COLOR CHANGES IN BERRIES DURING PROCESSING AND STORAGE

by

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INTRODUCTION

The color of a food product is of prime importance because of its effect upon consumer preference and because of the fact that color is associated in many cases with the quality of the food. The color has an effect on consumer preference even when it does not reflect other desirable qualities. In many cases the color can be used as a quality index; i.e., it is an index of maturity in fruits and vegetables and freshness in meat.

The color is equally important in canned fruits and vegetables, as it is in the fresh products. There are two sources of color change in preserved fruits: the heat processing itself, and the storage of the product to the time of consumption. The coloring materials suffer a degradation during the heat processing where a relatively significant portion of anthocyanins is destroyed and brown material is created. The degree of this loss depends upon the temperature of the treatment, the duration of the process, the presence of traces of copper or

iron ions and, perhaps, other chemical components of the fruit.

Metal ions increase the rate of anthocyanin degradation. On the contrary some other substances such as lyophilic colloids have a protective effect upon the anthocyanin pigments.

The second source of pigment loss is the change which takes place during the storage of the product. The rate of this destruction depends upon the temperature of the storage, the lower the temperature the less the loss of the pigment. At low storage temperatures the loss is negligible.

The main pigments of the berries belong to the group of natural pigments known as anthocyanins. Strawberry, raspberry, blueberry and blackberry do not have the same anthocyanin as the major pigment. A great deal of research has been carried on to determine causes for, and to develop methods of preventing changes of color in fruits. Some of these studies have been made in model systems and some in actual systems at various temperatures. The object of this study was to evaluate color changes in strawberries, raspberries, blueberries and

blackberries during the storage at 100° F. in glass and tin containers.

LITERATURE REVIEW

A. Strawberry

(1) Nature of the Pigments

Pelargonidin-3-monoglucoside is the main pigment of the strawberry (61, p 648; 63, p 3476; 54, p 1650-1664). Besides this pigment, cyanidin-3-glucoside, kaempferol and quercetin have been identified in this fruit (40, p 790). The strawberry is a comparatively poor source of anthocyanin, containing only 300-400 mg per kg of berries (63, p 3476).

The pelargonidin-3-glucoside has been identified in strawberries by Robinson and Robinson (54, p 1663). Robinson found pelargonidin-3-galactoside in wild strawberries (Fragazia vesca). Sondheimer and Kertesz (62, p 245-248) developed a method for the isolation and purification of crystalline anthocyanin from cultivated strawberry varieties (63, p 3476).

The red pigment of strawberry and strawberry products is unstable in heating and storage and many factors can affect the rate at which this pigment degrades (37,

p 180; 29, p 106). These factors are:

(a) Cooking time and temperature.

(b) Storage time and temperature.

(c) Nature of sugar in the preserves.

(d) Concentration and nature of carboxylic acids.

(e) Presence of ascorbic acid.

(f) Nature of headspace gas.

The pigment determination constitutes an inadequate measure of actual color change, since other factors, such as the formation of brown pigments and metal induced discoloration, take place concurrently with storage losses in anthocyanin pigment.

(2) Method of Pigment Determination

The amount of red anthocyanin pigment in strawberry products can be quantitatively determined by the method developed by Sondheimer and Kertesz (62, p 245). This method consists in the measuring of the light absorption in extracts made therefrom at 500 mu at pH 3.40 and 2.00. The measurement consists of subtracting the absorption at 500 mu of an anthocyanin solution at pH 3.4 from its

absorption at pH 2.00. The increase in color intensity is proportional to the concentration of anthocyanin in the solution (62, p 246). The pH of the medium strongly affects the light absorption of anthocyanin (55, p 7). The predominant effect of increasing hydrogen ion activity on the spectral properties of pelargoindin-3-monoglucoside is an increase in the intensity of absorption in the visible region (60, p 1507).

Anthocyanins are amphoteric substances which form oxonium salts with mineral and organic acids (27, p 562). It is highly probable that in neutral or nearly neutral solutions the pigment exists in the free state and upon acidification the equilibrium between the color base and the oxonium salt is shifted, resulting in a molecule of higher resonance and therefore, exhibit greater light absorption (60, p 1507; 5, p 358).

The hydrolysis reaction may be shown as:

$$R^{+} + HOH \quad = \quad ROH + H_3O^{+}$$

The pK is calculated as : (70, p 116):

$$pK = \log \frac{R^{+}}{ROH} + pH$$

For the pH range in which the R^{+} concentration

varies between 98.4 and 10.8 percent, the pK is constant within the experimental error and equal to 2.98 at 25° C. (60, p 1507).

(3) Degradation of the Pigment

As for the effect of cooking time and temperature, Decereau et al. (12, p 126) obtained an excellent correlation between thermal treatment, expressed as "temperature summation" i.e., degrees Fahrenheit above a base temperature multiplied by minutes at each temperature and pigment loss or brightness of the product. The pigment loss or reduction in brightness varies with processing temperatures as well as with the temperature summation. Assuming that heating is necessary to prevent only microbiological spoilage in a strawberry product containing an organism having the thermal death time characteristics of the penicillium described by Williams et al. (72, p 69) the highest level of pigment retention would be obtained by the use of a short-time-high-temperature treatment. (8, p 126).

Markakis et al. (46, p 118) have studied the kinetics of degradation of pelargonidin-3-monoglucoside in

buffer solutions, at pH 2.0 and 3.4 under exclusion of oxygen and in a temperature range from 45° C. (113° F.) to 110° C. (230° F.). First order reaction rates and straight thermal destruction time lines were obtained (46, p 128).

Decereau et al. (12, p 127) studied the effect of storage at 100° F. on strawberry jellies and found the extent of pigment loss. The retention of the anthocyanin was 26 percent after 19 days of storage. Visually, the onset of browning tended to mask what little differences existed in color due to the anthocyanin present.

Ascorbic acid has a significant effect on the rate of degradation of pelargonidin-3-monoglucoside and this effect has been studied in model systems (52, p 367; 4, p 395; 50, p 1; 65, p 475).

Pederson, Beattie and Stotz (50, p 1) observed parallel losses of ascorbic acid and anthocyanin during storage. The best correlation between ascorbic acid and red color losses was obtained with strawberry juice. Pederson and coworkers (50, p 1) postulated that an interaction between ascorbic acid and anthocyanin pigment

may occur.

Sondheimer and Kertesz (65, p 476) have demonstrated that the accelerating effect of the ascorbic acid on the rate of pigment breakdown is associated with the oxidation of the ascorbic acid. That the color loss is related to the rate of ascorbic acid oxidation was demonstrated in two ways.

(1) In anaerobic systems the anthocyanin loss was not significantly different from that observed in aerated solutions containing no ascorbic acid. Therefore, when lack of oxygen is inhibiting the ascorbic acid oxidation, no demonstrable anthocyanin deterioration can be attributed to the ascorbic acid.

(2) Thiourea is a metal complexing agent which has been used to decrease the rate of cupric-ion catalyzed, aerobic oxidation of ascorbic acid. Thiourea in the absence of ascorbic acid has no demonstrable effect on the rate of pigment destruction.

The transient presence of hydrogen peroxide in strawberry products is a distinct possibility (64, p 288) and therefore, the loss of some of the strawberry anthocyanin pigments through reaction with this

hydrogen peroxide is a reasonable assumption. There are a number of reactions which may give rise to hydrogen peroxide in strawberry products. It is known, for instance, that in the presence of oxygen and cupric ions the oxidation of ascorbic acid to dehydroascorbic acid is accompanied by the formation of hydrogen peroxide (64, p 288).

Headspace (65, p 478) has an undesirable effect on the red pigments of strawberry juice. The color loss is not due to a direct oxidation of the pigment by air since pelargonidin-3-monoglucoside is fairly stable at a pH of 3.4 when shaken with air. It is likely that the harmful effect of headspace on color stability in strawberry juice may be attributed largely to the oxidation of ascorbic acid.

Meschter (48, p 575) has observed the rate of pigment degradation in the presence of different sugars at 38° C. Sugars such as arabinose, levulose and sorbose which are relatively labile, produced a higher rate of pigment degradation than more stable sugars such as maltose and sorbitol. Sugar degradation products, 5-hydroxymethyl-furfural and furfural, also

increased the rate of degradation (48, p 578; 46, p 119). Further work in model systems by Mackinney, Lukton and Chichester (45, p 326) showed fructose to be more active than sucrose. These workers also demonstrated an added effect in a sugar amino acid system which was presumably due to the interaction of the sugar and amino acid (45, p 326). Decereau, Livingston and Fellers (12, p 126) have made some observations on the rate of loss of pigments in strawberry jellies. Contrary to expectation, replacement of sucrose by fructose increased the half-life of the pigment. Some work by Aref, Sidwell and Litwiller (2, p 294) indicated sugars could have some effect on the color of frozen strawberries.

Lukton, Chichester and Mackinney (41, p 428) have shown that the pigment is more stable at lower pH and that there is an increase of decolorizing activity with increase in pH in the range 3.0 to 4.5 (67, p 53). The percentage of pigment existing in the R^+ form is a function of pH and the rate constant of degradation is proportional to the percentage of R^+.

The effect of different chemical substances on the

strawberry pigment has been studied. Sondheimer and Kertesz (64, p 289) found that the addition of hydrogen peroxide to strawberry juice causes a decrease in the red color by a reaction which has the characteristics of the ferrous-ion catalyzed, anthocyanin-hydrogen peroxide reaction in the artificial mixture. Markakis et al. (46, p 119) observed that thiourea has a protective effect on both strawberry juice and buffered pigment solution. Propyl gallate and quercetin show a slight protective effect on the color of both juice and pigment solution. Decereau et al. (12, p 127) reported that several additives were tested for their effect on the rate of pigment destruction in processing. Their effectiveness was determined by heating jellies containing these additives at several bath temperatures, drawing samples at different time intervals and analyzing them for the anthocyanin pigment. From the data obtained, the half-life of the pigment under each set of conditions was determined by using the regression equation:

$$\log Y = \bar{Y} + b\,(x - \bar{x})$$

Where $\bar{x}$ is the mean of the exposure time in hours, $\bar{Y}$ is

the mean of the logarithm of the percent pigment retention, b is the slope of the regression line and x is the half-life value obtained by giving Y the value of 50 percent. The results are summarized in the following table.

