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# WHEY BASED NONFAT DRIED MILK SUBSTITUTES FOR BREADMAKING[1]

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## ABSTRACT

*A number of commercial whey products were evaluated at the 4% (flour basis) level, using a straight dough pup loaf baking procedure. The loaf volume and crumb texture of the breads were compared to controls made with and without nonfat dried milk (NFDM). Untreated sweet whey produced poor quality bread, but demineralized whey, whey protein concentrates, and a blend of whey plus NFDM plus soy flour gave loaf volumes and crumb grains equal to the NFDM controls. Potassium bromate requirements increased as the protein content of the whey product increased. Lactose is more concentrated in whey than in NFDM, but lactose concentration does not appear to cause the loaf depression. Contrary to literature reports with an acid whey, use of 0.2% diammonium phosphate (flour basis) alone does not totally replace NFDM in terms of both loaf volume and crumb structure. However, diammonium phosphate can correct for most of the suppressant activity of sweet whey. A correlation was found between the ash to protein ratio and baking performance of products.*

## INTRODUCTION

Nonfat dry milk (NFDM) traditionally has been included as an ingredient in bread. There are several reasons for using milk, including improved nutritional properties of the product, improved dough handling characteristics, improved bread quality (color, flavor, crumb color, and texture), and increased loaf volume (Ling *et al.* 1977; Volpe and Zabik 1975; Meade 1972). Recently, the utilization of NFDM has decreased and the utilization of various whey-based milk replacers has increased (Mann 1982; Hugunin 1980).

There is an immense variety of whey products available to bakers today.

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The purpose of this study was to examine a number of commercial whey products (Table 1). The products were tested at the 4% level (flour basis) with optimum bromate. Performance was measured by loaf volume and crumb texture and compared with control loaves made with NFDM.

Table 1. Baking performance of whey products tested[a/]

| Product Description | $KBrO_3$ Requirement | Performance | |
|---|---|---|---|
| | | Overall | Volume |
| A - Sweet whey | 20 | Poor | Low |
| B - Treated whey (nonhygroscopic) | 10 | Poor | Low |
| C - Delactosed whey | 10 | Poor | Low |
| D - Demineralized (25%) whey | 10 | Poor | Low |
| E - Demineralized (90%) whey | 10 | Good | Good |
| F - Protein concentrate (34.5% protein) | 20 | Good | Good |
| G - Protein concentrate (33.1% protein) | 20 | Good | Good |
| H - Partial delactosed whey | 20 | Poor | Low |
| I - Whey plus soyflour | 15 | Poor | Low |
| J - Whey, soyflour, buttermilk | 20 | Poor | Low |
| K - Whey, NFDM, Soyflour[b/] | 15 | Good | Good |
| L - Whey, soyflour, $CaSO_4$[b/] | 10 | Good | Good |
| M - Whey, soyflour, $CaSO_4$[b/] | 10 | Good | Good |
| N - Whey, soyflour, NFDM[b/] | 10 | Poor | Low |
| O - Whey, cornflour, Na caseinate | 10 | Poor | Low |
| P - Whey, $Na_2CO_3$, NFDM, Na casinate, $CaHPO_4$ | 10 | Poor | Low |
| Q - NFDM (control) | 30 | Good | Good |

a/ All products were tested at 4% addition flour basis
b/ Ingredient listing the same but different suppliers

## MATERIALS AND METHODS

Whey fractions used in this study included samples from four different U.S. manufacturers. The flour used was a malted hard red winter flour (moisture = 12.9%, protein = 12.4%).

A straight dough pup loaf procedure was used. Doughs contained 100 g flour (14% moisture basis), 6 g sucrose, 1.5 g NaCl, 4 g shortening, 4 g nonfat dry milk or whey-based substitute, optimum potassium bromate, optimum water, and 0.75 g Fermipan yeast (Gist-Brocades NU), which is equivalent to 2.0 g bakers compressed yeast (Bruinsma and Finney 1981). Doughs were mixed to minimum mobility and fermented at 30°C and 85% relative humidity for 180 min. Punches were at 105 to 155 min. After 55 min proof the loaves were baked at 218°C for 24 min. Loaf weights and volumes were determined immediately after baking. After cooling completely, loaves were sliced and scored. Scoring involves visually examining the grain of the cut

loaf of bread. When the bread contains the optimum level of oxidants the grain will be elongated and uniform. Loaf containing insufficient oxidant will be "green" or have small round cells with no elongation. Overoxidized loaves have grains with large open cells and a very uneven appearance.

