Progressive Freeze-Concentration of Tomato Juice

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Progressive freeze-concentration was applied to concentrate tomato juice. Effective partition constants of the solute between the solid and liquid phases were experimentally determined for total solid and potassium chloride (KCl)-equivalent salts. The partition constants were strongly dependent on the stirring rate at the ice front and the advance rate of that front. Increasing stirring rate and reducing advance rate of the ice front lowered the effective partition constant and improved freeze concentration performance. The partition constant was different between total solid and salts suggesting a different mechanism in the partition phenomena between the two components. Tomato juice of 4.3 wt% in solid content was concentrated up to 18.8 wt%. After the reconstitution of freeze concentrated tomato juice based on Brix, no substantial differences, except for salt content, were observed in acidity, vitamin C content, or color quality compared with before the concentration.

Freeze concentration has been applied to preconcentration of solute for analytical purposes (Matthews & Coggeshall, 1959; Shampiro, 1961), desalination, concentration of fruit juice (Omran & King, 1974; Deshpande *et al.*, 1982; Bayindirli *et al.*, 1993; Tannous & Lawn, 1981; Braddock & Marcy, 1985), concentration of dairy products (Hartel & Espinel, 1993; Hartel & Chung, 1993) and waste water treatment (Muller & Sekoulov, 1992; Slade & Dare, 1993; Matsuda & Kawasaki, 1997).

Freeze concentration is known to be the best method to concentrate liquid food for high retention of the flavor and thermally fragile compounds as compared with other techniques such as evaporation and membrane concentration. Freeze concentration, however, is also the most expensive method because of the high initial investment. In conventional freeze concentration (Huige & Thijssen, 1972), many small ice crystals are formed, transferred into a ripening vessel to be enlarged by the Ostwald ripening mechanism, then transferred into a washing column and separated from the mother solution after washing with water. In this method of suspension crystallization, the whole system is complex involving ice nucleation, ice crystal growth, and ice crystal separation so that the cost of the system is very expensive.

As an alternative way of freeze concentration, we have investigated progressive freeze-concentration (Bae *et al.*, 1994; Liu *et al.*, 1997), in which only a single ice crystal is formed as a sheet on a cooled surface in a freezing vessel immersed in coolant. Thus, the separation of ice crystal from the mother solution is much easier than the suspension crystallization method. This makes the system much simpler. We successfully applied progressive freeze-concentration to concentrate

model solutions containing glucose and Blue dextran (Liu *et al.*, 1998). We also theoretically analyzed the effective partition constant of solute between the ice and liquid phases in the progressive freeze-concentration by a concentration polarization model (Miyawaki *et al.*, 1998).

In the present paper, we applied progressive freeze-concentration to tomato juice, and evaluated its effect on juice quality.

Theoretical

Effective partition constant of solute (K) between the solid and liquid phases at the ice-liquid interface is defined as follows:

$$K = C_S / C_L \qquad (1)$$

where C_S is the solute concentration in the ice phase at the boundary and C_L is the solute concentration in the bulk liquid phase, where complete mixing is expected by the stirring. This parameter, K, determines the effectiveness of progressive freeze-concentration and can be experimentally determined by the following equation (Liu *et al.*, 1997):

$$(1 - K)\log(V_L / V_0) = \log(C_0 / C_L) \qquad (2)$$

where V_0 and V_L, respectively, are liquid phase volumes at the beginning and at an arbitrary time and C_0 and C_L, respectively, are solute concentrations in the liquid phase at the beginning and at an arbitrary time.

Materials and Methods

Materials Blue dextran (MW=2,000,000) was purchased from Sigma Chemical (St. Louis, Mo.). Tomato juice was supplied by Kagome Co. (Tokyo). All other chemicals were of reagent grade.

Progressive freeze-concentration The apparatus for progressive freeze-concentration was composed of a cylindri-

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cal sample vessel of stainless steel (48 mmϕ, 197.5 mmH), a cooling bath, and a driving system to plunge the sample vessel into the cooling bath ($-10°C$) at a constant speed (0.16-2.37 cm/h) in order to control the advance rate of the ice front, which grows upward from the bottom of the sample vessel. The sample vessel was equipped with a propeller inside to stir the solution at the ice-liquid interface (Liu *et al.*, 1997). When it was necessary to see inside, an acrylic vessel with a stainless steel bottom was used. In this case, the advance rate of the ice front was controlled only by the coolant temperature.