TABLE 1

The effect of heating temperatures and additives on the half-life of pelargonidin-3-monoglucoside in processing (12, p 127)

Additive	Half-life in hours at 200° F.	220° F.	240° F.
None	1.38	0.73	0.28
Kojic acid (0.05%)	1.59	0.75	0.26
Quercetin (0.076%)	1.71	0.65	0.26
Rutin (1.0%)	1.66	0.76	0.31
Sequestrene (0.076%)	1.32	0.67	0.23
Thiourea (0.076%)	1.49	0.67	0.28

The principal breakdown products of the pigment in oxygen are an insoluble red-brown precipitate and a soluble brown material. In nitrogen only minute amounts of red-brown precipitate are formed for equivalent pigment losses, according to Lukton, Chichester and MacKinney (41, p 427). The soluble breakdown products absorb at 440 mu and the pigment itself at 500 mu. The

optical density of the pigment at 500 mu was calculated from the following equations (41, p 428; 70, p 120) which take into account the absorbance of pigment breakdown products.

$$D^{500} = D_B^{500} + D_p^{500}$$

$$D^{440} = 0.48\ D_p^{500} + 2.3\ D_B^{500}$$

Where D_p is the optical density of the pigment and D_B is that of the breakdown products. The value 0.48 is the ratio of absorption of the pigment at 500 mu to that at 440 mu at pH 1.25 and 2.70. However, at pH 3.25, 3.85 and 4.50 the ratios are 0.49, 0.57 and 0.69 respectively. The ratio of absorption at 440 and that at 500 mu of the breakdown products was determined from the absorption spectrum of the brown soluble material which had been separated and characterized by paper chromatography. So the change in pigment concentration can be calculated by solving the simultaneous equations for D_p^{500}.

Lukton et al. (41, p 429) found that the ratio of the absorption at 440 to that at 500 mu increased with time, approaching 2.3 as the pigment was completely destroyed. The absolute absorption at 500 mu decreased

with time.

It is not known how the brown material is formed in strawberry products. Hodge (21, p 928) reviewed the browning reactions in 1953. Three broad types of browning reactions were recognized:

(1) Carbonyl-amino reactions: This type includes the reactions of aldehydes, ketones and reducing sugars with amines, amino acids, peptides and proteins.

(2) Caramelization: It occurs when polyhydroxy carbonyl compounds (sugars, polyhydroxycarboxylic acids) are heated to relatively high temperatures in the absence of amino compounds. This type of browning characteristically requires more energy to get started than the carbonyl-amino reactions, other conditions being equal. Neither carbonyl-amino nor caramelization reactions are dependent upon the presence of oxygen to produce browning.

(3) A third broad type of browning frequently encountered by the food processor is the group of oxidative reactions, which for example, convert ascorbic acid and polyphenols into di- or polycarbonyl

compounds.

These three types of browning reactions are non-enzymatic (44, p 302). In the case of strawberry there are at least two possible pathways of formation of the red-brown precipitate. One is the conversion or polymerization of the pseudobase of the pigments to the red-brown precipitate (6, p 1573). The other is the hydrolysis of the pseudobase to the aglucone with subsequent conversion directly or through intermediates to the red-brown precipitate.

In both cases the brown pigment may arise from the glucose (20, p 667), the red-brown precipitate and from colorless breakdown products (58, p 517; 41, p 592). The formation of the red-brown precipitate from the aglucone is unlikely since no precipitate was observed when the aglucone was discolorized in solution. It follows, then, that the precipitate must be formed from the pseudobase of the oxonium salt of the glucoside, or possibly from both.

Mackinney, Lukton and Chichester (45, p 326) reported that one may consistently observe a linear relation between pigment loss (in mg/100 g preserve) and

browning (increase in optical density at 440 mu). The brown product arises either concomitantly with, or as a direct result of pigment degradation.

In strawberry juice there is an initial increase in browning not accompanied by a pigment loss. Subsequent to this loss which amounts to about 20 percent of the total browning (i.e., the total amount formed by the time most of the pigment has been destroyed) the ratio of pigment to browning becomes constant (45, p 325).

Because of the formation of the red-brown precipitate and the brown soluble pigment, the amount of the anthocyanin alone is no criterion of an acceptable color. The brightness of the product must be taken into account. This measurement can be done by using the Hunter Color and Color-Difference Meter (26, p 261). One may calculate hue, value, chroma and the chromaticity coordinates by using this instrument (11, p 536). The Hunter has two scales: L and R_D and gives three numbers for each color measurement. The use of either R_D (45^o - 0^o luminous reflectance) or L (visual lightness) depends upon the type of measuring circuit selected. The other two scales of the instrument measure "a" which is

redness when plus, gray when zero and greenness when minus and "b" which is yellowness when plus, gray when zero and blueness when minus. When using the R_D scale the a_L and b_L are slightly different from those measured in conjunction with L.

There are three different methods of presenting the sample to the instrument (66, p 14):

1. Spot reading: The sample is presented to the instrument in a polyethylene container. At different positions of the sample a set of readings are taken. The mean of these readings presents a reliable estimate of the sample.
2. Reading from rotation (57, p 666): These readings are obtained using the spinning attachment described by Sidwell and Cain (57, p 666). The sample is rotated above the window of the instrument at a rate sufficient to give a steady galvanometer reading.
3. Reading from blending: The sample is blended for 30 seconds in a Waring Blendor and then deaerated for 15 minutes using a water aspirator.

It has been shown in tomato juice that the ratio,

a/b, correlates with dominant wavelength and the function $(a^2 + b^2)^{\frac{1}{2}}$ represents saturation or chromaticity. "Dominant wavelength" is the wavelength of the spectrum light that, when combined in suitable proportions with the achromatic light, as daylight, yields a match with the light considered. The ratio of the amount of the spectrum light used, to the sum of the spectrum light and the achromatic light is called percent purity (26, p 281).

A rapid method for the measurement of red color in strawberries with the Hunter Color-Difference Meter using the R_D circuit was described by Hoover et al. (23, p 10). The relative color score of berries is determined by the formula

$$Y = \text{antilog } 0.40239/0.03125X$$

Where X represents the "a" value of the color meter. The formula is an expression of the response of the Hunter Color-Difference meter to different concentration of Congo Red ranging from 10 to 50 ppm when dispersed in a suspension of sugar, agar and MgO. From the L, a_L and b_L we can calculate the tri-stimulus values X, Y and Z by means of the formulas (26, p 282).

$$Y = \frac{L^2}{10000}$$

$$X = \frac{(0.5602 \times a_L) + (0.9804 \times L) \times L}{10000}$$

$$Z = \frac{(1.181 \times L - 1.687 \times b_L) \times L}{10000}$$

The tristimulus values of a light are the amounts of the three reference primary colors required to give by additive combination a match with the light considered. The tristimulus values are usually expressed as chromaticity coordinates, "x," "y" and "z," which are the ratio of each tristimulus value of the light to their sum, i.e., "x" = $\frac{X}{X + Y + Z}$. From these values and using a chromaticity diagram one can specify a color in terms of dominant wavelength and percent purity. The tristimulus values are based on a system of color specification adopted by the "International Commission on Illumination" in 1931. This system of color specification is generally referred to as the I.C.I. or C.I.E. system of color notation (10, p 354).

In the case of strawberry products MacKinney and Chichester (43, p 13) first pointed out that the anthocyanins were an inadequate measure of actual color

change, since other factors, such as the formation of brown pigments and metal-induced discoloration take place concurrently with storage losses in anthocyanin pigment. These authors suggested that the attractive color of strawberry preserves is rather more closely related to the brightness of the product, a measurable colorimetric dimension corresponding to the tristimulus Y value of the C.I.E. color solid, or the R_D or L values of the Hunter system.

Decereau et al. (12, p 127) used the Y value as a measure of desirable color in strawberry jellies and obtained excellent correlations between brightness values and temperature summations. These authors used the Beckman DU spectrophotometer, equipped with a reflectance attachment. Jelly samples were placed in a shallow, white enameled cuvette measuring 40 mm in diameter and 9 mm in depth, which was covered by a glass slide to present a reproducible sample thickness. C.I.E. brightness was calculated from the spectual reflectance data by means of the selected ordinate method.

In a study of Livingston et al. (38, p 303) four tristimulus colorimeters, the photovolt, Model 610

Reflection Meter, the Hunter Color Difference Meter, the Model C Color Eye and the Color Master Differential Colorimeter were evaluated for their ability to provide color data which could be significantly correlated to visual ratings, pigment contents and browning measurements. According to these authors the Hunter a_L values correlate significantly with visual scores and pigment contents. Hunter b_L values correlate with pigment content but not with visual scores. Visual scores were obtained by combination of ranking and acceptability tests carried out by twenty judges.

Aref, Sidwell and Litwiller (2, p 293) used the Hunter Color Difference Meter to determine whether or not the addition of various sweeteners to strawberries before freezing would affect the fruit differently with respect to quality characteristics. The color was measured by using the L scale. The sample was placed in a circular, transparent, clear plastic dish and four spot readings were taken at random. The Hunter L readings and the dominant wavelength after three months of storage were significantly different due to

lots, treatments and sweeteners, while the purity values were significantly different due to lots only. After six months of storage the Hunter L readings were significantly different due to lots, treatments and sweeteners.

Guadagni, Nimmo and Jansen (16, p 389; 17, p 306) found that the major color changes in frozen strawberries were represented best by changes in the Hunter a_L value. The decrease in a_L value was essentially linear for all temperatures from 0° F. to 25° F. and the rate of decrease varied logarithmically with increasing temperatures.

In studying methods for presenting raspberry and strawberry samples to the Hunter Color and Color Difference Meter, Tinsley (66, p 39) concluded that in sliced strawberries, the A.M.S. score for color increased fairly regularly with the appropriate change in brightness up to a certain point. There was a tendency to rate samples higher with a higher L value, until a critical value was attained after which the rating fell off rapidly with increase in Hunter L.