## RESULTS AND DISCUSSION

The potassium bromate requirement, in general, increased as the protein content of the milk solids replacer increased. The greatest bromate requirement, 30 ppm, was with the NFDM with 35.9% protein (Table 1 and 2). The optimum bromate for whey protein concentrates with 34.5% and 33.1% protein (F and G) was 20 ppm, while 15 ppm bromate was optimum for the partially delactosed whey (H) with 20% protein and 10 ppm bromate or less was required for the remaining samples with approximately 13% protein.

Whey (A) by itself produced a poor loaf of bread with low volume. When 90% demineralized whey (E), whey protein concentrates (F and G), or a blend of whey plus NFDM plus soy flour (K) were used the volumes and crumb textures were comparable to the NFDM control. Another blend of whey plus NFDM plus soy flour (N), which contained different proportions of components, was unsatisfactory.

Whey mixed with soy flour and calcium sulfate (L and M) produced slightly improved loaves compared to whey, as did a mixture of whey, sodium carbonate, NFDM, sodium caseinate, and calcium phosphate (P). There seems to be little logic to the selection of useful whey additives except that the closer one approaches NFDM, the better the performance.

Previous work (Ling *et al.* 1976, 1977 and Hoseney and Ling 1977) in which milk solids were fractionated by isoelectric precipitation at pH 4.5 and dialyzed, showed that the whey fraction was responsible for the increased loaf volume produced when NFDM was incorporated into bread. The protein precipitated under such conditions is essentially total casein and free of inorganic ions. Commerical sweet whey, as used in this study, is the result of rennin precipitation at pH 6.15 (Webb and Johnson 1965). Under

Table 2. Chemical analysis of milk and whey products

| Product | Protein % | Carbohydrate % | Fat % | Ash % | Moisture % | pH | Ash Protein |
|---|---|---|---|---|---|---|---|
| Q - NFDM | 35.9 | 52.3 | 0.8 | 8.0 | 3 | | 0.22 |
| A - Sweet whey | 12.7 | 71.3 | 1.1 | 8.0 | 4.5 | | 0.63 |
| H - Partial delactosed | 20 | 54 | 2 | 18 | 3 | 7.0 | 0.90 |
| F - Whey prot. concn. | 34.5 | 52 | 4 | 6 | 3.5 | 6.5 | 0.17 |
| D - Demineralized (25%) | 13.0 | 74.9 | 0.9 | 5.5 | 4.5 | 6.5 | 0.42 |
| E - Demineralized (90%) | 13-15 | 80-85 | 1-1.5 | 1-1.25 | 4-5 | 6.5 | 0.08 |

those conditions, more of the salts are retained with the curd than with acid formed curd. Therefore, sweet whey contains lower ash than does acid whey. This is probably the cause for the different performances of sweet whey (A) and acid whey (Ling *et al.* 1976).

The whey protein concentrates tested (F and G) both performed well, giving loaf volumes and grains similar to NFDM control loaves. It is possible that the heat treatment of the sweet whey protein concentrates (F and G) and the sweet whey (A) could account for the difference in baking performance. It is also possible that the difference in protein content is also a factor.

Lactose is more concentrated in sweet whey (73.5%) than in NFDM (35.9%) and, therefore, might be a key to the low volume of sweet whey (A) breads. However, delactosed whey (C) gave the worst performance at the 4% level of all the products tested. A product with a high lactose content (F) produced loaves comparable to those containing NFDM. It thus appears that concentration of lactose does not cause in the loaf depressant effect.