Tomato juice was first cooled to 0°C and poured into the sample vessel to start the freeze concentration. Prior to initiating this, a small amount of pure water was poured onto the bottom of the sample vessel to form an ice lining on the cooling surface and prevent supercooling at the initial moment of ice crystal formation. Initial supercooling negatively affects freeze concentration by increasing the amount of impurity in the ice crystal (Liu *et al.*, 1998; Shirai *et al.*, 1998). In sampling, the progressive freeze-concentration process was stopped and the solution and the ice phase were removed from the sampling vessel for assay. The amount of ice was measured volumetrically after melting. For data at a different sampling time, the entire procedure was repeated from the beginning.

Analytic procedure Total solid content was determined by drying a 5 ml sample in the oven at 135°C for 2 h. Concentration of salts was measured as KCl-equivalent salt by a conductivity meter (CM30S, TOA, Tokyo) calibrated with a standard KCl solution. Brix was measured by a refractometer (N-1E, Atago, Tokyo). Acidity was determined by the titration of the sample after filtration through paper (5A, Advantech Toyo, Tokyo). Vitamin C content was analyzed by the 2,6-dichloroindophenol method (AOAC, 1975) and color index was measured by a color meter (ND-Σ80, Nippon-Denshoku-Kogyo, Tokyo).

Results and Discussion

A typical result of the progressive freeze-concentration is shown in Fig. 1 for 0.05% Blue dextran (coolant at $-20°C$), 1% tomato juice (coolant at $-23°C$), and 5% toamato juice

(coolant at $-18°C$). Stirring rate was 1400 rpm in each case. It is clear that an ice crystal with high purity was obtained to make the freeze concentration effective both for Blue dextran and tomato juice under appropriate operating conditions.
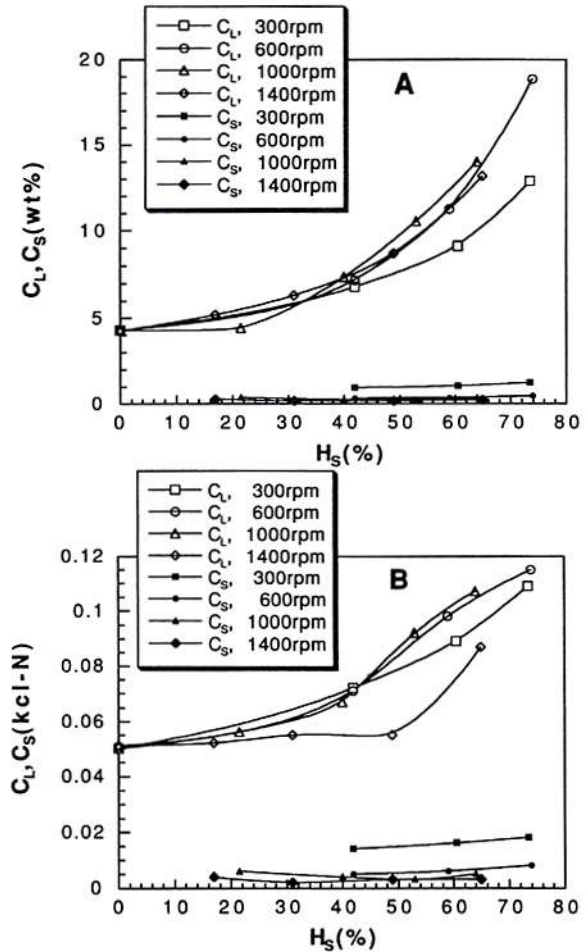
Fig. 2. Effect of stirring rate on change in concentrations of total solid (A) and salts (B) in solution phase (C_L) and ice phase (C_S) with increase in the ice fraction (H_S) in progressive freeze-concentration. Advance rate of ice front was fixed at 0.5 cm/h.

