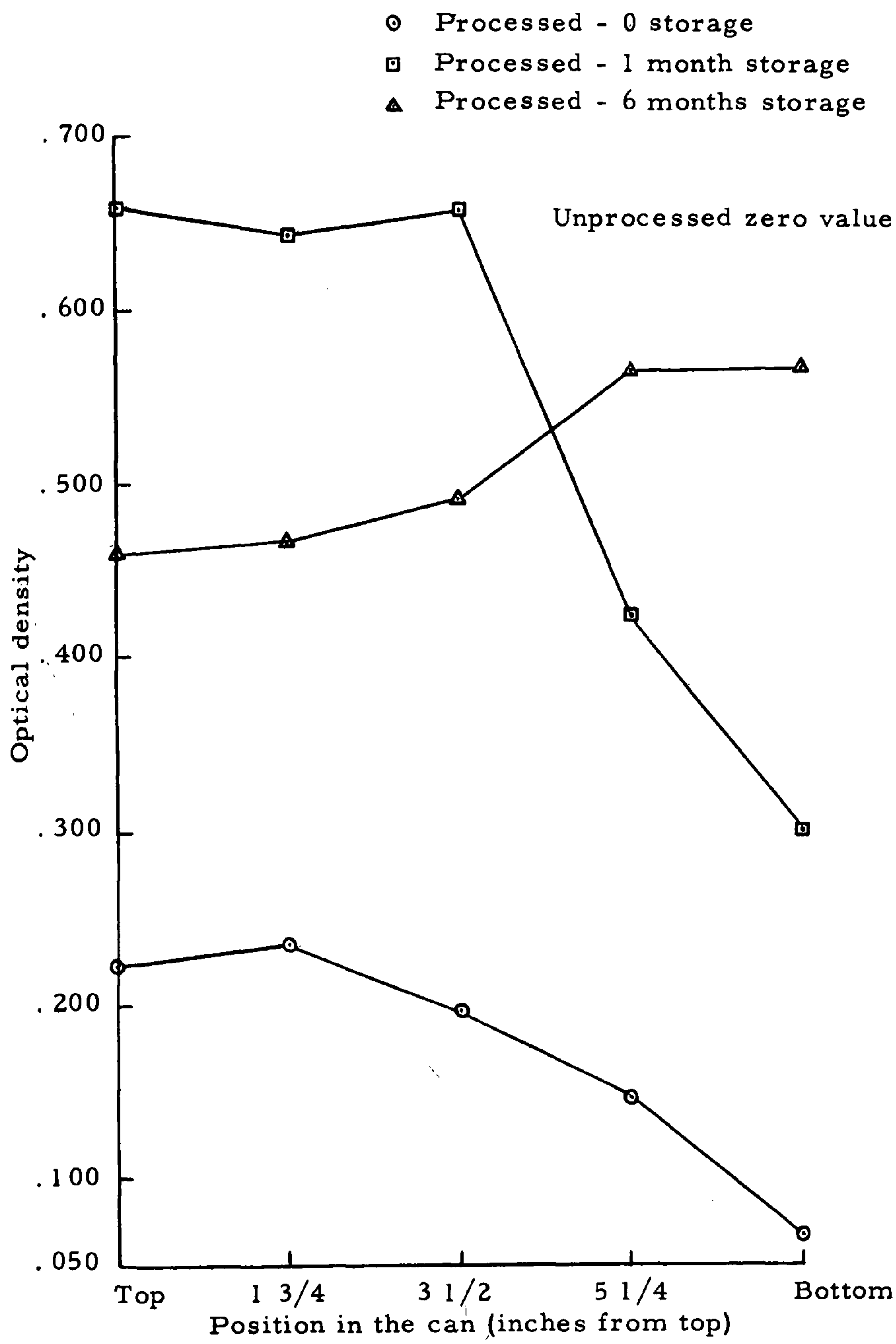


Figure 32. Diffusion of Pigments in Canned Blueberries (side)

124, 95, 59, 64, 19, 20) Table 2.