B. Raspberry

Guadagni and Nimmo (15, p 633) in a study of the effect of time and temperature on color distribution of frozen raspberries (56, p 121) found that maximum absorption occurred at approximately 513 mu. The effect of pH on the absorption of raspberry pigment is similar to that reported by Sondheimer and Kertesz (63, p 3476) for the anthocyanin pigment in strawberry. Storage at 30° F. for two weeks does not cause any shift in the characteristic absorption spectra of fresh frozen raspberries but merely causes a certain amount of pigment transfer from berries to syrup. The extent of pigment transfer depends on the original pigment concentration in the berries and the time and temperature of storage. At 0° F. only a slight increase in the color of the syrup had occurred after one year of storage.

The pH of the medium and the gas of the headspace have an influence on the pigment destruction in canned raspberries, as in the strawberry. Harib et al. (19, p 482) canned raspberry and strawberry fruits at pH

values of 3.5, 5.5, 7.5 and 8.5, with or without air in the headspace, and the effects on color were measured by spectrophotometric determinates on extracted anthocyanins and by determination with the Hunter Color Difference Meter on homogenized samples of the products. Destruction of red pigments and change of color to purple and finally to greyish-blue, increased with rise of pH and with the presence of air. The red color in fresh products was shown chromatographically, by these authors, to be due to four components in raspberries and five in strawberries.

W. H. Case (8, p 16) reported another study of the effect of storage on raspberry and strawberry pigments. Canned raspberries and strawberries and raspberry jams were stored at -20° F., 70° F. and 100° F. Decrease in color at -20° F. was very slow for nine months (33, p 9). At 70° F. about one-half of the pigment was lost in one month and all in twelve months. At 100° F. two-thirds of the pigment was lost in one month.

Kitson (32, p 16) studied the effect of temperature and length of storage on berry pie fillings. Frozen strawberries were cooked, filled into pint sealers with

glass tops and the containers were sealed, inverted and cooled in air and the products were stored at different temperatures from 32° to 100° F. The color of the products was examined by reflectance measurements. After one month at 100° F. the pie fillings became dark brown and wholly unacceptable. Loss of the desirable red color was associated with a shift towards a shorter dominant wavelength and a decrease in percent spectral purity.

It is known that colloids help improve the quality of frozen raspberries. The principal objection to frozen raspberries is that when thawed the raspberry fruit tends to break down, releasing an excess of free liquid (34, p 51). Colloidal materials such as pectin and plant gums have been of value in improving the quality of frozen fruit. When such agents are used there is a considerable increase in the drained weight of the fruit and in the color. Barton (3, p 50) dissolved the colloidal agents in 50 percent syrup. The agents were: (1) gum tragacanth, (2) 150 grade high-methoxyl pectin, (3) 320 grade low-methoxyl pectin. A photovolt reflectionmeter was used for color

measurement. The added colloids were effective in retaining the color in both red and purple raspberries.

C. Blackberry

Karrer and Pieper (28, p 519) found that the pigment of the blackberry consists of a monoglucoside of a cyanidin either identical to, or an isomer of, chrysanthin or asterin in asters and chrysanthemums. The identity of the pigment with chrysanthemin required it to be a b-glucoside.

The major isolated pigment of blackberry showed all the color properties and reactions attributed to chrysanthemin-chloride (23, p 142).

D. Blueberry

The anthocyanin can be extracted (1, p 2; 73, p 387; 9, p 1) from the dried fruit and adjusted to a fixed pH. The anthocyanin absorbs at 500 mu. As the color of the juice becomes a beautiful rose color by acids, Watson (69, p 246) proposed that the juice of this berry could be used as an indicator in volumetric

analysis.

Brody, A. L., et al. (7, p 367) stored commercially packed blueberry pie filling in No. 2 cans at two different temperatures, 34°-36° F. and 75°-78° F. Colorimeter readings showed a slightly more blue hue in the low temperature samples than in the high temperatures at two months.

MATERIALS AND METHODS

Raw Material

The purpose of this experimental work was the investigation of the influence of the process and subsequent storage at 100° F. upon the absorption spectrum of the pigments of strawberries, raspberries, blackberries and blueberries and the study of the L, a_L and b_L values of the Hunter Color Meter.

The Northwest strawberry, the Willamette raspberry, the Marion blackberry and the Jersey blueberry were used. The fruits were selected to have the average physical properties which can be found in commercial packs. These fruits were obtained from the University farm and precooled overnight at 35° F., before processing. The berries were mixed, washed and trimmed to remove any dirt or blemished berries in a McLauchlan vibratory washer and drained on 8-mesh stainless steel trays before hand filling into cans or jars. Very small or very large fruits were removed during this operation.

Containers

Fruit enamel cans (303 x 406) and Duraglass 303 jars were used in these experiments for the canning of the berries. The fruits used for the first replication of the cans and jars were taken from the same lot. The same is true for the fruit used for the second replication.

Preparation for Processing

Cans and jars were weighed individually and 300 grams of washed berries and 182 grams of 60° Brix syrup at 170° F. were filled in the container. Before syruping, each can or jar was held at 25 inches vacuum for one minute in a manually operated vacuum closing machine. The vacuum was released by filling with syrup at 170° F. The cans were steam flow closed at 20 inches vacuum. The jars were sealed with a steam sealer maintaining 20 inch vacuum.

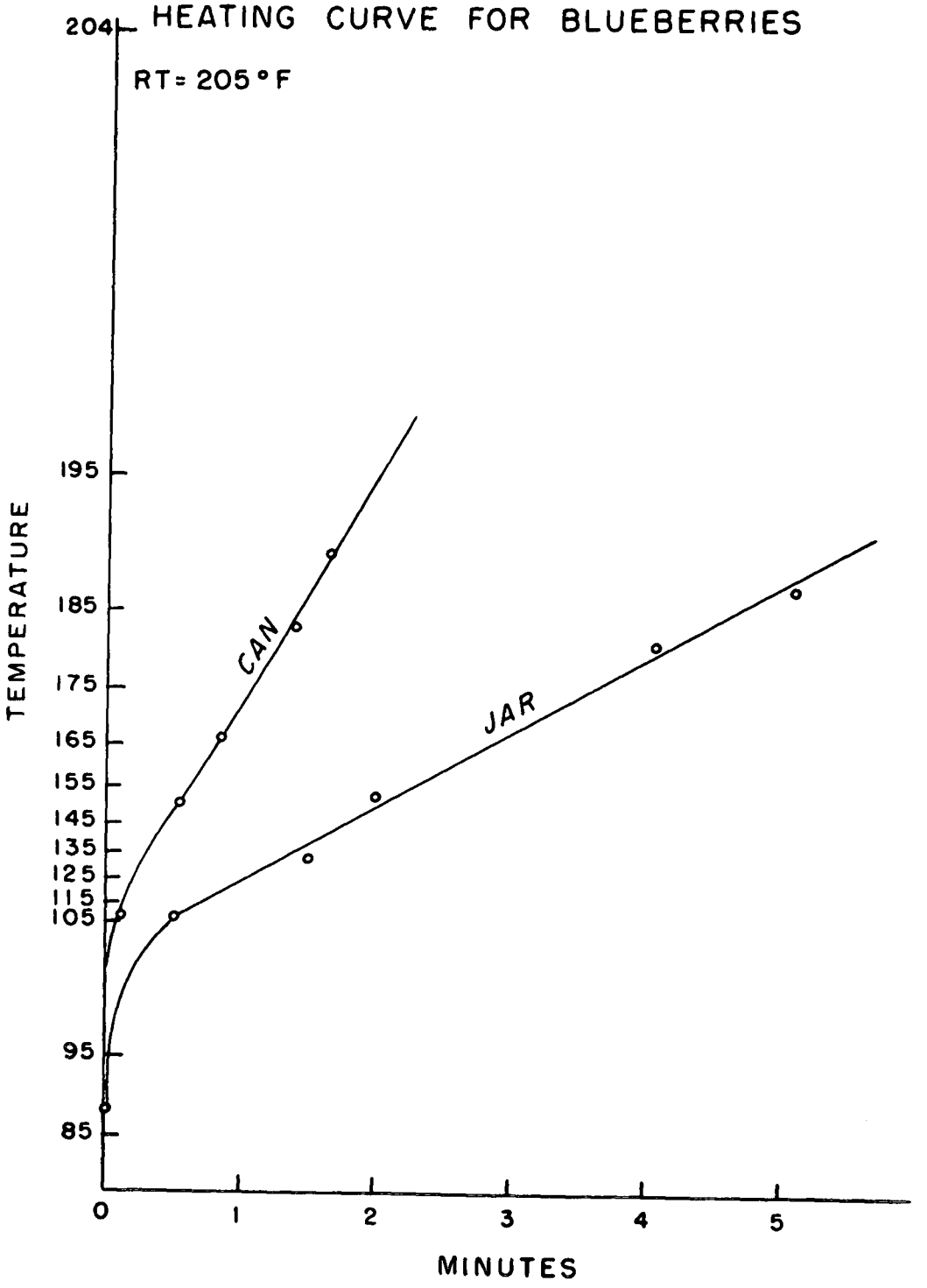
Heat Processing Method

The cans were spin-processed in a modified Roll-Thru machine, spinning the cans or jars with coaxial rotation. The speed used for the cans was 100 r.p.m., and the processing time was 5 minutes. The spin-cooking machine was preheated for 1 minute before the cans were processed. The heating curves for blueberries are shown in Fig. 1. The jars were cooked for the same time at the same speed, with the exception of the blueberries. In the case of the blueberries, because of released gas, a relatively high pressure was developed in the jars, and so the cooking time was reduced to 4 minutes. The cans and jars were cooled in the Roll-Thru machine with spraying water and stored at 100° F.

Product Examination Methods

Two replications of four samples, for each one of the four berry fruits examined, and for each of the two different containers were made. Analyses of samples were run immediately after processing, and after storage

Figure 1.