Blue dextran (0.05%)   **Tomato juice (1%)**   **Tomato juice (5%)**
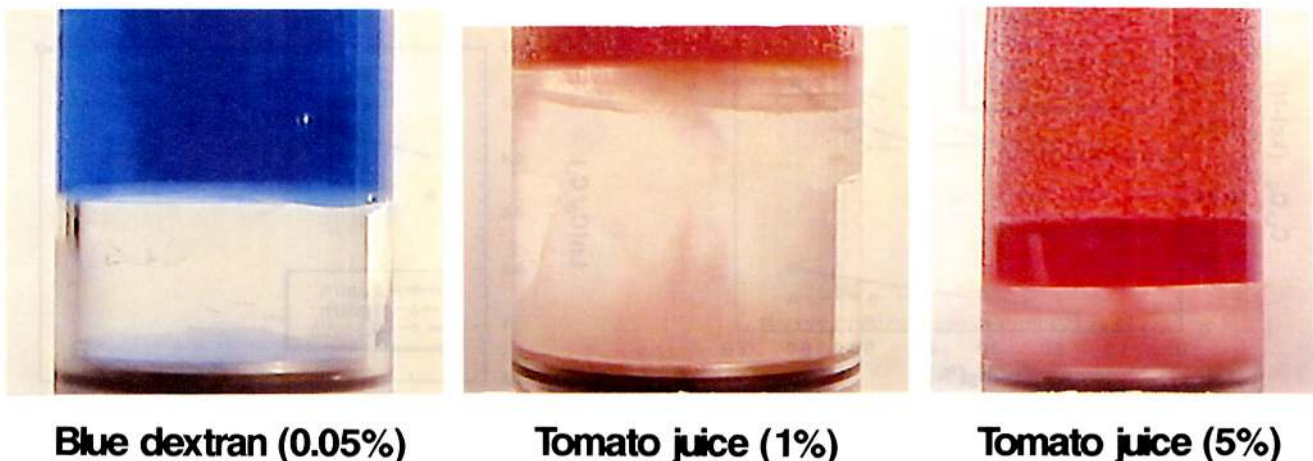
Fig. 1. Typical results of progressive freeze-concentration of 0.05% Blue dextran (A), 1% tomato juice (B), and 5% tomato juice (C).

Figure 2 shows the effect of stirring rate at the ice front on the change in concentrations of total solid (Fig. 2A) and KCl-equivalent salts (Fig. 2B) of tomato juice in the solution phase (C_L) and the ice phase (C_S) in progressive freeze-concentration with advance rate of ice front fixed at 0.5 cm/h. A large difference between C_L and C_S and increase in C_L with an increase in the ice fraction (H_S) were observed, showing the effectiveness of this technique to concentrate the juice. An increase in the stirring rate at the ice-liquid interface caused an increase in purity of the ice phase and subsequent higher efficiency of the freeze concentration.

Figure 3 shows the effect of the advance rate of ice front on the change in concentrations of total solid (Fig. 3A) and KCl-equivalent salts (Fig. 3B) in the solution and the ice phase in the progressive freeze-concentration with a fixed stirring rate of 1400 rpm. A decrease in the advance rate of the ice front caused an increase in the ice purity.

Figure 4 shows the plot according to Eq. (2) to obtain K for total solid (Fig. 4A) and salts (Fig. 4B) at a constant advance rate of the ice front of 0.5 cm/h with the stirring rate varied. A good linear relationship between $\ln(C_0/C_L)$ and $\ln(V_0/V_L)$ was obtained for total solid as was expected by Eq. (2). From the slope of linear lines in Fig. 4A, the effective

partition constant was obtained. At a stirring higher than 600 rpm, the slope of the plot was almost 1, which corresponds to K value of zero showing a good freeze concentration effect for solid content. The plots for salts in Fig. 4B, however, are scattered and the slopes were lower than 1, which corresponds to K value above zero. This means that salts are more easily incorporated into the ice phase at the ice front in the progressive freeze-concentration as compared with solid component. Halde (1979) pointed out that a smaller size solute is more easily incorporated into the ice phase than those of larger size in the progressive freeze-concentration.

