

It is not the intent of the authors to encourage careless handling and cold storage practices for apples and pears in the Pacific Northwest. They do feel, however, that the popular conception of the possible hazard presented by a few ripe apples in commercial fruit cold storages has been distorted beyond its true economic significance; and that prompt handling, adequate refrigeration capacity to cool the fruit quickly, proper air distribution to get uniform temperatures throughout the room, and maintaining favorable temperatures and humidities are the really important factors in successful cold storage of pears and apples.

### Summary

Unripe Bartlett and Anjou pears and Starking Delicious apples were stored continuously at 31° F. during 1950-51 in volatile-free atmospheres and in those containing measured quantities of ethylene and nonethylenic volatiles from ripened fruits of similar variety. Certain indexes associated with the rate of ripening (respiration, firmness, and soluble pectins) failed to reflect any significant difference in the degree of ripeness between the fruit held in fresh outside air and that exposed to the emanations from ripe fruit. A qualified panel of judges

was unable to distinguish any impairment in the cold storage life or the texture, flavor, dessert quality, and freedom from physiological disorders during subsequent ripening of the pears and apples, as a result of their previous storage along with ripened fruit.

Storage temperatures of 31°, 45°, and 65° F. were employed in the 1951-52 experiment wherein ripe and unripe Anjou pears were held in the presence of each other, as were also Starking Delicious apples. The presence of ripe fruit hastened the respiratory climacteric in Anjou pears by about 2 days when the experiments were conducted at 65°. This stimulatory effect was not detected organoleptically. The ripening of Anjou pears at 45° and 31° was not hastened by the presence of previously ripened fruit. Starking Delicious apples were not adversely affected at any of the temperatures tested when they were stored along with ripened fruit of the same variety.

The commercial implications of these and related studies are discussed with regard to the successful storage of apples and pears at 31° F.

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## FOOD DISCOLORATION

# Darkening of Food Purees and Concurrent Changes in Composition of Head-Space Gas

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Studies on the nonenzymatic browning of foods have shown that carbon dioxide and oxygen are involved in these reactions. In an attempt to clarify further the relationship between composition of head-space gas and change in color, the concentration of these gases in the head space of sealed tubes of puréed fruits and vegetables was determined periodically. Reflectometric measurements of the color of the purées were made concurrently. Oxygen was absorbed and carbon dioxide evolved by all the food studied. There was a significant correlation between oxygen absorption and discoloration in all foods except pears. The correlation between carbon dioxide evolution and discoloration was significant only for beets, carrots, green beans, and squash. Significant correlation between oxygen absorption and carbon dioxide evolution was observed for all except spinach purée. Development of nonenzymatic discoloration in the puréed vegetables closely paralleled absorption of oxygen, indicating that inhibition of darkening in these puréed foods may be assisted by maintenance of low oxygen levels.

**O**XYGEN AND CARBON DIOXIDE may be involved in the development of nonenzymatic darkening in foodstuffs.

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The present study was undertaken to try to clarify the relationship between gas changes and changes in color. The rates of oxygen absorption and carbon dioxide production by eight puréed foods were studied. Darkening occurred concur-

rently in most of these purées and was evaluated by a reflectometric method. Correlation coefficients between changes in composition of head-space gas and discoloration are presented.

Although Maillard (9) noted that the

reaction between amino acids and sugars proceeds in the presence or absence of oxygen, oxidation has been found to play an important part in many nonenzymatic food discolorations. Relatively large quantities of oxygen have generally been associated with a greater degree of darkening in citrus products (3, 4, 8). The influence of oxygen in bringing about undesirable changes in color in wines (10), apricots (12), evaporated milk (14), applesauce (6), and other products has also been described.

Maillard (9) also reported the evolution of carbon dioxide from reaction mixtures of glucose and glycine. Stadtman, Chichester, and Mackinney (13) concluded from experiments employing radioactive tracer techniques that about 80% of the carbon dioxide produced was derived from glycine and about 10% from glucose, in the Maillard reaction.

According to Reithel and Wither (11) carbon dioxide may form from ascorbic acid reactions. Degradation of pectin produced carbon dioxide in investigations by Dore (2).

Carbon dioxide evolution from apricots is described by Stadtman and co-workers (12) and from citrus products by Loeffler (8) and Curl (7). Lewis, Esselen, and Fellers (5) gave details of a sealed tube technique for studying production of carbon dioxide. They reported amounts of carbon dioxide produced by various foods and reaction mixtures under specified conditions.

### Experimental

**Preparation of Tubes of Purée.** The edible portion of green beans and of spinach and the pulpy portion of beets, carrots, squash, apples, peaches, and pears were blanched and comminuted to produce purées. Slight variations in procedure were necessary in these preliminary steps, depending on the nature of each individual foodstuff. Purées were centrifuged to remove air bubbles and momentarily subjected to a vacuum equivalent to 684 mm. of mercury or more, to reduce to a minimum the content of dissolved oxygen.