The loss in weight of fruits after canning is a general phenomenon due to osmotic pressure gradient of heavy syrups. A shrinkage and shrivelling of the fruits during the first days after canning (low drained weights) result from the rapid movement of water from the less concentrated solution inside the fruit to the more concentrated solution outside. A simultaneous movement of sugars from syrup to berries favors rapid (about three days) reduction of the osmotic pressure gradient.

Ross (95) reported that "the algebraic sum of sugars and water translocations would represent the drained weight increase of syrup, on the drained weight decrease of fruit after three months storage."

The drained weights and the rate of translocation varies greatly with cover syrup concentration, type of the syrup, type of the fruit, pH of the fruit juice, temperature during processing and storage.

The unprocessed packs of the berries showed losses of weight of about one-half the magnitude of the processing losses. These changes are due to the osmotic process because of the large difference in sugar concentration. No hydrolysis had happened which could give products with a higher penetration efficiency into the fruit tissue. From the average value of syrup which was about 40^{o} Brix for

TABLE 2

DRAINED WEIGHT BEHAVIOR OF PROCESSED BERRIES

Type of Berry	Days After Processing	Drained Weight in Grams[1]	Drained Wt. /Fresh Wt.
Strawberry	Unprocessed*	1618	75.07
	0	1045	48.54
	30	1018	47.26
	180	1113	51.64
Raspberry	Unprocessed*	1797	83.39
	0	1414	65.62
	30	1470	68.21
	180	1501	69.68
Blackberry	Unprocessed*	1802	83.64
	0	1482	68.78
	30	1613	74.86
	180	1692	78.53
Blueberry	Unprocessed*	1725	84.49
	0	1700	83.27
	30	1725	84.49
	180	1720	84.24

* About five hours delay at room temperature after syruping.

[1] Mean of three cans.

the unprocessed packs, it is assumed that little of the sugars of the difference from the initial 60° Brix syrup had moved in to fruit cells, but that the juice translocated into the syrup resulting in a lower concentration and a corresponding reduction of drained weight. Syrup entering the fruit would be found in the intercellular spaces from which it would readily drain.

The diffusion of sugars in the berry packs during processing has a higher rate. The amounts of sugar and water present in the fruit cells and syrup is much different than in the unprocessed packs. The main reason for this change is that processing destroys the semi-permeable membrane of the cells and facilitates diffusion and exchange of the solvent and solute molecules between the cover syrup and the berry cells. At this point, all of the four berry packs showed the lowest drained weight, although the soluble solids of the syrup were lower. This indicated that more water came out to the syrup phase than sugars entered the fruit tissue.

Except blueberries which showed little change in drained weight after six months storage, all the other berries showed a slight increase in their drained weights.

The gain in weight of strawberries was less because heat processing caused strawberry cells to bind together more firmly, with a possible polymerization of phenolic materials, resulting in a shrinkage of the cells which have lost their ability to recover and gain weight by sorption of sugars from the syrup. Isherwood (39, p. 147), Gallop (20, p. 31).

All the samples after six months storage showed an increase in their drained weights. The gain in weight during storage resulted from the gradual movement of sugars into the fruit tissue. The rate of this diffusion was accelerated because more invert sugar was present in the syrup. Adams (1) reported a 2 percent inversion in canned cherry syrup immediately after canning which increased to 27.9 percent after 6 months storage.

The behavior of blueberry drained weights was different from that of the three other fruits. The loss in drained weight happened mostly during the packing period and was low in comparison to the losses to the other fruits. During processing, another slight decrease appeared, but a gain in weight takes place during storage reaching after 6 months storage the same weight that the berries had after packing.

The rate of change in drained weights in the cans of the blueberries showed the same trend as the diffusion of sugars and their translocation through the cans governed by a smooth movement.