Figure 5 shows a similar plot of $\log(C_0/C_L)$ against $\log(V_0/V_L)$ at a fixed stirring rate at 1400 rpm with the advance rate of the ice front varied. A good linear relationship was again obtained for total solid (Fig. 5A) but plots are a little scattered for salts (Fig. 5B). Figures 4 and 5 show that the higher stirring rate along with the slower advance rate of the ice front gives the better freeze concentration performance.

Figure 6 shows the effect of stirring rate on the effective partition constant for solid and salts with the advance rate of the ice front fixed at 0.5 cm/h. There are difference between the effective partition constant of total solid and that of salts, showing a difference in the mechanism of the partition phenomenon between the two components. In both cases, however, an increase in stirring rate decreased the partition
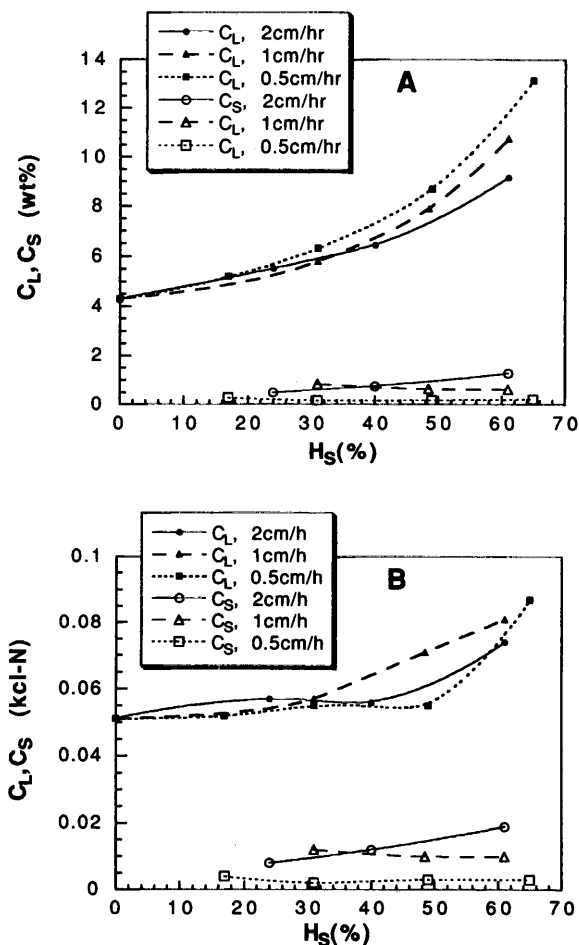

Fig. 3. Effect of advance rate of ice front on change in concentrations of total solid (A) and salts (B) in solution phase (C_L) and ice phase (C_S) with increase in ice fraction (H_S) in progressive freeze-concentration. Stirring rate was fixed at 1400 rpm.
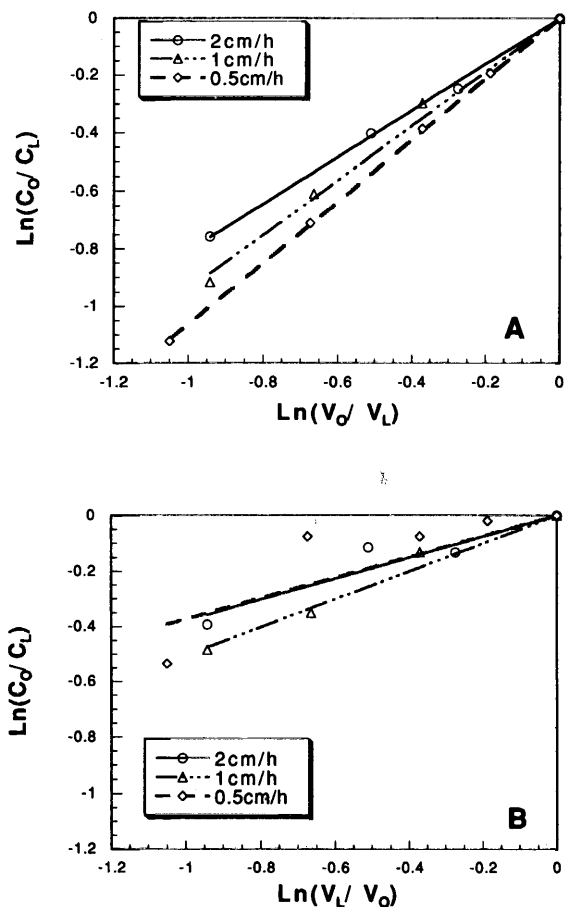
Fig. 4. Effect of stirring rate on the plot based on Eq. (2) to obtain K for total solid (A) and salts (B). Advance rate of ice front was fixed at 0.5 cm/h.