HEATING CURVE FOR BLUEBERRIES
RT= 205 °F
204
195
185
175
165
155
145
135
125
115
105
95
85
TEMPERATURE
CAN
JAR
0
1
2
3
4
5
MINUTES

times of 3, 7, 14, and 28 days. The following measurements were obtained for each sample: Vacuum, head space, drained weight, degrees Brix of the syrup, titratable acidity and pH of the syrup, Hunter Color Meter measurements and absorption spectra.

Vacuum readings were taken on cans or jars with a checked U. S. Gauge puncture gage, after cans or jars had cooled to approximately 25° C.

The gross headspace was measured with two small rulers as the distance between the top of the can double seam and the top of the product.

The procedure used for the determination of the drained weights was the U.S.D.A.-A.M.S. method for canned foods as described in the Almanac of the Canning Industries, edited by E. E. Judge, 1960 ed. (p 148-149).

The color study of the processed fruits was carried out by the use of the Hunter Color and Color Difference Meter for the study of color changes of the solids and by the use of the Beckman DK-1 spectrophotometer for the study of changes in the absorption spectra of the liquid taken from the cans or the jars.

Hunter Color and Color Difference Meter Measurements

These measurements were made by the spot reading method. The sample was presented to the instrument in a polyethylene plastic container, 6 inches in diameter and 1½ inches deep. Readings were taken at four different positions of the sample. The average of these readings was considered as the measurement. The sample consisted of the solid fruit taken from the cans or the jars. A small amount of liquid from the can or the jar was added to the plastic dish in order to fill the small spaces between the solid particles in the container.

The L scale was used in this experiment. In the case of strawberries, raspberries and blackberries the instrument was standardized against the National Bureau of Standards Standard "Panel 70 Red" having the following L scale values:

$$L = 29.2$$
$$a_L = 47.7$$
$$b_L = 17.7$$

In the case of blueberries the standard "Panel 45 Royal Blue" having the following L scale values was used for the standardization of the instrument:

$L = 22.1$
$a_L = 13.5$
$b_L = 43.4$

Absorption Spectra

An appropriate volume of the syrup taken from the cans or the jars was diluted with citrate buffer. The dilution factor for strawberries was 1:10, for the other fruits 1:25. The final pH of the buffer-diluted syrup was 3.4. The buffer was prepared by mixing 0.1N 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 1.0 N sodium hydroxide solution and diluting the mixture to one liter. The pH 3.4 was chosen because it was close to the pH of the liquid taken from the cans and the jars of the strawberries. The solution was filtered by means of a No. 4 Whatman filter paper. After holding the diluted liquid for one hour, the absorption spectrum from 700 mu to 400 mu was taken in a Beckman, Model DK-1, Spectrophotometer. The scanning time used was 30 minutes

corresponding to 1.2 mu per 1 mm distance on the chart. The cell used was a Beckman 1 cm absorption cell.

The cans and jars were stored at a constant temperature of 100° F. in the absence of light.

The "Camco Roll-Thru"[1] pasteurizer-cooler. This machine is a continuous unit in which the cans or jars are rolled through two ten-foot decks set beneath hot or cold water sprays. The containers are held within the pockets of a continuous moving link belt. Reversal of the direction of the can rotation takes place at each end of each deck. The cooker temperature was 205-207° F. for 5 minutes, except for the blueberries in glass, where the time was 4 minutes.

Heating rates of tin and glass containers.

The center temperatures of the containers were measured at appropriate time intervals by means of Ecklund thermocouples connected to a 16 point Brown Electronik Recorder. The containers were removed from the cooker during the temperature measurement. Plotted points (Figure 1) represent the time-temperature relationships of separate containers.

1. Manufactured by: Horvic Manuf. Co., Pittsburg, Pa.

RESULTS AND DISCUSSION

The methods described in the previous section were used for the analysis of the berry fruits processed and stored in tin or glass containers. The mean headspace in the cans and jars was 12/16 inches with a range of 4/16 inches. The average vacuum in the cans was 15 inches, range 2 inches, and in the jars, 21 inches, range 1.5 inches. The drained weight increased with the storage time in the case of strawberries, raspberries and blackberries. For blueberries there was a slight decrease. The average percent drained weight increase for strawberries for 28 days storage was 8.5 percent, for raspberries 7.7 percent, for blackberries 10 percent over the zero storage time. The decrease in the case of blueberries was 15 percent for the first replication and 2 percent for the second. As far as the color was concerned the following results were found.

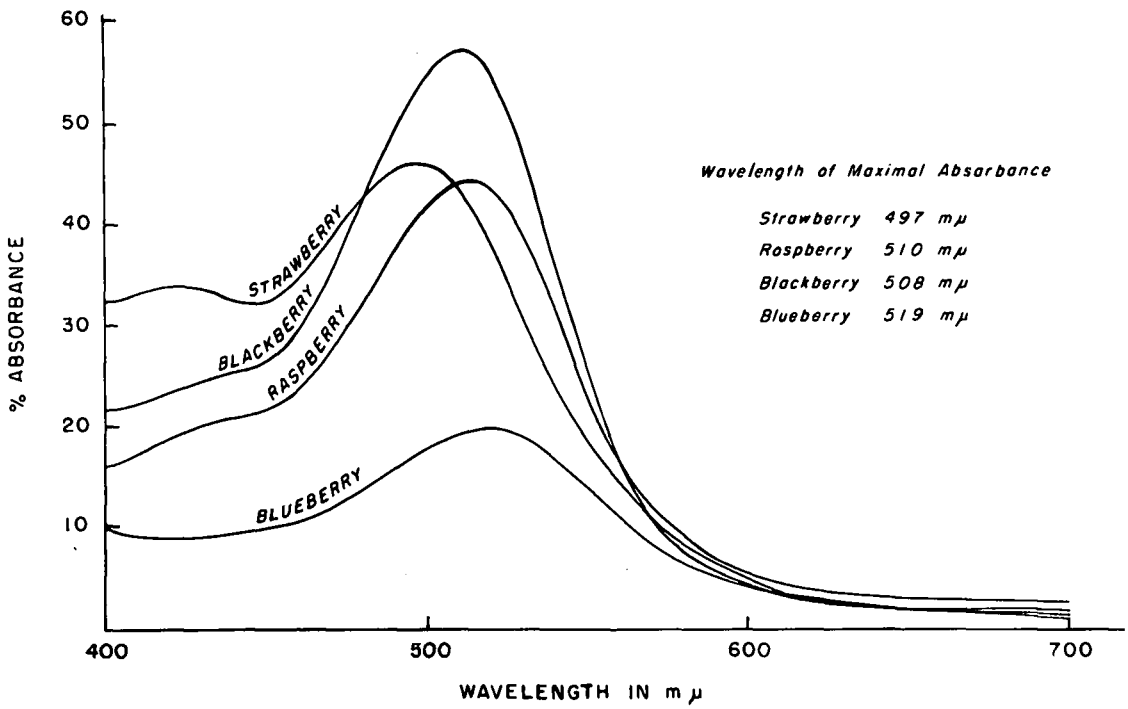
1. Northwest Strawberries

Absorption Spectrum

Liquid samples from the cans and the jars were diluted 1:10 with citrate buffer and the pH was adjusted to 3.4. The solution was filtered through a No. 4 filter paper. After that, the absorption spectrum was taken from 700 mu to 400 mu. In the case of the fresh fruit an appropriate amount of fresh fruit was mixed with citrate buffer in a Waring blender and the homogenized mixture was filtered and appropriately diluted to give a 1:10 solution of the original amount of the fruit. Two absorption peaks appeared in this region of the spectrum. These peaks corresponded to wavelengths 497 mu and 423 mu. The peak at 497 represented the absorption maximum of the spectrum in this region (Fig. 2). Between these two absorption peaks an absorption minimum appeared at wavelength 440 mu. The wavelengths of the peaks did not change with the storage time. The absorbance became less during the processing of the fruit and decreased during the storage period. The means of the absorbance at 497 mu and 440 mu calculated on the basis

Figure 2.

ABSORPTION SPECTRUM OF STRAWBERRY, RASPBERRY, BLACKBERRY AND BLUEBERRY PIGMENTS IMMEDIATELY AFTER PROCESSING



of four samples (dil 1:10, pH 3.4) are tabulated in Table 2.

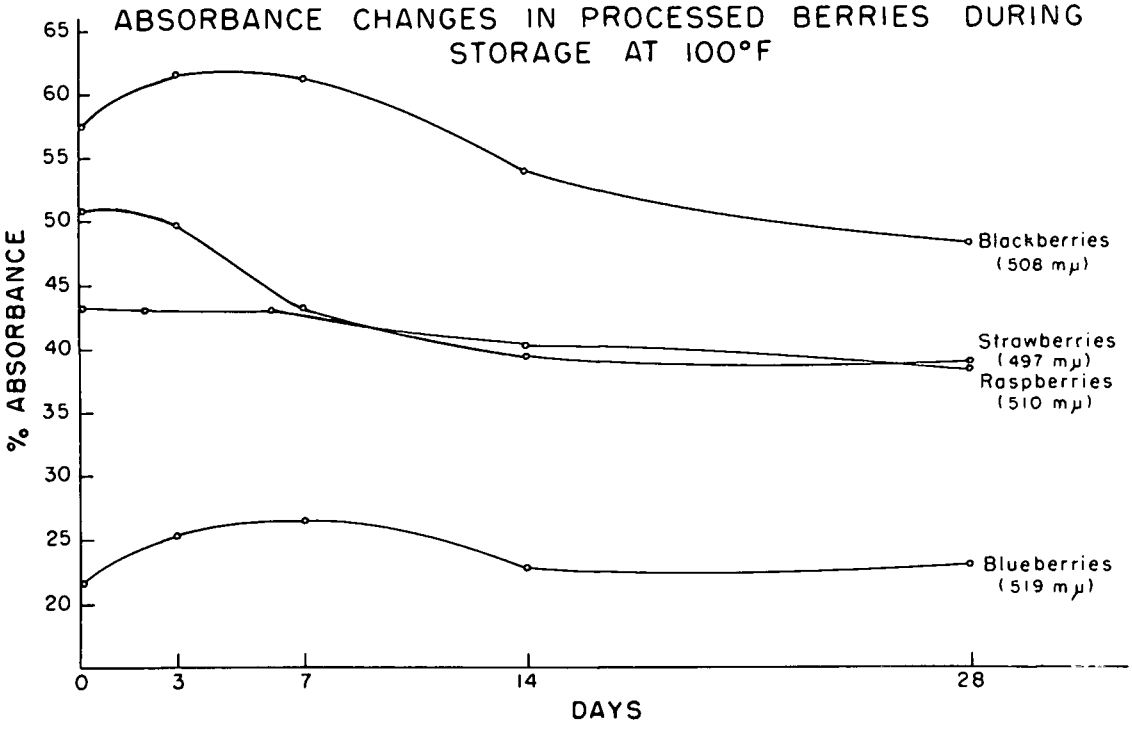
The absorbance of the fresh fruit of the first replication was 63.7% at 497 mu, and 38.0% at 440 mu. The ratio of these two values was 1.67. The absorbance of the fresh fruit of the second replication was 65.5% at 497 mu, 38.0% at 440 mu and the ratio of these two values, 1.72. The data tabulated in Table 2 shows that the absorbance at 497 mu decreased with processing and during storage (Fig. 3). The absorbance at this wavelength is due mainly to the anthocyanin pigments of the strawberry, which undergo degradation during processing and storage. Brown pigments, which are among the products of the degradation of the anthocyanin, absorb stronger at 440 mu than the anthocyanin pigments. For this reason the rate of decrease of the absorbance at 440 mu is less than the rate at 497 mu. The ratio of the absorbance at 497 mu over the absorbance at 440 mu decreased with the storage time. The decrease in this ratio between the different storage times was significant at the 5 percent level. The differences between the peak absorbances at different times of storage were