Although the concentration of inorganic salts, as expressed by ash content, does not increase during the conversion of milk to whey, there is a considerable increase in the ratio of salts to protein content. In milk there is a close association between the proteins (especially casein) and inorganic salts. It may be that the increase in "free" salts is a detrimental factor. The ash to protein ratio for several products is shown in Table 2. There is a correlation between this ratio and baking performance. Samples E and F have ash to protein ratios below that for NFDM and show comparable baking performances. Sample D, with a ratio between NFDM and whey (A) produced loaves comparable to the no milk sample, whereas sweet whey (A) produced inferior loaves. Sample H, showing the highest ash to protein ratio, produced more inferior loaves than the sweet whey (A).

Ling *et al.* (1976) showed that loaf volume could be maintained if NFDM was replaced by ammonium salts in the form of diammonium phosphate at the 0.2% level. Under the present experimental conditions the loaf volume could be maintained through the use of 0.2% diammonium phosphate at the same bromate level as used with the 4% NFDM (30 ppm). However, the loaves were over-oxidized. The optimum bromate level was considered to be 20 ppm with a slight decrease in loaf volume (Table 3). It must be concluded, therefore, that 0.2% diammonium phosphate cannot totally replace 4% NFDM in terms of both loaf volume and crumb structure.

When sweet whey (A) was supplemented with 0.2% diammonium phosphate the optimum bromate was judged to be equivalent to that required for NFDM. The volume was slightly lower than the control but significantly greater than for sweet whey alone. Therefore, most of the suppressant activity of sweet whey (A) can be corrected by diammonium phosphate supplementation.

Table 3. Baking data with diammonium phosphate

| | Potassium Bromate ppm | Loaf Vol. cc |
|---|---|---|
| Control (no milk) | 10 | 836 |
| 4% NFDM | 30 | 868 |
| 0.2% $(NH_4)_2HPO_4$ | 20 | 849 |
| 0.2% $(NH_4)_2HPO_4$ | 30 | 866 |
| 0.2% $(NH_4)HPO_4$ + 4% Whey (A) | 30 | 854 |
| 4% Whey (A) | 20 | 813 |

The greatest suppressant activity was found with delactosed whey (C). Table 4 lists the results of a test bake series in which levels of delactosed whey and potassium bromate were varied. At the higher levels of delactosed whey and at the levels of bromate found optimum for doughs containing diammonium phosphate, the delactosed whey (C) had a severe volume-reducing effect. When 0.5% delactosed whey (C) was baked with 30 ppm potassium bromate the loaf volume and grain approached that of the NFDM control. At levels greater than 1% delactosed whey (C), grain structure tended to be somewhat disorganized and optimum bromate levels difficult to assess. It may be that much higher levels of oxidant are necessary.

Because whey products containing a high lactose concentration (E)

Table 4. Baking data for combinations of delactosed whey and diammonium phosphate

| Ingredient | Potassium Bromate ppm | Loaf Volume cc |
|---|---|---|
| NFDM (4%), control | 30 | 900 |
| $(NH_4)_2HPO_4$ (0.2%) | 20 | 865 |
| $(NH_4)_2HPO_4$ plus | | |
| Delactosed whey (C, 0.1 g) | 15 | 847 |
| (0.2 g) | 15 | 840 |
| (0.5 g) | 30 | 902 |
| (1.0 g) | 40 | 851 |
| (2.0 g) | 40a/ | 784 |
| (3.0 g) | 20a/ | 708 |
| (4.0 g) | 20a/ | 673 |

a/ Optimum Potassium bromate level could not be determined

showed good baking performance, it was of interest to observe the effect of lactose per se when adequate levels of ammonium and phosphate ions were present (Table 5). Lactose levels up to 2 g, equivalent to the concentration in 4 g NFDM, do not have any detrimental effects upon loaf volume or crumb structure. At higher levels, equivalent to the concentration when 4 g whey are added, loaf volume shows a slight decrease. Complete replacement of NFDM by lactose reduces volume further, but the decrease was not dramatic. Lactose concentration is unlikely to be a major factor responsible for the adverse effect of sweet whey as a milk solids replacer.