constant between the solid and liquid phases. According to the concentration polarization model (Miyawaki *et al.*, 1998), an increase in the stirring rate caused a decrease in the extent of concentration polarization due to rise in the mass

transfer at the ice front which reduced the partition constant. To increase the mass transfer at the ice front, ultrasonic radiation is also applicable (Matsuda & Kawasaki, 1997).

Figure 7 shows the effect of advance rate of the ice front on the effective partition constant at a fixed stirring rate of 1400 rpm. In this case again, the effective partition constants were
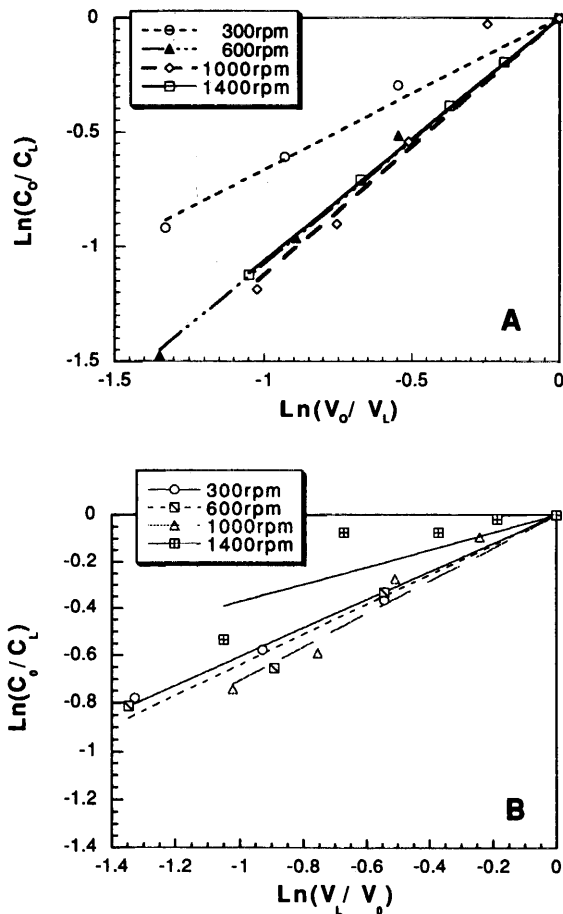

Fig. 5. Effect of advance rate of ice front on the plot based on Eq. (2) to obtain K for total solid (A) and salts (B). Stirring rate was fixed at 1400 rpm.
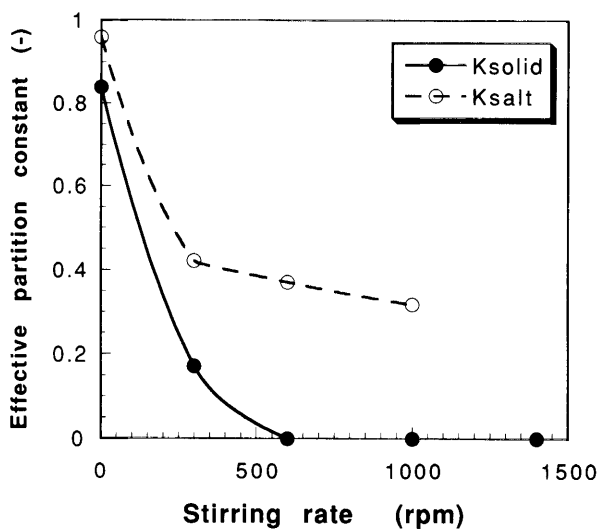

Fig. 7. Effect of advance rate of ice front on effective partition constant of solute between ice and liquid phases in progressive freeze-concentration. Stirring rate was fixed at 1400 rpm.