Table 2

Absorbance Means at 497 mu and 440 mu of Processed Strawberries

Days After Processing	% Absorbance At 497 mu	% Absorbance At 440 mu	Ratio 497/440 mu
	CANS		
	I REPLICATION		
0	50.6	30.3	1.67
3	49.8	33.5	1.48
7	43.1	30.9	1.41
14	39.3	29.8	1.32
28	38.7	30.7	1.26
	II REPLICATION		
0	55.93	32.53	1.72
3	50.16	32.33	1.53
7	46.47	31.97	1.50
14	43.25	30.65	1.41
28	39.75	29.73	1.33
	JARS		
	I REPLICATION		
0	52.9	31.7	1.67
3	52.3	33.9	1.54
7	45.9	31.6	1.45
14	41.6	31.2	1.33
28	39.0	30.0	1.30
	II REPLICATION		
0	55.90	33.0	1.69
3	48.97	31.0	1.58
7	49.10	32.67	1.50
14	45.93	32.83	1.40
28	41.85	30.12	1.38

Figure 3.


ABSORBANCE CHANGES IN PROCESSED BERRIES DURING STORAGE AT 100°F
% ABSORBANCE
65
60
55
50
45
40
35
30
25
20
0
3
7
14
28
DAYS
Blackberries (508 mμ)
Strawberries (497 mμ)
Raspberries (510 mμ)
Blueberries (519 mμ)

significant as found by statistical analyses of this factorial experiment. The F value for the difference between tin and glass was 3.4 with 1 and 30 degrees of freedom. The 5 percent critical region was beyond 4.1709. The error was 1.12 with 30 degrees of freedom. The F value for the hypothesis that there was no difference in the absorbance with the storage time was 6.7 with 4 and 30 degrees of freedom and the critical region beyond 2.6896. The error was 1.120 with 30 degrees of freedom.

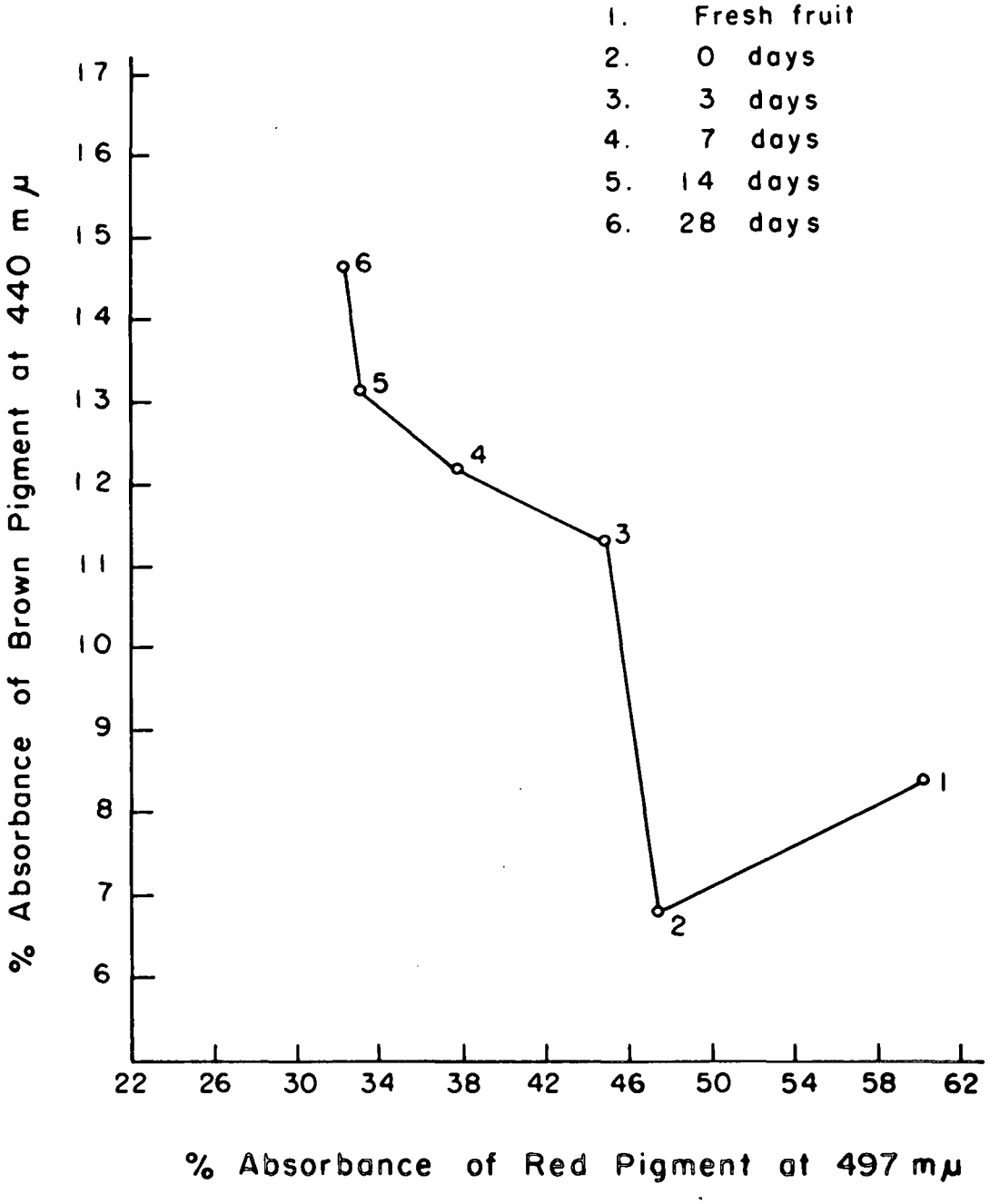
The plot of the absorbance or the ratio of the absorbances at 497 and 440 mu as a function of time did not give a straight line relationship. A logarithmic plot of the absorbance versus time did not give a straight line relationship. This does not mean that the anthocyanin degradation does not follow first-order reaction, because the absorbance is not due solely to the anthocyanin pigments. Brown products of the anthocyanin degradation interfere with the absorbance of the anthocyanin at these wavelengths.

Even after separating the absorption of the brown pigment from that of the anthocyanin pigment, the

anthocyanin degradation did not follow a first-order reaction in this experiment. This is probably due to the fact that parallel reactions were taking place in this system. The oxidation of the ascorbic acid has been reported to have an accelerating effect upon the pigment breakdown (65, p 476). The transient presence of hydrogen peroxide in strawberry products is a distinct possibility (64, p 288) and loss of some of the strawberry anthocyanin pigment through reaction with hydrogen peroxide is a reasonable assumption. Sugar degradation products, 5-hydroxy-methyl-furfural and furfural could increase the rate of degradation (48, p 578; 46, p 117). It is possible that some of these factors began to influence pigment degradation after some time of storage. For this reason the over-all reaction, which was observed in this experiment did not follow the first-order reaction. By using the equations proposed by Meschter (49, p 110; 41, p 428), the red pigments were separated from the brown pigment. The results are shown in Fig. 4. The values of the absorbance due to red pigment and that due to brown products do not give sufficient information for color evaluation

Figure 4.

COLOR CHANGES IN PROCESSED STRAWBERRIES DURING STORAGE AT 100° F



(49, p 114). Fig. 4 suggests that probably there was a formation of precursors of the brown pigment during the processing. These precursors were products of the degradation of the anthocyanin, which gave the brown pigments formed during storage.

Hunter Color Meter

The L, a_L and b_L scales of the Hunter Instrument were used for the determination of the color of the fruit solids taken from the cans or the jars. The data obtained from these measurements are tabulated in Table 3.

