# Product-Induced Stratification of Covering Syrups [a, b, c]

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PRODUCT-INDUCED stratification is the name given the concentration gradient of soluble solids which results when foods of high water and low solids content are placed in sugar syrup. When the syrup is first poured over the product, the concentration of solids in the syrup is uniform throughout the jar; when the product is marketed some months later, the soluble solids concentration of the syrup, although lower than it was initially, is again uniform. However, soon after the syrup is added to the product, a non-uniform gradient of soluble solids concentration is created because water leaving the product rises to the top of the jar, instead of diluting the surrounding syrup. Moreover, this non-uniform gradient is large enough to inhibit convection *(2)*, and continues to increase throughout the heating period.

This investigation is primarily concerned with a description of the dynamic processes which result in product-induced stratification in sweet fresh cucumber spears.

## EXPERIMENTAL

**Measurements.** The following measurements were made: soluble solids concentrations in the syrup at the top and bottom of both heated and unheated jars of sweet, fresh cucumber spears at times ranging from 15 sec to 64 min after adding the syrup; soluble solids concentrations at 6 points (top to bottom) in heated and unheated jars of cucumber spears at 64 min and 24 hr after adding syrup; both product and syrup soluble solids concentrations at top and bottom of heated jars of cucumber spears at times from 1 hr to 213 days after adding syrup; acetic acid concentration in the syrup at the top and bottom of heated jars of cucumber spears at times from 64 min to 128 days; and pH in both syrup and product at top and bottom of heated jars of spears at times from 64 min to 8 days after adding syrup.

## MATERIALS AND METHODS

The cucumbers used in this study were a slicing variety 1.5 to 2 in (3.8 to 5.1 cm) in diameter and 6 to 8 in (15 to 20 cm) long. A product known as cucumber spears was used in nearly all the work in this study; however, cucumber slices, cherries, and peaches were also tested for stratification. The details of the cucumber spear studies only will be reported here. The cucumber spears were prepared by cutting off the ends of whole cucumbers to obtain a nearly uniform cylindrical section 4.12 in (10.5 cm) long and then cutting this section lengthwise into 6 equal wedges. All the containers used in the tests were 16-oz glass jars (sometimes called 16-oz vegetable or No. 303 jars) with a lug finish. The spears were hand packed to a weight of 10.6 ± 0.2 oz (300 ± 5 g). Each spear was placed vertically in the jar, and the cut surface of the outer row of spears placed against the glass. The covering liquor was 50.0% sucrose and 2.8% acetic acid, by weight. The acetic acid had to be added to insure preservation because the heat process given the cucumber spears is adequate only for acid products. In most of the tests the jars were filled to the same distance below the top of the finish (0.5 cm) with 148 ± 15 ml of covering liquor. In the tests made to determine the vertical soluble solids concentration gradient and the tests made to determine the amount of stratification from 0.04 to 8 days, the volume of added syrup was fixed at 150 ± 2 ml. Both covering liquor and spears were initially at room temperature. Jars to be heat processed were immersed for 40 min in an agitated water bath maintained at 180° F (82° C) and cooled for 15 min in a water spray at about 54° F (12° C). Jars for the final equalization tests were stored at 74.0 ± 2.0° F (23.3 ± 1.1° C) in closed cases. The jars were handled carefully throughout the investigation to minimize agitation of the contents.

Hypodermic syringes and needles were used to remove 0.2 to 0.3 ml of syrup for each concentration measurement. Each pair of product soluble solids concentrations was measured at top and bottom in a single spear one end of which was at the top of the jar and the other at the bottom. Each spear taken was blotted to remove the surrounding syrup; a 0.5 cm section was cut from each end and pressed between the fingers to express the juice directly onto the refractometer prism.

The soluble solids concentrations were measured using a Bausch and Lomb Abbe-3L double scale refractometer, the sucrose scale of which is based on the International Sucrose Tables refractive indices at 20° C. The experimental data in this study are the refractive indices of the samples reported as per cent sucrose corrected to 20° C. It is recognized that these values include the contribution of the acetic acid to the refractive index.

The acetic acid concentrations, taken at the top and bottom of heated jars of cucumber spears, were determined by titration of 5.0 ml samples with 0.1N NaOH. The pH measurements of both syrup and product at the top and bottom of heated jars were made with a Beckman Model G pH meter equipped with "one-drop" electrodes. The liquid for the product pH measurements was obtained in the same way as that for the product soluble solids measurements.