Borosilicate glass tubes 15 x 125 mm. were used as containers for the purées. Twenty-six tubes of each of the eight foods named above were prepared for head-space gas studies. Ten milliliters of purée were added to each test tube. The open end of each tube was drawn into a capillary and shaped for gas analysis in a manner similar to that described by Lewis, Esselen, and Fellers (5).

The head-space oxygen content of all tubes in a group was adjusted to 6 to 7% concentration before sealing, to provide conditions approaching those present in packaged foods. This oxygen level was achieved by subjecting each group of prepared tubes to a specific vacuum, releasing the vacuum to atmos-

pheric pressure with nitrogen, and quickly sealing the capillaries in a flame.

**Thermal Process.** Before storage, all tubes, except those for immediate examination, were processed to prevent microbial spoilage. Vegetable purées were processed 15 minutes at 240° F. (115.5° C.), and fruit purées were processed 15 minutes at 212° F. (100.0° C.).

**Head-Space Gas Analysis.** In order to show the original head-space gas composition, two tubes of each purée were analyzed immediately after sealing by the modified Blacet-Leighton technique described by Lewis, Esselen, and Fellers (5). Two additional tubes of each purée were analyzed immediately after processing to show the effect of

**Table I. Relationship of Head-Space Gas Content and Discoloration of Purées during Storage at 85° to 90° F. (29.4° to 32.2° C.) in Sealed Tubes**

Purée	Storage, Days	Head-Space Gas, Millimole		Discoloration, R.U. <sup>a</sup>
		O <sub>2</sub>	CO <sub>2</sub>	
Vegetable Purées				
Beet	0 (unprocessed)	0.012	0.000	2.3
	0 (processed)	0.011	0.000	3.0
	2	0.008	0.001	3.3
	6	0.002	0.011	...
	10	0.003	0.015	9.5
	16	0.002	0.012	11.8
	24	0.002	0.010	...
Carrot	0 (unprocessed)	0.013	0.000	2.3
	0 (processed)	0.013	0.000	1.8
	2	0.012	0.001	...
	6	0.011	0.000	4.5
	10	0.008	0.020	6.3
	16	0.004	0.024	7.8
	24	0.005	0.025	8.5
Green beans	0 (unprocessed)	0.012	0.000	2.8
	0 (processed)	0.012	0.000	4.5
	2	0.011	0.000	...
	6	0.008	0.003	7.5
	10	0.007	0.011	8.0
	16	0.006	0.014	10.0
	24	0.004	0.014	11.3
Squash	0 (unprocessed)	0.013	0.000	2.3
	0 (processed)	0.013	0.000	2.8
	2	0.011	0.001	3.8
	6	0.009	0.005	4.5
	10	0.007	0.006	5.0
	20	0.005	0.008	6.5
	36	0.003	0.006	7.8
Spinach	0 (unprocessed)	0.014	0.000	0.0
	0 (processed)	0.012	0.000	1.8
	2	0.011	0.000	4.5
	6	0.007	0.007	3.8
	10	0.006	0.007	2.0
	20	0.006	0.005	4.5
	36	0.003	0.005	6.5
Fruit Purées				
Apple	0 (unprocessed)	0.013	0.000	0.3
	0 (processed)	0.013	0.000	1.0
	2	0.012	0.002	2.8
	6	0.009	0.002	4.0
	10	0.009	0.002	3.5
	20	0.008	0.002	9.0
	36	0.009	0.002	7.0
Peach	0 (unprocessed)	0.014	0.000	2.3
	0 (processed)	0.013	0.001	1.3
	2	0.012	0.001	1.8
	6	0.010	0.004	4.8
	10	0.008	0.005	6.5
	20	0.008	0.003	...
	36	0.009	0.002	10.5
Pear	0 (unprocessed)	0.013	0.000	0.5
	0 (processed)	0.012	0.001	0.3
	2	0.012	0.000	0.8
	6	0.012	0.001	1.3
	10	0.009	0.004	1.8
	20	0.011	0.002	5.8
	36	0.011	0.002	6.0

<sup>a</sup> Reflection units increase with increased darkening.

processing on head-space gas composition. Thereafter, tubes were analyzed in pairs at regular intervals during storage at 85° to 90° F. (29.4° to 32.2° C.) in the dark.

**Evaluation of Darkening.** Reflection measurements were made on each tube from which a gas sample was taken. The method described by Livingston and Vilece (7) was employed. In-tube reflection readings were made of the top and bottom portions of each tube. For an in-tube reflection reading of the top portion of a purée, the slit of the tube holder was placed so that it exposed to the search unit an area from 1 to 8 mm. below the head-space region of the tube. For a reflection reading of the bottom portion of the purée, the slit was placed so that it exposed to the search unit an area from 10 to 17 mm. above the bottom of the tube.