The fresh fruit of the first replication gave the following readings:

$$L = 20.7$$
$$a_L = 14.3$$
$$b_L = 8.5$$

The same readings obtained from fresh fruit of the second replication were:

$$L = 24.7$$
$$a_L = 18.1$$
$$b_L = 10.7$$

The readings of the three Hunter Instrument scales decreased as the storage time increased. The visual

Table 3

Mean Values of Hunter Color Meter Readings for Processed Strawberries

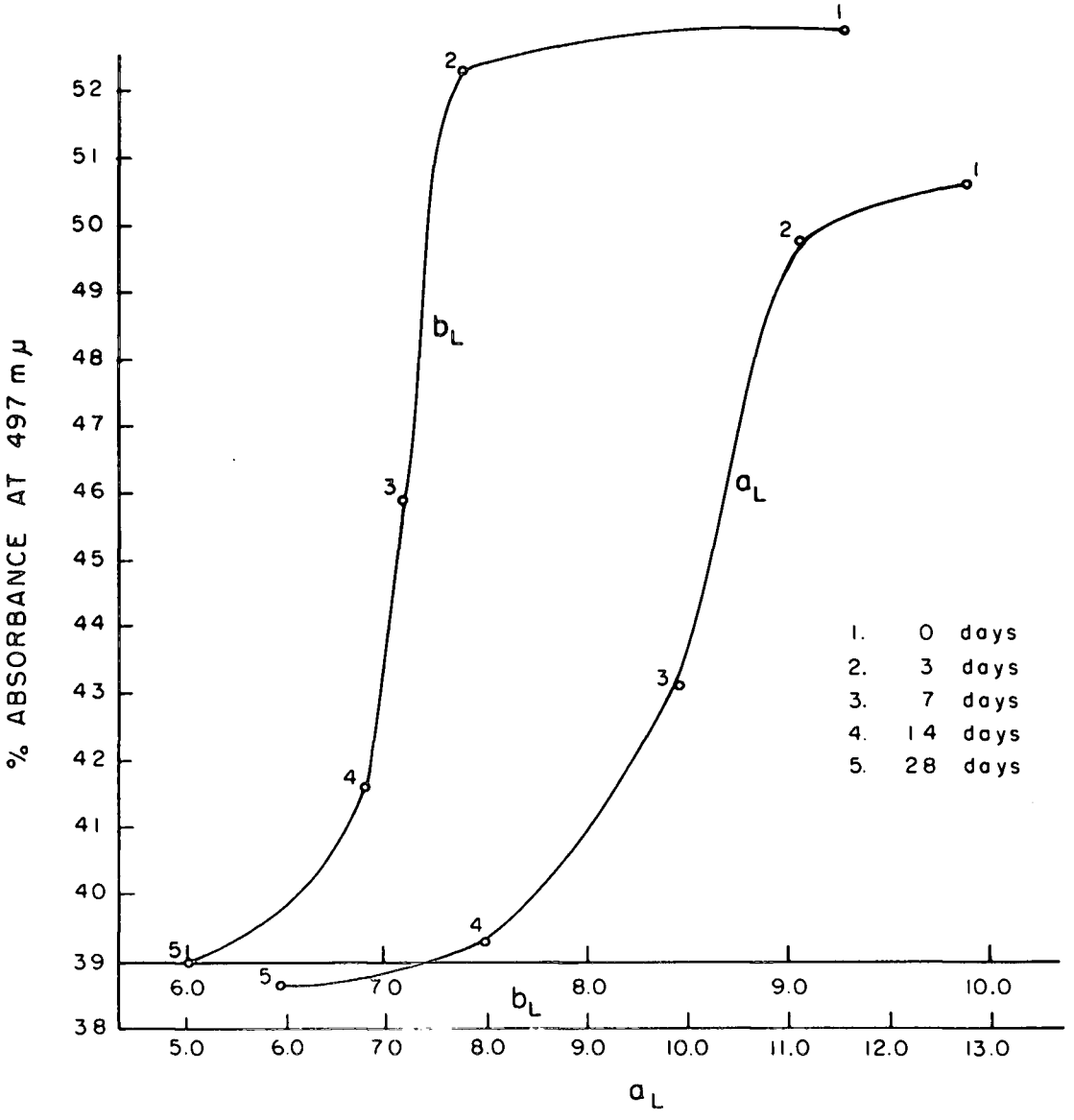
Days After Processing	CANS				JARS			
	L	a_L	b_L	a/b	L	a_L	b_L	a/b
	I REPLICATION							
0	21.5	12.8	8.9	1.4	22.4	12.7	9.3	1.4
3	21.1	11.2	7.2	1.5	21.2	11.4	7.4	1.5
7	20.7	9.9	7.3	1.4	20.8	9.9	7.1	1.4
14	19.8	8.0	6.6	1.2	19.7	8.7	6.9	1.3
28	19.0	5.9	6.4	0.9	18.7	6.5	6.0	1.1
	II REPLICATION							
0	23.1	16.3	9.7	1.7	24.7	15.2	10.1	1.5
3	21.8	12.0	8.6	1.4	22.0	13.6	9.1	1.5
7	21.3	11.7	7.7	1.5	21.8	12.2	7.9	1.5
14	20.9	10.4	7.8	1.3	20.9	10.5	7.6	1.4
28	20.1	7.7	7.3	1.0	19.9	8.3	7.0	1.2

lightness, L, decreased with the storage time, probably because of the formation of the brown products of the anthocyanin degradation. The a_L scale is a measure of the redness of the product under consideration when positive and of the greenness when negative. Decreasing of the a_L positive value means that the redness of the strawberries decreased. This change might be explained on the basis of the fact that the absorbance at 497 mu decreased at a faster rate than the absorbance at 440 mu. The b_L reading is yellowness when positive and blueness when negative. The b_L reading for the strawberries decreased with time. Therefore, the color of the product shifted to a darker region.

Neither of these three readings gave a straight line when plotted against time. The plot of each one of these three readings versus the absorbance at 497 mu (Fig. 5) and the ratio of the absorbances at 497 mu and 440 mu did not give a straight line. There are some qualitative relationships between the change in the absorbance and the change in the readings of the Hunter Color Meter. The decrease in the absorbance at 495 mu and the decrease in the a_L reading means a change in the

Figure 5.

CHANGES OF ABSORBANCE AT 497 mμ AND a_L OR b_L HUNTER METER VALUES DURING STORAGE AT 100°F OF PROCESSED STRAWBERRIES



redness of the sample. The decrease in the absorbance at 440 mu and the decrease in b_L means decreased yellowness. The ratio a_L/b_L is a measure of the hue change.

Comparison of Tin and Glass

Spectrophotometer

The means of the absorbance of the diluted liquid (dilution 1:10) taken from cans and jars are tabulated in Table 2. The shape of the spectra were exactly the same in both cases. There was no difference in the wavelength of the peak absorbance. Generally the absorbance at 497 mu was higher for the fruit processed in glass. Statistical analysis of the factorial experiment type showed that there was no significant difference at the 5% significant level between the absorbance of the fruit preserved in glass and tin containers. The rate of the anthocyanin degradation remained the same, at least for the storage time and the storage temperature used in this experiment. Seemingly the cans had no harmful influence upon the anthocyanins, as long as the containers were sealed.

Hunter Color Meter

The data obtained from this instrument are tabulated in Table 3. Statistical analysis, as in the case of the absorbance showed that there was no significant difference between the L, a_L and b_L readings for the fruit preserved in cans or jars. It appeared from these measurements that the tin container had no harmful influence upon the color of the fruit at least for the storage time and the storage temperature used in this experiment.

2. Willamette Raspberries

Absorption Spectrum

Appropriate amounts of the liquid taken from the cans or the jars were diluted with citrate buffer. The final pH was 3.4. The spectrum of the dilute solution in the region 700 mu to 400 mu was taken by using a DK-1 spectrophotometer. Only one peak appeared in this region of the spectrum. The wavelength of this peak was 510 mu. The means of the absorbance at this wavelength

of four samples are tabulated in Table 4.

Fresh raspberries were homogenized with citrate buffer in a Waring blender and appropriately diluted (dilution 1:25, pH 3.4). The absorbance at 510 mu for the fresh fruit of both replications was 52.0%. The wavelength of the peaks did not change during the storage. The absorbance increased during the first 14 days of the storage at 100° F. After the fourteenth day there was a definite decrease in the absorbance. The change of the absorbance during the storage is quite different from that of the strawberries. It seems that the equilibrium was attained during the first 14 days in the case of the raspberries. The difference in the rate of change of the absorbance in strawberries and raspberries was due to the difference in the time which the pigment took to be distributed between the solid and the liquid phases. The rate of the diffusion of the pigment from the solid phase to the liquid phase was greater than the rate of the degradation the first 14 days. The plot of the absorbance or of the logarithm of the absorbance versus time did not give a straight line relationship. The absorbance at 440 mu did not

Table 4

Means of Absorbance at 510 mu of Diluted Liquid (Dilution 1:25, pH 3.4) of Processed Raspberries

Days After Processing	% Absorbance CANS	JARS
	I REPLICATION	
0	43.1	39.0
3	43.0	40.5
7	43.1	43.0
14	40.1	39.8
28	38.3	37.9
	II REPLICATION	
0	40.8	39.2
3	43.3	45.6
7	41.7	46.0
14	37.2	40.0
28	34.1	34.5

seem to have the significance that it had in the case of the strawberries. Statistical analysis showed that there was no significant difference in the absorbance between the fruit processed in cans and the fruit processed and stored in jars, for the storage time and temperature used in this experiment.

Hunter Color Meter

The L, a_L and b_L scales of the Hunter Color Meter were used for the determination of the color of solid samples taken from the cans or the jars. The standard "Panel 70 Red" was used for the standardization of the instrument, as in the case of the strawberries. The data obtained from these measurements are tabulated in Table 5.

The L reading remained almost constant during storage. The a_L reading decreased with storage time. At the end of the 28th day of storage the a_L reading was about one-half of the value immediately after processing. The b_L reading decreased during the first week of storage and after that it remained practically constant. The plot of any one of three Hunter readings against time

Table 5

Mean Values of Hunter Color Meter Readings for Processed Raspberries

Days After Processing	CANS L	CANS a_L	CANS b_L	CANS a/b	JARS L	JARS a_L	JARS b_L	JARS a/b
			I REPLICATION					
0	17.6	16.9	6.1	2.7	18.3	17.5	6.6	2.7
3	17.4	13.9	5.1	2.7	17.7	17.2	5.6	3.0
7	17.6	13.3	4.9	2.7	17.6	15.0	5.2	2.9
14	17.7	12.2	4.9	2.5	17.0	12.5	4.7	2.7
28	17.9	7.5	4.9	1.5	18.6	9.8	5.3	1.8
			II REPLICATION					
0	17.0	15.8	5.8	2.7	17.7	16.9	6.6	2.6
3	17.4	15.2	5.3	2.8	18.1	15.0	5.3	2.8
7	17.3	14.0	4.8	2.9	17.3	13.2	4.7	2.8
14	17.3	9.9	4.7	2.1	16.4	12.4	4.6	2.7
28	18.2	7.1	4.8	1.5	18.1	9.0	4.8	1.9

did not give a straight line.