## RESULTS AND DISCUSSION

Figure 1 shows the rate of formation of the soluble solids gradient in both heated and unheated jars. These data are the averages of 4 unheated jars and 3 heated jars. It should be pointed out that each unheated jar can easily be sampled at more than one time during the test period. The same 4 jars were used throughout the unheated jar test, and, consequently, a total of 16 samples (total sample volume of about 4 ml) had been removed from each jar by the end of the test. In the heated jar tests, a jar could be used to supply only one pair of top and bottom samples. Each heated jar was removed from the bath at the stated time and the top and bottom samples taken quickly. Two people were required for this sampling; one took the top sample, the other the bottom. As a result, 24 heated jars were required for the whole test, 3 jars for each pair of top and bottom soluble solids concentration readings. A comparison of the soluble solids concentrations of heated jars with unheated jars (Figure 1) shows that more dilution of the syrup had taken place in the heated jars at the top and the bottom of the jar at any time after 8 min; however, the difference in concentration between top and bottom was about the same for heated jars as for unheated jars (see Table 1). The principal result to note is that the amount of stratification is not appreciably affected by the heating and cooling process.

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[a] Journal Paper No. 2548, Michigan Agricultural Experiment Station, East Lansing, Michigan.

[b] Presented before the Nineteenth Annual Meeting of the Institute of Food Technologists, Philadelphia, May 19, 1959.

[c] This research is a portion of the thesis presented by T. R. Mulvaney for the M.S. degree, Michigan State University, 1958.

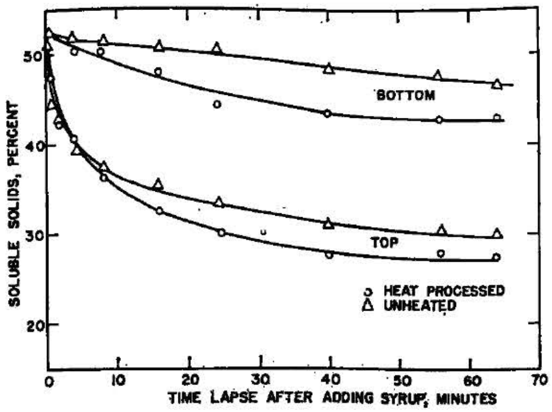


**Figure 1.** Soluble solids concentrations in the syrup in jars of sweet fresh cucumber spears.

**TABLE 1**

Differences in per cent soluble solids (bottom–top) in sweet, fresh cucumber spear covering liquor

| Time, minutes after syrup addition | Heated | Unheated |
|---|---|---|
| 4 | 9.9 | 12.3 |
| 16 | 15.6 | 15.6 |
| 64 | 15.8 | 17.8 |

The product-induced soluble solids concentration gradient was not constant throughout the jar. Figure 2 shows the soluble solids concentrations in the syrup measured at several points in heated and unheated jars at 64 min and 24 hr after adding syrup; each point is the average of two readings. The gradient in unheated jars, as a function of time and position in the jar, is primarily of academic interest; however, these unheated jar gradients are presented for contrast with the gradients in heated jars. Mulvaney *(1)* shows data for the gradient in unheated jars as a function of position at several times in the interval from 1 to 64 min after adding syrup. The soluble solids concentration in the syrup in unheated jars at 4 min was nearly constant from the bottom of the jar to within half an inch from the top and dropped from 50% to 41% in the last half-inch; at 16 min the gradient had the same shape as it did at 64 min (see Figure 2), but the concentrations were higher at every point. Soluble solids measurements at 6 points during the heating period were not made because of the problems in obtaining samples.

Twenty-four hours after adding syrup, the gradient in the heated jars was about the same as that in the unheated jars, but there was a pronounced difference in gradients at 64 min (about 10 min after the end of the cooling period for the heated jars) even though the average gradient was about the same (see Table 1). The authors draw two tentative conclusions from the evidence presented in Figure 2: first, that the gradient is not constant at any time in heated jars; and, second, that the gradient in heated jars during the heating period cannot be deduced from the gradient at the corresponding time in the unheated jars.