This slow rate of movement and the small changes in drained weights indicates that the skin of the blueberries offers greater resistance to movement of fruit fluid to the syrup. Whittenberger (121) reported a hypothesis for cherries, which has a structure similar to blueberries, that:

> High drained weight in heat-processed cherries seems to be associated with a high degree of tissue cohesiveness, which in turn is dependent on the strength or heat stability of the intercellular cement. Microscopic examination reveals that from tissues exhibiting low drained weight, single intact cells and clusters of cells may slough off their own accord or may be separated easily with a microneedle. This indicates that the intercellular cement is comparatively weak. On the other hand, single intact cells cannot readily be separated from freshly processed tissues showing high drained weight.

F. Shear-Press Measurements

Samples of a 100 g from top, middle and bottom positions of the drained berries were used for measuring the texture according to the previously described method. The readings obtained were converted to pounds force which are tabulated in Table 3.

It was observed that in all cases the unprocessed samples had maximum values which dropped off immediately after processing. However, in the case of blackberries there was an initial slight increase in the firmness of the berries obtained from both top and bottom, upon processing followed by a gradual softening in the texture up to six months of storage.

TABLE 3

TEXTURE MEASUREMENTS OF PROCESSED BERRIES

Type of Berry	Days	Maximum force in Pounds Position in the Can		
		Top	Middle	Bottom
Strawberry	Unprocessed	52.93	47.13	48.20
	0	33.00	38.20	38.50
	30	18.87	33.13	33.13
	180	25.73	30.07	28.40
Raspberry	Unprocessed	54.60	59.73	63.60
	0	51.47	48.60	58.07
	30	43.33	49.07	45.93
	180	55.00	57.33	61.73
Blackberry	Unprocessed	98.13	97.93	93.33
	0	99.00	91.53	98.00
	30	70.00	74.00	83.33
	180	62.73	69.33	74.33
Blueberry	Unprocessed	192.27	209.33	183.73
	0	100.80	118.13	108.53
	30	67.67	118.13	105.27
	180	59.87	86.00	78.33

* All samples on 100 g drained weight basis. Means of three cans.

In case of blueberries there was a progressive softening of the fruit at all the three positions in the can and with processing and subsequent storage up to six months.

Strawberries behaved similarly with the exception of the samples obtained from the top position of the can, where a large decrease in firmness was observed at the end of one month as compared to the zero time and six months storage.

The berries in this area may be more ripe and thereby softer due to a density separation of the berries during processing. The graphs from the recorder showed a flat area at the top of the curve for the three samples of this treatment. This suggests a change in the seed fraction, probably due to acid hydrolysis of the external seeds in this high acid area of the can.

The firmness of raspberries decreased gradually from unprocessed, processed zero time of storage, to processed 30 days of storage. Upon subsequent storage up to six months there was a reversal of this trend and the berries seemed to firm up. This was true of all the samples from the three different positions. This is a most significant finding in that firmness is apparently a reversible change in at least some fruits. When using maximum force as the criteria of measuring texture, the proportion of seeds in the fruits has a pronounced affect. Strawberries and blueberries, behave somewhat similarly regarding the nature of these seeds. The seeds are rather small and few as compared to the amount of flesh. Thus, upon processing there is an immediate decrease in firmness which continues to decrease with storage. The position of berries in the can did not have any effect on this general pattern of continued softening as is evident from Table 3.

Raspberries and blackberries behaved somewhat differently in this respect. The seeds are large and contribute considerably to the total weight of the berries. Upon processing, the effect on texture is not as pronounced owing to the fact that the seeds are not as readily affected as the flesh. Thus, there was a slight softening in case of raspberries where as in blackberries a slight increase in the firmness was obtained. However, upon subsequent storage the seeds became somewhat soft and as in blueberries give a softer fruit at the end of six months of storage. The firming of the raspberries upon six months of storage might be due to a toughening of the seed coats as a consequence of prolonged storage. More probable is the effect of syrup concentration on the drained weight in the three can locations. The syrup concentration in the top of the can after one months storage is close to the soluble solids. Concentration of the fruit juice in the case of raspberries, and consequently there would be little osmotic shrinkage of the fruit in this area. A 100 g sample of drained weight solids would contain a higher percentage of juice and less of the structural cell solids and would exhibit a softer texture upon shearing.