The same is true for the plot of the Hunter readings against absorbance.

Correlation of the absorbance with the Hunter readings appeared more difficult than in the case of the strawberries. The a_L value decreased with the storage, while the absorbance increased the first days of the storage.

The difference in Hunter readings between the fruit processed and stored in tin and glass containers was not significant. The L and b_L values were almost the same, while more definite differences existed between the a_L values.

3. Marion Blackberries

Absorption Spectrum

The same technique was used for the preparation of the sample which was presented to the spectrophotometer. The dilution was 1:25 and the pH 3.4. The spectrum was taken from 700 to 400 mu. The results are tabulated in Table 6.

Table 6

Means of Absorbance at 508 mu of Diluted Liquid (Dilution 1:25, pH 3.4) of Processed Blackberries

Days After Processing	% Absorbance CANS	JARS
	I REPLICATION	
0	57.3	57.6
3	61.5	61.1
7	61.3	58.2
14	53.9	54.8
28	48.3	50.5
	II REPLICATION	
0	59.7	56.1
3	59.4	52.9
7	55.6	54.2
14	53.4	48.0
28	42.1	38.7

There is only one peak of absorption in this region of the spectrum. The wavelength of this peak was 508 mu and remained constant during storage. The absorbance at 508 mu underwent a slight increase the third day of the storage and after that showed a continuous decrease. This increase did not appear in the second replication. The rate of degradation of the pigment of the blackberries was similar to that of the strawberries. The diffusion of the blackberry pigment from the solid phase to the surrounding liquid phase was faster than in the raspberries and the equilibrium of the pigment between the solid and the liquid phase was attained during the thermal processing or in the first three days of storage.

An appropriate amount of fresh blackberries was mixed with buffer and homogenized in a Waring blender. The mixture was filtered and diluted to 1:25 in relation to the original amount of the fruit. The pH of the final solution was 3.4. This solution showed an absorbance 65.0% at 508 mu. Statistical analysis showed that there is no significant difference in the absorbance at 508 mu between the blackberries processed and stored in tins and those processed and stored in glass containers.

Hunter Color Meter

As in the previous fruits, the L, a_L and b_L scales of the Hunter Color Meter were used for the determination of the color of solid samples taken from the cans and the jars. The standard "Panel 70 Red" was used for the standardization of the instrument. The data obtained from these measurements are tabulated in Table 7.

The L value increased after 14 days of storage. At the end of the 28 days the L value had the highest values obtained in this experiment. The a_L value increased the first three days of storage, showed a slight decrease the seventh day and increased again towards the end of the storage period. The b_L value remained almost constant. The Hunter Color Meter readings for blackberries did not show the regular changes found in the corresponding readings for strawberries. The L reading showed the largest value the 28th day of the storage.

The plot of any one of the L, a_L and b_L against time did not give a straight line. The same was the result of the effort to relate the Hunter Color Meter readings and the absorption at 508 mu. Between the readings for

Table 7

Mean Values of Hunter Color Meter Readings for Processed Blackberries

Days After Processing	CANS L	CANS a_L	CANS b_L	CANS a/b	JARS L	JARS a_L	JARS b_L	JARS a/b
		I REPLICATION						
0	14.4	6.8	2.5	2.7	14.5	7.0	2.7	2.6
3	14.7	6.7	2.4	2.8	15.2	9.0	2.8	3.2
7	14.5	9.6	2.8	3.4	14.5	9.1	2.8	3.2
14	16.1	5.5	3.0	1.8	14.7	6.5	2.6	2.5
28	16.8	4.6	3.6	1.3	16.3	4.7	3.6	1.3
		II REPLICATION						
0	15.0	6.3	3.2	2.0	14.4	6.2	3.0	2.1
3	15.7	5.9	3.3	1.8	15.3	6.3	2.7	2.3
7	15.3	6.3	3.2	2.0	14.7	6.3	2.7	2.3
14	16.1	4.1	3.4	1.2	16.0	5.4	3.5	1.5
28	16.1	4.6	2.1	2.2	16.0	4.4	2.1	2.1

fruit processed and stored in tin and glass containers, there was no significant difference.

4. Jersey Blueberries

Absorption Spectrum

Appropriate amounts of liquid taken from the cans or the jars were diluted with citrate buffer and the pH was adjusted to 3.4. As in the case of the three other berry fruits the spectrum of the diluted solution was taken in the region 700 mu to 400 mu. In this region of the spectrum, only one peak appeared at 519 mu (Fig. 2). The wavelength of this peak remained constant during the storage period. The means of the absorbance are tabulated in Table 8. The absorbance changes with the time of the storage. The maximum value of absorbance was obtained at the end of the first week of the storage at 100° F. The diffusion of pigment from the solid phase to the liquid phase was more rapid than the degradation of the pigment.

In this respect, the blueberries behaved more like the raspberries and blackberries than strawberries.

Table 8

Means of Absorbance at 519 mu of Diluted Liquid (Dilution 1:25, pH 3.4) of Processed Blueberries

Days After Processing	% Absorbance CANS	JARS
	I REPLICATION	
0	10.5	10.8
3	15.9	16.3
7	21.9	21.0
14	22.8	19.4
28	19.0	19.6
	II REPLICATION	
0	21.3	23.0
3	25.2	24.9
7	26.5	29.3
14	22.6	23.3
28	22.8	21.9

In general, the pigment diffused from the solid phase to the liquid phase of the can or the jar, till equilibrium was attained. In strawberries the equilibrium was attained during the processing, so the diffusion rate was nil during storage and the decrease in absorbance occurred from the beginning of the storage period. In raspberries, blackberries and blueberries the diffusion was more significant than the degradation of the pigment and the absorbance increased during the first week of the storage in spite of the anthocyanin degradation.

A fresh sample from the first replication showed an absorbance of 32.0% at 519 mu, pH 3.4, dilution 1:25. Under the same conditions the fresh sample of the second replication showed an absorbance of 39.0%. There was no significant difference in the absorbance between fruit processed and stored in tin or glass containers, at the 5% significance level as statistical analysis of the results tabulated in Table 8 showed.

Hunter Color Meter

As in strawberries, raspberries and blackberries the L, a_L and b_L scales of the Hunter Color Meter were

used for the color measurement, with the difference that the standard "Panel 45 Royal Blue" was used in the case of the blueberries. The results are tabulated in Table 9.

The L value remained almost constant during storage. The a_L and b_L values did not show significant differences with the storage time. The a/b represents the change in hue. In general, the Hunter readings showed little change during storage.

Table 9

Mean Values of Hunter Color Meter Readings for Processed Blueberries

Days After Processing	CANS				JARS			
	L	a_L	b_L	a/b	L	a_L	b_L	a/b
			I REPLICATION					
0	12.1	6.6	-1.2	-5.5	12.3	6.4	-1.9	-3.3
3	11.2	6.8	-1.5	-4.5	11.7	7.0	-1.9	-3.7
7	11.2	6.9	-1.5	-4.6	11.2	7.6	-1.7	-4.5
14	11.4	8.3	-1.9	-4.4	13.0	8.7	-1.9	-4.5
28	13.7	7.1	-3.4	-2.1	13.5	9.0	-3.3	-2.7
			II REPLICATION					
0	10.9	4.4	-1.6	-2.8	10.0	5.0	-2.6	-3.1
3	10.5	5.1	-1.8	-2.8	10.9	5.2	-1.8	-2.9
7	11.0	5.7	-1.5	-3.8	10.4	5.7	-1.7	-3.4
14	12.9	5.9	-3.2	-1.8	12.9	6.1	-3.3	-1.9
28	11.7	6.2	-2.3	-2.7	11.8	6.1	-2.2	-2.8

SUMMARY AND CONCLUSIONS

In this thesis a study was made of color changes in strawberries, raspberries, blackberries and blueberries spin-cooked and stored at 100° F. for a period of four weeks.

The results indicated the following conclusions:

1. There is no appearance of new peaks or shift of the wavelength of the peaks of absorption in the spectrum from 700 mu to 400 mu, as a result of the processing or storage.

2. The absorbance in the case of the strawberries decreased with the process and the storage right from the beginning of the storage. The absorbance in the cases of raspberries, blackberries and blueberries increased during the first days of storage and decreased after that.

3. The L, a_L and b_L Hunter Color Meter values changed with storage time. In strawberries and raspberries the values decreased, in blackberries and blueberries the values increased the first days and decreased after that.

4. There was no significant difference at the 5% level in any one of the above discussed changes between berry fruits processed and stored in tin and glass containers for a storage time of 28 days at a temperature of 100° F.

BIBLIOGRAPHY

1. Anderson, R.J. Chemical studies of grape pigments. Geneva, 1923. 16 p. (New York Agricultural Experiment Station Technical Bulletin 96.)

2. Aref, M., A.P. Sidwell and E.M. Litwiller. Effect of various sweetening agents on frozen strawberries from preserve manufacture. Food Technology 10:293-297. 1956.

3. Barton, R.R. Colloids help improve the quality of frozen raspberries. Food Packer 34(2):50. 1953. (Abstracted in Food Science Abstracts 26:194. 1954.)

4. Beattie, H.G., K.A. Wheeler and C.S. Pederson. Changes occurring in fruit juices during storage. Food Research 8:395. 1943.

5. Berson, J.A. Ring-chain tautomerism of pyrylium pseudobases. Journal of the American Chemical Society 74:358-360. 1952.

6. Blackburn, M., et al. Reaction of flavylium salts with dimethylaniline and malonic acid. Journal of the Chemical Society 1957, p. 1573-1576.