A detailed knowledge of the gradient during the heating period is important. The slowest heating point is near the bottom of the jar and is a point of high sucrose concentration, and, therefore, a point of high lethality for many microorganisms associated with spoilage of fresh cucumber pickles *(3)*, primarily because of the high sucrose concentration. The top of the jar, which is the point lowest in sucrose concentration, is the point of highest temperature, and, therefore, a point of high lethality because of the temperature. The point of least lethality in a syrup-packed jar, formerly identified with the slowest heating point, will be that point at which the combined lethal effects of sucrose concentration and temperature give the least integrated lethality for the entire heating and cooling process.

Figure 3 shows the relationship between syrup and product at both the top and bottom of the jar for heat-processed sweet, fresh cucumber spears. These points are the averages of readings from three jars for each time; the first measurements were taken 64 min after adding syrup. Figure 1 shows the changes in soluble solids concentration in the syrup only for the first 70 min; no data are available to show the changes in the soluble solids concentration in the product during this interval. The maximum top-bottom difference in soluble solids concentration occurred in the syrup about 1 day after adding the syrup and amounted to about 21%; the corresponding maximum difference in the product occurred at about 2 days and amounted to about 17%. The difference between the product and its surrounding syrup is a maximum at the moment the syrup is added. A period of 6 to 8 days was required for the soluble solids in the product and its surrounding syrup to reach equilibrium; during this period water was still leaving the product at the bottom, rising to the top, and there diluting the syrup. The maximum dilution of the syrup at the top of the jar was reached at 6 to 8 days at which time the soluble solids concentration in the syrup was 15%. The maximum water loss by the product, which produces product shrinkage and consequent poor appearance,

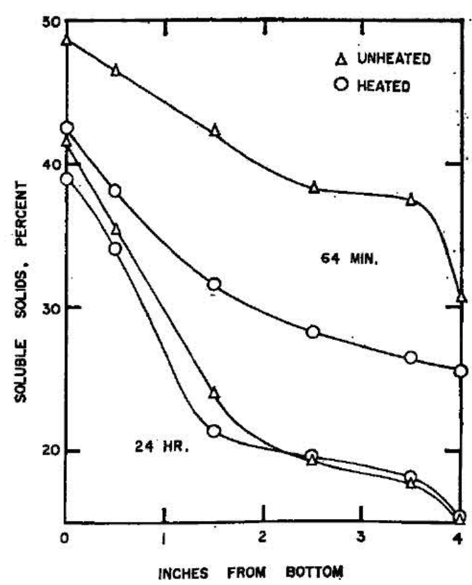


**Figure 2.** Soluble solids concentration gradients in the syrup in jars of sweet fresh cucumber spears.

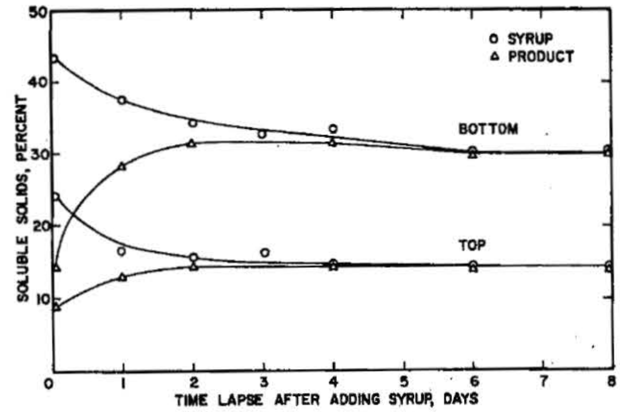


**Figure 3. Soluble solids concentrations in heat processed sweet fresh cucumber spears.**

was at the bottom of the jar. In this test this maximum loss occurred about 3 days after adding syrup at which time the soluble solids concentration in the product reached 31%.

Figure 4 shows the entire range of product and syrup soluble solids concentrations from just after the heating and cooling period to the time of final equalization [d] 213 days later. The data are shown on a logarithmic scale for convenience; each plotted point is the average of readings from 6 jars. At the end of 213 days the difference between soluble solids concentrations in the syrup at the top and bottom was 0.5%; the corresponding difference for the product was 0.1%. There was still a difference between product and syrup soluble solids of about 1%. The measured final equalization (average of top and bottom for both product and syrup) of 21.8% is in good agreement with the calculated final equalization of 22.3%, based on 148 ml of syrup (soluble solids concentration of 52.8%, specific gravity 1.24) and 300 g of cucumber spears (soluble solids 3.2%, specific gravity 1.00).