The position of the berries in the can seemed to have an effect on texture in the case of strawberries and blueberries. The middle samples were found to be slightly firmer upon six months of storage in strawberries and blueberries, whereas the bottom samples seem to be the firmest in the case of raspberries and blackberries.

In the case of blueberries the texture measurements were generally higher as compared to the other three berries. This is due to the structural makeup of the blueberries. They have firm skins with a wax covering and many small seeds. Thus, they offer high resistance to shearing. Even after processing the seeds and skins are not as much affected as the flesh and hence blueberries even after processing give higher texture measurements though less than the unprocessed samples. A marked loss of firmness occurred upon long storage and probably represents changes in the seed and skin fractions.

G. Head Space and Vacuum

The mean headspace in the cans was 11/16 inches with a range of 3/16 inches.

The vacuum readings of the cans have been tabulated in Table 1. The relative low vacuum in the cans during packing except strawberries which showed a higher vacuum, permitted an amount of oxygen to remain in the container. During processing, oxidation phenomena are accelerated and the consumption of oxygen produces a higher vacuum into the can.

An increase in vacuum appeared during storage due to the same probable reason.

The initial low vacuum readings are the result of two factors. The large amount of intercellular gases entrapped in the berries and somewhat compressed under hydrostatic pressures is released to the headspace area during processing and results in a lowered vacuum. Secondly, the high metabolic activity of berry fruits and accompanying microflora results in considerable gas formation unless the cans are immediately processed and even then there is a considerable lag time before enzyme inactivation temperatures are reached.

The rate vacuum increase in the cans depends on the initial vacuum of the container, where the amount of oxygen is proportional to the type of product.

Blueberries showed a two-fold vacuum increase after six months storage. It could be explained by the fact that blueberries during still processing as Gallop (19, p. 112) reported that: "The natural cuticle wax melted off the fruits and subsequently deposited during cooling as a white scum in the headspace region and wherever berries were in a contact with the can." The wax deposition plays probably a protective role and retarded hydrogen swelling.

Hartwell (32, p. 377) pointed out that corrosion problems at tin plate containers are associated with two factors, the product and how it is handled and the container itself. In the chapter of mechanism of corrosion (32, p. 335) he writes:

> Typically, if all conditions are satisfactory, vacuum losses during storage of cans tend to be relatively small until the point is reached where a great part of the protective influence of tin is lost, whereupon hydrogen evolution from the steel commences at an accelerating rate.

Livingston, et al. (62, p. 116-120) found that headspace oxygen appears to be an essential reactant in the formation of the surface darkening "ring discoloration." This darkening was entirely prevented by the elimination of oxygen from the headspace.

Livingston's results are in agreement with our observations in blackberry cans after six months storage which showed the berries on top darker than the rest, Figure 27 and in raspberries, one months storage, Figure 26, which showed a dark surface layer.

SUMMARY

Chemical and physical changes taking place in berry fruits prepared and stored under similar conditions were studied from the point of diffusion and distribution of the constituents in the can.

The present work was planned to study characteristic behaviors of four different kinds of berries for some of the commonly occurring substances in fruits as sugars, acids, and pigments.

Structure differences between the berries gave the most characteristic results in diffusivity ability of the constituents as is further indicated.

1. The distribution patterns of sugars for strawberries, raspberries, and blackberries were similar in nature. There was a decrease in the percent soluble solids immediately after processing. This was more pronounced in the case of blackberries. In case of blueberries the variation in the sugars with the position in the can and storage time was of much less magnitude. However, all four berries show an initial difference in the percent soluble solids between the can top and bottom. A gradual increase was observed in the amount of sugars as the bottom of the can is approached. With storage this difference minimizes and approaches an equilibrium condition at the end of six months storage at 78° F.