7. Brody, A.L. and K. Bedrosian. Effect of room temperature vs. refrigerated storage on quality of canned fruit and vegetable products. Food Technology 15:367-370. 1961.

8. Case, W.H. Color problems in fruit spread rations. Canner 114(19):16-17. 1952.

9. Chandler, F.B. Composition and uses of blueberries. Orona, 1944. 12 p. (Maine. Agricultural Experiment Station Bulletin 428.)

10. Committee on Colorimetry. Optical Society of America. Concept of Color. Journal of Optical Society of

America 33:544. 1953.

11. Davis, R.B., and W.A. Gould. A proposed method for converting Hunter Color Difference Meter readings to Munsell hue, value and chroma denotations. Food Technology 9:536. 1955.

12. Decereau, R.V., G.E. Livingston and C.R. Fellers. Color changes in strawberry jellies. Food Technology 10:125-128. 1956.

13. Desrosier, N.W., et al. Meter simplifies color grading of fruits and vegetables. Food Engineering 24(5):92-93. 1952.

14. Eastman, E.J., et al. Observations of color changes in some processed and stored food. Food Technology 5:121-128. 1951.

15. Guadagni, D.G., C.C. Nimmo and E.F. Jansen. The time-temperature tolerance of frozen foods. X. Retail packs of frozen raspberries. Food Technology 11:633. 1957.

16. Guadagni, D.G., C.C. Nimmo and E.F. Jansen. The time-temperature tolerance of frozen foods. VI. Retail packs of frozen strawberries. Food Technology 11:389. 1957.

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

18. Hardy, A.C. Handbook of colorimetry. Cambridge, Mass., Technology Press, 1936. 87 p.

19. Harib, A.T., and H.D. Brown. The effect of oxygen and hydrogen ion concentration on color changes in processed beets, strawberries and raspberries. Proceedings of the American Society of Horticultural Science 68:482-490. 1956.

20. Haworth, W.M. The conversion of sucrose into furan compounds. Journal of the Chemical Society 1944,

p. 667-670.

21. Hodge, J. E. Chemistry of browning reactions. Journal of Agricultural and Food Chemistry 1:928. 1953.

22. Hoover, W.M., and R.A. Dennison. A rapid objective method for evaluation of color in strawberries. Proceedings of the 51st Annual Meeting of the American Society of Horticultural Science, Florida. 1954. 28 p.

23. Huang, H.T. Decolorization of anthocyanins by fungal enzymes. Journal of Agricultural and Food Chemistry 3:141. 1955.

24. Huang, H.T. Enzyme identification of the anthocyanin pigment of blackberry. Nature (London) 177:39. 1956.

25. Joslyn, M.A. Color retention in fruit products. Industrial and Engineering Chemistry 33:308. 1942.

26. Judd, Dean. Color in business, science and industry. New York, Wiley, 1959. 401 p.

27. Karrer, Paul. Organic chemistry. New York, Elsevier, 1950. 983 p.

28. Karrer, Paul and B. Pieper. The pigment in the forest and in the large garden blackberry. Helvetica Chimica Acta 13:1067-1070. 1930. (Abstracted in Chemical Abstracts 25:519. 1931.)

29. Kertesz, Z.I., and E. Sondheimer. To reduce color losses in strawberry preserve. Food Industries 20: 106-108. 1948.

30. Kertesz, Z.I. Investigations of color changes in fruit spreads. Glass Packer 27:229-231. 1948.

31. Kertesz, Z.I. Color problems in fruit spreads. Glass Packer 27:609-610. 1948.

32. Kitson, J.A. Measurement of color changes in berry pie fillings. Effect of temperature and length of storage. Canadian Food Industry 28(4):15-16. 1957.

33. Lee, Frank, and George Slate. Chemical composition and freezing adaptation of raspberries. Geneva, 1954. 12 p. (New York. Agricultural Experiment Station. Bulletin No. 761.)

34. Leinbach, L., et al. Composition of red raspberries including pectin characterization. Food Technology 2:51-54. 1951.

35. Lewis, V.M., W.B. Esseley and C.R. Fellers. Nitrogen free carboxylic acids in the browning reaction. Industrial and Engineering Chemistry 41:2591-2592. 1949.

36. Livingston, G.E. Malic acid-fructose reaction. Journal of the American Chemical Society 75:1342-1344. 1953.

37. Livingston, G.E., et al. The discoloration of pectin gels. Food Technology 9:180-184. 1955.

38. Livingston, G.E., Tan Chee-Teek and Z.I. Sabry. Colorimetry of strawberry preserves. Food Technology 13:303-306. 1959.

39. Link, Karl Paul. The anthocyanins and the flavones. In: Henry Gilman's Organic Chemistry, Vol 2. New York, Wiley, 1943. p 1315-1340.

40. Lukton, A., C.O. Chichester and G. Mackinney. Characterization of a second pigment in strawberries. Nature 176:790-792. 1955.

41. Lukton, A., C.O. Chichester and G. Mackinney. The breakdown of strawberry anthocyanin pigment. Food Technology 10:427-432. 1956.

42. Macara, T. The composition of raspberries. Analyst 60:592-596. 1953.

43. Mackinney, G., and C.O. Chichester. Color deterioration in strawberry preserves. Canner 114:13. 1952.

44. Mackinney, G., and C.O. Chichester. The color problem in foods. In: Advances in Food Research, Vol 5. New York, Academic Press, 1954. p 301-351.

45. Mackinney, G., A. Lukton and C.O. Chichester. Strawberry preserves by a low temperature process. Food Technology 9:324-326. 1955.

46. Markakis, Perikles, Gideon Livingston and Carl Fellers. Quantitative aspects of strawberry pigment degradation. Food Research 22:117-130. 1957.

47. Mayer, Fritz. The chemistry of natural coloring matters. New York, Reinhold, 1943. 354 p.

48. Meschter, E.E. Effect of carbohydrates and other factors on strawberry products. Journal of Agricultural and Food Chemistry 1:574-579. 1953.

49. Meschter, E.E., and R.W. Liggest. Color measurement in strawberry preserves. Color in foods, a symposium. Washington, National Academy of Sciences, Natural Resources Council, 1954. 186 p.

50. Pederson, C.S., H.G. Beattie and F.H. Stotz. Deterioration of processed fruit juices. Cornell, 1947. 28 p. (New York. Agricultural Experiment Station. Bulletin 728.)

51. Pigman, William Ward. Chemistry of the carbohydrates. New York, Academic Press, 1948. 902 p.

52. Pratt, Dan E., et. al. Interaction of ascorbic acid, riboflavin and anthocyanin pigments. Journal of Agricultural and Food Chemistry 2:367-372. 1954.

53. Robinson, R. Natural coloring matters and their analogues. Nature 132:625. 1933.

54. Robinson, R., and G.M. Robinson. A survey of anthocyanins. Biochemical Journal 26:165-1664. 1932.

55. Robinson, W.B., et. al. Chemical composition and freezing adaptability of strawberries. Geneva, 1947. 14 p. (New York. Agricultural Experiment Station. Bulletin 726.)

56. Shah, J.N., and O.J. Worthington. Comparison of methods

and instruments for specifying the color of frozen strawberries. Food Technology 8:121-125. 1954.

57. Sidwell, A.P., and R.F. Cain. A new method of presentation of food samples to the Hunter Color and Color-Difference Meter. Science 120:666-667. 1954.

58. Singh, B., G.R. Dean and S.M. Cantor. The role of 5-(hydroxymethyl)-furfural in the discoloration of sugar solutions. Journal of the American Chemical Society 70:517-522. 1948.

59. Slate, G.L., et al. The blueberry in New York. Geneva, 1942. 26 p. (New York. Agricultural Experiment Station. Circular 189.)

60. Sondheimer, Ernest. On the relation between spectral changes and pH of the anthocyanin pelargonidin-3-glucoside. Journal of the American Chemical Society 75:1507-1508. 1953.

61. Sondheimer, E., and C.B. Carash. The major anthocyanin pigment of the wild strawberry. Nature 178:648-649. 1956.

62. Sondheimer, E., and Z.I. Kertesz. Colorimetric determination of anthocyanin pigments in strawberry and strawberry products. Analytical Chemistry 20:245-248. 1948.

63. Sondheimer, E., and Z.I. Kertesz. The anthocyanin of strawberries. Journal of the American Chemical Society 70:3476-3479. 1948.

64. Sondheimer, E., and Z.I. Kertesz. The kinetics of the oxidation of strawberry anthocyanin by hydrogen peroxide. Food Research 17:288-297. 1952.

65. Sondheimer, E., and Z.I. Kertesz. Participation of ascorbic acid in the destruction of anthocyanin in strawberry juice and model systems. Food Research 18:475-479. 1953.

66. Tinsley, Ian James. Methods of presenting raspberry

and strawberry samples to the Hunter Color and Color-Difference Meter. Master's thesis. Corvallis, Oregon State University, 1955. 53 numb. leaves.

67. Tinsley, Ian James. The degradation, in model systems, of the anthocyanin of the Marshall strawberry. Ph.D. thesis. Corvallis, Oregon State University, 1958. 58 numb. leaves.

68. Townsend, C.T. Problems in the processing of fruits. Berkeley, California, National Canners Association, 1951. 2 p. (Information letter No. 1325.)

69. Watson, G.N. The juice of the blueberry as an indicator. American Journal of Pharmacy 85:246. 1913.

70. Willard, H. Hobart, Lynne L. Merritt and John A. Dean. Instrumental methods of analysis. New York, D. Van Nostrand, 1960. 626 p.

71. Williams, B.L., and S.H. Wender. The isolation of kaempferol and quercetin from strawberries. Journal of the American Chemical Society 74:5919-5920. 1952.

72. Williams, C.C., E.J. Cameron and O.B. Williams. A facultative anaerobic mould of unusual heat resistance. Food Research 6:69-73. 1941.

73. Woodruff, E.E., D.H. Dewey and H.M. Sell. Chemical changes of Jersey and Rubel blueberry fruit associated with ripening and deterioration. Proceedings of the American Society of Horticultural Science 75:387-401. 1960.