The facts presented in Figure 4 help to explain why these products are customarily held in storage for some time before being released for sale. This problem can be discussed by considering three phases of the final equalization of soluble solids concentrations between product and syrup throughout the jar. First is stratification, the movement of water leaving the product at the bottom of the jar and rising to the top because the density of the surrounding syrup is higher; stratification is the most rapid phase and reached a maximum in one to two days. Second is the equalization of the soluble solids in the product with that of the surrounding syrup; this phase of equalization takes longer than stratification and was reached in 6 to 8 days. Third is the final equalization between top and bottom soluble solids concentrations in product and syrup; this phase of final equalization takes the longest and required over 200 days in these experiments. Some processors of sweet, fresh cucumber products make a practice of inverting the finished jars after they are put in cases and before the cases are placed in the warehouse; that is, about an hour after adding syrup. If the jars are inverted at that time (see the first set of points in Figure 4) the product at the top will be at 18% soluble solids and the product at the bottom will be at 10%. If there were no mixing of the syrup, then the syrup would be the same; that is, 28% at the top and 44% at the bottom. If there were perfect mixing of the syrup, then the syrup concentration at the time of inverting would be about 30% (see Figure 2). Even in the case of perfect mixing restratification will take place because the solids content of the product at the bottom (formerly at the top) would still be less than the concentration in the surrounding syrup. It is a known fact that this practice does reduce the time required for final equalization, probably primarily because there is some mixing of the syrup and a resulting reduction in the high sucrose concentration at the bottom of the jar. The authors hazard the opinion that the best time to invert the jars, with the object of reducing the time required for final equalization, is at about 1 week. This time is not critical; any time between 5 days and 2 weeks should give similar results. At 8 days the maximum loss of water by the product at the bottom of the jar has taken place, and, therefore, maximum product shrinkage. If the jar were inverted at this time, the product having 15% soluble solids would be placed in syrup at 31% soluble solids, and the product at 30% (now at the top) would be placed in syrup at 15% (assuming no mixing of the syrup). If there were perfect mixing, the syrup would be at some value between 15% and 32%, perhaps 20%. The product now at the top should fill out by gaining water at the much faster rate of the second phase of equalization, equalization between product and surrounding syrup which should take place in 6 to 8 days. There would be some further stratification because soluble solids leaving the product at the top would be in a lower density region and should fall toward the bottom of the jar. The exact details of final equalization, if the jars are inverted, will depend on the time at which the jar is inverted and the degree of mixing of the syrup.

Table 2 gives the pH in syrup and product at top and bottom of heated jars at several times from 64

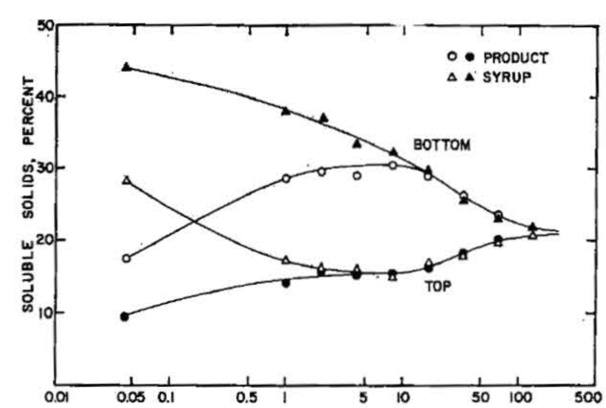


**Figure 4. Soluble solids concentration equalization in heat processed sweet fresh cucumber spears.**

[d] The diffusion probably proceeds according to an exponential function, and, theoretically, would reach equalization at infinite time.

min to 8 days after adding syrup; the data are averages of values from 3 jars. The largest pH difference found between top and bottom in both the syrup (difference in pH of 0.62) and product (difference in pH of 0.54) was at the first sampling time, 64 min. No pH measurements were made after the 8th day.