There was no appreciable difference between the samples taken from the center and the side of the can.

2. An increase in the titratable acidity of the syrup was observed, immediately after processing and also upon further storage at 78° F.

In the case of strawberries and blueberries the titratable acidity was observed to reach a near equilibrium state in the can at the end of six months storage, whereas in the case of raspberries and blackberries difference between the titratable acidity content at the top to the bottom was still evident at the end of six months.

Little difference in acidity patterns was observed between samples taken from center and the side of the can.

3. pH changes were noticed to be characteristic of the berries. In the case of raspberries, blackberries and blueberries, there was an increase in pH values of the syrup immediately after processing, where as in strawberries the increase was slight. In all four berry packs the top samples were more acidic than the bottom ones when the berries were not processed and also immediately after processing. However, upon further storage this difference between the top and bottom samples decreased and at the end of six months of storage a tendency to reach an equilibrium throughout the can was observed.

There was no noticeable difference in the pH distribution patterns of the samples analyzed from the center and the side of the can.

4. An increase in the amount of pigments of the syrup was observed upon processing and subsequent storage at 78° F as measured by the optical density. However, in the case of strawberries and raspberries, there was a tendency for the pigments to reach an equilibrium and then decrease. The pigment concentration in these two berries was lower at the end of six months storage than the unprocessed berries, indicating a degradation of the pigments.

In the case of blackberries the amount of pigments in the syrup increased with processing and storage and was highest at the end of six months storage and there was little tendency of reaching an equilibrium in six months. In most cases samples obtained from the top position of the can showed the maximum concentration of pigments with the bottom samples having the lowest.

No pigments diffused from the berries to the syrup in unprocessed blueberries. However, upon processing pigments showed up in the syrup and increased at the end of one months storage. Upon further storage up to six months, the concentration of pigments decreased and the diffusion pattern seemed to reverse from that of one month; that is, at the end of one month, bottom samples showed the lowest concentration whereas at the end of six months it had the highest concentration of pigments.

No noticeable differences in the pattern of pigment diffusion was observed between samples collected from the center and the side of the can.

5. An initial decrease in the texture of strawberries, raspberries and blueberries was observed as a consequence of processing and storage. In case of blackberries a slight increase was observed for samples from top and bottom locations with the middle region showing a decrease. Upon subsequent storage there was a gradual softening of fruits in case of strawberries, blackberries and blueberries. The softening was very slight in the case of raspberries, where an actual firming up was observed at the end of six months as compared to the one month storage. All the top, middle and bottom samples of the four berries showed similar patterns.

6. All berries were shrunken after syrup addition becoming more pronounced upon processing. The degree of shrinkages was characteristic for each berry.

A lower drained weight compared with the fill weight was observed. An increase in drained weight was realized after six months of storage.

Blueberries showed a slight decrease after processing, but after a month of storage they gained their weight at the point of the unprocessed control.

7. An increase in vacuum readings of the cans appeared after processing and during storage. In the case of blueberries, the vacuum was twice as high after six months of storage than at the packing period.

CONCLUSIONS

1. Immediately following processing, there was a decrease in the percent soluble solids and an increase in the amount of pigments in the syrup of all four berries. Diffusion of sugars neared equilibrium at the end of six months storage. The pigments in the case of strawberries and raspberries behaved similarly but did not reach an equilibrium in the case of blackberries and raspberries.
2. There was an increase in the titratable acidity of the syrup immediately after processing which continued to increase upon storage. Equilibrium was almost reached in the can at the end of six months in the case of strawberries and blueberries. Lower pH values were obtained in the syrup following processing which further decreased upon storage without obtaining any equilibrium in the packs of blackberries and raspberries.
3. An increase in the drained weights of strawberries, raspberries, blackberries was obtained at the end of six months. In the case of blueberries there was an initial slight decrease up to one month followed by an increase at the end of six months. Immediately after processing there was a softening of all the fruits except blackberries. All the four berries progressively softened with storage.

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