Table 1. Concentration of total solid content of tomato juice by progressive freeze-concentration.

Initial conc. (wt%)	Stirring rate (rpm)	Advance rate (cm/h)	H_s (%)	C_L (wt%)	C_s (wt%)
4.3	1400	2	61.8	9.17	1.28
4.3	1400	1	63.7	10.8	0.62
4.3	1400	0.5	68.5	13.2	0.21
4.3	1000	0.5	71.1	14.0	0.33
4.3	600	0.5	79.2	18.8	0.46
4.3	300	0.5	74.9	12.9	1.24
4.3	0	0.5	68.7	4.58	3.84
0.9	1400	0.5	80.3	4.6	0.0
0.5	1400	0.85	74.7	2.09	0.0

Fig. 6. Effect of stirring rate on effective partition constant of solute between ice and liquid phases in progressive freeze-concentration. Advance rate of ice front was fixed at 0.5 cm/h.
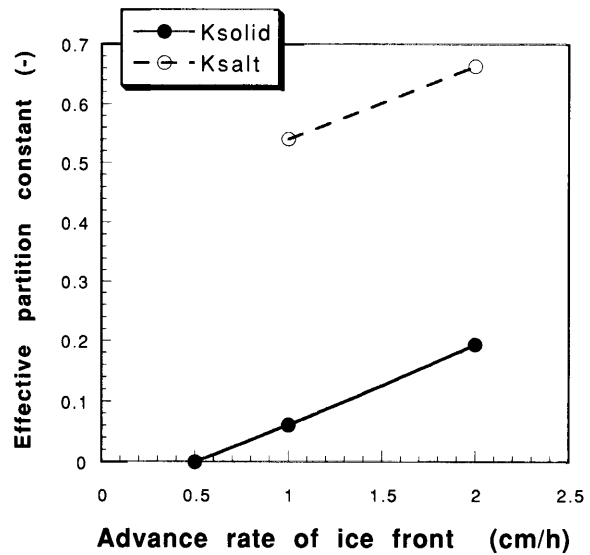
Table 2. Quality of reconstituted tomato juice after progressive freeze-concentration.

	Control	Reconstituted (1)[a]	Reconstituted (2)[b]
Brix (%)	2.8	2.8	2.8
Concentration ratio (−)	−	2.7	4.1
Conductivity (mS/m)	365	304	242
Acidity (%)	0.25	0.23	0.23
Vitamin C (mg%)	5.4	5.3	5.4
Color index			
L	24.1	22.2	22.1
a	5.28	5.76	5.94
b	13.1	11.7	11.7
a/b	0.4	0.49	0.51

[a]Freeze concentrated at u=0.5 cm/h and 1400 rpm.
[b]Freeze concentrated at u=0.5 cm/h and 600 rpm.

different between total solid and salts. An increase in the advance rate increased the partition constant of solutes between the ice and the liquid phases. The advance rate of the ice front affects the extent of concentration polarization and changes the partition constant (Miyawaki et al., 1998). The advance rate also affects the dendritic structure of the ice front (Miyawaki et al., 1992), which further influences the partition constant.

Table 1 summarizes the final results of the progressive freeze-concentration of tomato juice (4.3 wt%) along with those of diluted juice. In general, the slower advance rate of the ice front and the higher stirring rate at this front gave better results in the freeze concentration; the maximum concentration obtained was 18.8 wt% in solid content, a 4.4 fold concentration. This figure seems to be attractive for the practical applicability of the method. When the juice was diluted to 0.5 or 0.1%, the purity of ice increased to almost 0% in solid content, showing that the progressive freeze-concentration favors a diluted system for its effectiveness (Miyawaki et al., 1998).

Table 2 shows a comparison of analytic results for tomato juices before and after the concentration-reconstitution based on Brix value. Although the salt content was reduced because of its incorporation in the ice, no substantial differences were observed in acidity, vitamin C content, or color index after the concentration-reconstitution, showing the practical applicability of the present method to the concentration of tomato juice.