**TABLE 2**
**pH changes in syrup and cucumber spears after heat processing**

| Time, days after adding syrup | pH | | | |
|---|---|---|---|---|
| | Syrup | | Product | |
| | Top | Bottom | Top | Bottom |
| 0.04 | 3.93 | 3.31 | 4.13 | 3.59 |
| 1 | 4.06 | 3.54 | 4.11 | 3.69 |
| 2 | 4.02 | 3.60 | 4.05 | 3.66 |
| 4 | 4.09 | 3.70 | 4.03 | 3.73 |
| 6 | 4.03 | 3.73 | 4.07 | 3.75 |
| 8 | 4.02 | 3.71 | 4.04 | 3.75 |

Table 3 gives the acetic acid concentration in the syrup, percentage acid by volume, at top and bottom of heated jars at several times from 64 min to 128 days after adding syrup; the data are averages of values taken from 3 jars. The maximum difference found in the acetic acid concentration in the syrup between the top and bottom of the jar was at the first sampling time. Equalization of acetic acid concentration between top and bottom occurred at about 64 days after processing. The data given in Table 3 were not taken from the same jars as the data in Table 2; however, the pH and acetic acid concentration should be comparable unless there is lot-to-lot variation.

A limited number of tests were made using cucumber slices, pitted sour cherries and sliced peaches. Suffice it to say that these products stratified and then equilibrated at about the same rate as shown for cucumber spears.

Evidence has been presented for the existence of stratification in syrup-packed products. There remain the questions of why does stratification occur and what should be done about it?

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 occurs 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.

**TABLE 3**
**Syrup acetic acid concentration in heated sweet, fresh cucumber spears**

| Time, days after adding syrup | Percentage acetic acid[1] | |
|---|---|---|
| | Top | Bottom |
| 0.04 | 1.33 | 2.82 |
| 1 | 1.12 | 2.23 |
| 2 | 1.14 | 2.41 |
| 4 | 1.18 | 1.98 |
| 8 | 1.17 | 1.90 |
| 16 | 1.34 | 1.71 |
| 32 | 1.47 | 1.53 |
| 64 | 1.48 | 1.47 |
| 128 | 1.48 | 1.45 |

[1] By volume.

Since there is a region of high sucrose at the bottom of the jar, there will be some retardation of convection currents *(2)*. The jars could be agitated during the heating process; this practice would presumably improve the heat transfer characteristics and decrease process time requirements. However, any gain in process time must be offset against the increased cost of agitation; moreover, even if the jars were thoroughly agitated during the heating and cooling periods, the syrup in the jars would still stratify as soon as agitation is stopped because at that time the product and syrup soluble solids are not in equilibrium. After agitation is stopped, water leaving the product at the bottom of the jar would encounter a high density syrup and rise to the top of the jar.

## SUMMARY

These results indicate conclusively that when a high-moisture food product is placed in a sugar solution, the water leaving the product does not diffuse uniformly into the syrup throughout the jar, but instead rises to the top thereby giving rise to a density gradient. This stratification begins as soon as the syrup is added to the product. In one test with a heat processed sweet, fresh cucumber spear product, two minutes after adding the syrup, a difference of over 9% was found between top and bottom soluble solids concentrations in the syrup. This top-bottom difference in soluble solids concentrations continued to increase up to about one day after adding syrup. The soluble solids concentrations in the product lagged behind the concentrations in the syrup; appreciable differences persisted up to four days after adding syrup; equalization of soluble solids between the product and its surrounding syrup was reached at about eight days after adding the syrup, but final equalization throughout the jar was reached only after several months. Acetic acid concentrations and pH were also found to be different between top and bottom of the jars. There was no salt in the covering liquor used in these tests, but the authors think that salt would also stratify. It should be emphasized that stratification takes place during heat processing. Comparisons between heated and unheated jars of cucumber spears show that although both the top and bottom soluble solids concentrations in heated jars are lower than those in unheated jars at corresponding times up to an hour after addition of the syrup, the differences, and, therefore, the average gradients are about the same. Stratification during the heating period should retard convection. Agitation of the jars is discussed as a means of eliminating stratification during the heating period and, thereby improving heat transfer, but agitation is not recommended without qualification.

Arguments are presented to suggest that there are ways to minimize the time required for final equalization of soluble solids between syrup and product throughout the jar.

The present study has shown that during heat processing of syrup-packed products the water leaving the product selectively dilutes the syrup (sugar and acid). Given this fact, the question of heat destruction of microorganisms in syrup packs should be reexamined to take account of the constantly changing sugar and acid conditions to which these microorganisms are exposed during processing. In some regions of the jar the sugar and acid conditions may be significantly lower than were anticipated when the heat process was designed.

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