For most purées, the tristimulus green filter was used and Munsell color standard 5Y 4/4 was set equal to 70% reflectance. For beets, unfiltered light was used and Munsell color standard 5Y 4/4 was set equal to 100% reflectance. For spinach, unfiltered light was also used, but Munsell color standard 5G 2/2 was set equal to 100% reflectance.

### Results and Discussion

Reflectometric values, as reported in this paper, are expressions of "ring browning." They were found by subtracting the reflection reading on the top portion of the tube from that on the bottom portion. This value was convenient for use because the greatest visible change occurred in the top portion of the tubes. In general, the contrast in appearance of top and bottom portions was the outstanding development in tubes, as judged by both eye and reflectometer.

Gas content of head spaces was calculated after a preliminary experiment showed that neither pressure nor vacuum developed in tubes as a result of sealing and processing. The results of gas analyses and the head-space volumes of tubes were used in these calculations.

The data in Table I indicate that oxygen is absorbed and carbon dioxide is evolved by all the purées tested. These tables show the relationship between oxygen absorption, carbon dioxide evolution, and formation of discoloration as measured reflectometrically. The development of discoloration was rapid except in apple, pear, and spinach purées.

The production of carbon dioxide seems to be related to the pH of the food, since the vegetables produced more than the fruits. The concentration of carbon dioxide in the head space of tubes of carrot purée after 36 days' storage is about twice the original concentration of oxygen. For green beans, the concentration is slightly more than the original

**Table II. Coefficients of Correlation for Reflectance Values and Head-Space Gas Changes in Puréed Foods**

Purée	O <sub>2</sub> vs. R.U. <sup>a</sup>	CO <sub>2</sub> vs. R.U.	O <sub>2</sub> vs. CO <sub>2</sub>
Beet	0.911 <sup>b</sup>	0.962 <sup>b</sup>	0.767 <sup>b</sup>
Carrot	0.911 <sup>b</sup>	0.866 <sup>b</sup>	0.951 <sup>b</sup>
Green Bean	0.876 <sup>b</sup>	0.855 <sup>b</sup>	0.835 <sup>b</sup>
Squash	0.925 <sup>b</sup>	0.890 <sup>b</sup>	0.879 <sup>b</sup>
Spinach	0.714 <sup>b</sup>	0.365	0.396
Apple	0.754 <sup>b</sup>	0.455	0.642 <sup>c</sup>
Peach	0.839 <sup>b</sup>	0.552	0.837 <sup>b</sup>
Pear	0.049	0.311	0.974 <sup>b</sup>

<sup>a</sup> Reflectance units.

<sup>b</sup> Highly significant (0.01 level).

<sup>c</sup> Significant (0.05 level).

oxygen concentration. Smaller amounts were evolved by other purées after the same period of storage.

Beet purée seems to absorb oxygen most quickly and most completely. The more acid foods do so more slowly and less completely.

The development of discoloration, as measured by means of the reflectometer, shows a gradual increase, in most cases, except for a relatively rapid initial phase. In general, this change parallels the absorption of oxygen, which is a slow, gradual process. Beet purée is the exception. The comparatively rapid initial development of darkening and the comparatively slow initial absorption of oxygen are, however, at variance with one another. Evolution of carbon dioxide is characterized by an initial lag period, followed by a period of relatively rapid production.

Table II presents the correlation coefficients for reflectance values and head-space gas changes in the purées studied. The data indicated a highly significant correlation between oxygen absorption and reflectance values in all foods except pear purée. The lower correlation values of spinach and apples should be noted, as darkening in spinach is not evident visually, and darkening other than "ring" type is observable in apple purée.

Correlation between carbon dioxide evolution and reflectance values is very high for beet, carrot, green bean, and squash purées, but not for the other foods tested. In all cases, except beet and pear purées, the correlation of oxygen absorption with reflectance values was higher than that of carbon dioxide evolution. This observation supports the view that oxidation is more closely associated with darkening than carbon dioxide evolution.

A very good correlation exists between oxygen absorption and carbon dioxide evolution, except for spinach purée. Spinach was unusual in behavior, however. Although no discoloration was visible in spinach purée, reflection measurements indicated a decrease in reflected light during storage.

### Summary

Purées absorb oxygen and evolve carbon dioxide to different extents during storage. Acid foods generally absorb oxygen less quickly. Development of discoloration more closely resembles oxygen absorption, as both increase gradually. After an initial lag period, carbon dioxide evolution increases at a rapid rate, in most cases.

Evaluating tubes by means of the in-tube reflection method was found to be rapid and satisfactory.

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