Progressive freeze-concentration was proved to be effective for the concentration of tomato juice with a good concentration ratio and retention of vitamin C, color quality etc. after reconstitution. Progressive freeze-concentration is believed to be an alternative to the suspension crystallization method (Huige & Thijssen, 1972) because of its simplicity in separating ice crystals from the mother solution, thus substantially reducing the cost of the apparatus. The design of the present system, however, is not suitable for scaling up or high productivity because of the limited cooling surface area. To improve this, a tubular reactor design with a falling film inside (Muller & Sekoulov, 1992; Flesland, 1995; Shirai et al., 1998) would be preferable as it would increase the cooling surface area of the system.

References

AOAC. (1975). Official Method of Analysis of the Association of Official Analytical Chemists. p. 829.

Bae, S.K., Miyawaki, O. and Arai, S. (1994). Control of freezing front structure and its effect on the concentration efficiency in progressive freeze-concentration. Teion Seibutsu Kogaku Kaishi, 40, 29-32 (in Japanese).

Bayindirli, L., Ozilgen, M. and Ungan, S. (1993). Mathematical analysis of freeze concentration of apple juice. J. Food Eng., 19, 95-107.

Braddock, R.J. and Marcy, J.E. (1985). Freeze concentration of pineapple juice. J. Food Sci., 50, 1635-1639.

Deshpande, S.S., Bolin, H.R. and Salunkhe, D.K. (1982). Freeze concentration of fruit juices. Food Technol., May, 68-82.

Flesland, O. (1995). Freeze concentration by layer crystallization. Drying Technol., 13, 1713-1739.

Halde, R. (1979). Concentration of impurities by progressive freezing. Water Res., 14, 575-580.

Hartel, R.W. and Espinel, L.A. (1993). Freeze concentration of skim milk. J. Food Eng., 20, 101-120.

Hartel, R.W. and Chung, M.S. (1993). Contact nucleation of ice in fluid dairy products. J. Food Eng., 18, 281-296.

Huige, N.J.J. and Thijssen, H.A.C. (1972). Production of large crystals by continuous ripening in a stirred tank. J. Crystal Growth, 13/14, 483-487.

Liu, L., Miyawaki, O. and Nakamura, K. (1997). Progressive freeze-concentration of model liquid food. Food. Sci. Technol. Int. Tokyo, 3, 348-352.

Liu, L., Fujii, T., Hayakawa, K. and Miyawaki, O. (1998). Prevention of initial supercooling in progressive freeze-concentration. Biosci. Biotech. Biochem., 62, 2467-2469.

Matsuda, A. and Kawasaki, K. (1997). Concentration and separation of impurities in liquid by freezing with supersonic radiation. J. Chem. Eng. Jpn., 30, 825-830.

Matthews, J.S. and Coggeshall, N.D. (1959). Concentration of impurities from organic compounds by progressive freezing. Anal. Chem., 31, 1124-1125.

Miyawaki, O., Abe, T. and Yano, T. (1992). Freezing and ice structure formed in protein gels. Biosci. Biotech. Biochem., 56, 953-957.

Miyawaki, O., Liu, L. and Nakamura, K. (1998). Effective partition constant of solute between ice and liquid phases in progressive freeze-concentration. J. Food Sci., 63, 1-3.

Muller, M. and Sekoulov, I. (1992). Waste water reuse by freeze concentration with a falling film reactor. Water Sci. Technol., 26, 1475-1482.

Omran, A.M. and King, C.J. (1974). Kinetics of ice crystallization in sugar solutions and fruit juices. AIChE J., 20, 795-803.

Shampiro, J. (1961). Freezing-out, a safe technique for concentration of dilute solutions. Science, 133, 2063-2064.

Shirai, Y., Wakisaka, M., Miyawaki, O. and Sakashita, S. (1999). Effect of seed ice on formation of tube ice with high purity for a freeze waste water treatment system with a bubble-flow circulator. Water Res., in press.

Slade, A.H. and Dare, P.H. (1993). Measuring maximum specific growth rate and half saturation coefficient for activated sludge systems using a freeze concentration technique. Water Res., 27, 1793-1795.

Tannous, R.I. and Lawn, A.K. (1981). Effects of freeze-concentration on chemical and sensory qualities of apple juice. J. Food Sci. Technol., 18, 27-29.