Another fraction of whey tested was a commercial whey permeate. The permeate would be expected to contain vitamins, minerals, and lactose. As might be expected, at the 4% level of permeate dough fermentation was retarded. The permeate, at a 2% level, required less oxidant than did the control and also gave a lower loaf volume (Table 6). When the dough was overoxidized (30 ppm) the loaf volume approached that of the control.

Table 5. Baking data with lactose

| Level of Lactose | Potassium Bromate ppm | Loaf Volume cc |
|---|---|---|
| NFDM (4%) | 30 | 900 |
| 1.0 g | 20 | 881 |
| 2.0 g | 20 | 883 |
| 3.0 g | 20 | 845 |
| 4.0 g | 20 | 822 |

Table 6. Baking data for whey permeate

| Sample | $KBrO_3$ ppm | Loaf Volume cc | Grain |
|---|---|---|---|
| Control | 20 | 920 | optimum |
| Permeate (2%) | 0 | 832 | green |
| | 10 | 863 | optimum |
| | 20 | 885 | slightly over-oxidized |
| | 30 | 893 | over-oxidized |

## SIGNIFICANCE

Milk, generally NFDM, has traditionally been an ingredient in bread. Heat-treated NFDM not only improves the crust color and nutritional quality of bread but also improves the loaf volume. In recent years the cost of NFDM has increased substantially. Therefore, bakers have looked for a cheaper milk product to add to their bread. Whey appears to fill the bill as it is plentiful and relatively cheap.

However, as detailed herein, there are many whey products and mixtures of whey on the market. Some of the products are beneficial in breadmaking while others are detrimental.

## ACKNOWLEDGMENT

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# ROLE OF COFACTORS IN BREAKDOWN OF TMAO IN FROZEN RED HAKE MUSCLE

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## ABSTRACT

*Previously indicated results that cofactor concentrations were the rate-limiting factor in the production of DMA in frozen red hake muscle were confirmed. Both the Fe-reducing agent (ascorbate, cysteine) and the flavin-NADH systems which had been previously shown to be effective* in vitro, *were demonstrated to also function in minced muscle and in reconstituted muscle, i.e., muscle from which the low molecular weight fraction had been removed. The evidence implies that an oxidation-reduction cycle of Fe is involved in the breakdown of TMAO to DMA. Activity with the flavin system is greatly increased in the presence of glucose oxidase and glucose which would remove* $O_2$ *from the system.* $Fe^{+2}$ *was effective in increasing DMA production under all conditions, whereas* $Fe^{+3}$ *was effective only in the presence of reducing agents and/or anaerobic conditions. Enzymes capable of destroying cofactors when added to minced muscle tissue before frozen storage inhibited the rate of formation of DMA. The percentage of formaldehyde produced which was bound (unreactive to the Nash reagent) was much higher in minced muscle than in reconstituted muscle, indicating that a large fraction of the formaldehyde produced reacts with the low molecular weight fraction.*

## INTRODUCTION

A rapid textural toughening on frozen storage is typical of the flesh of fish from the gadoid family. It has been hypothesized that this toughening comes about via degradation of trimethylamine oxide (TMAO) by an endogenous enzyme with the production of dimethylamine (DMA) and formaldehyde. The latter is believed to act as a crosslinking agent forming extensive three-dimensional networks of the proteins which produce the toughness (Castell

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*et al.* 1973a). The texture of red hake has been shown to deteriorate especially rapidly and could be a basic drawback in the development of this underutilized species (Dyer and Hiltz 1974).

In earlier work from our laboratory we studied the removal of trimethylamine oxide and soluble protein (a possible measure of enzyme) from red hake muscle tissue by diffusion processes (Landolt and Hultin 1981). Data from that work indicated that under some conditions, neither soluble proteins nor TMAO were rate-limiting factors in the breakdown of TMAO during frozen storage of the flesh.

At least two major independent cofactor systems may be involved in the catalysis of TMAO breakdown to DMA and formaldehyde *in situ* (Phillippy 1983; Parkin 1983). One of these is flavin, the efficacy of which is greatly improved by the presence of NADH. The second system requires iron in either the ferrous or ferric state, and a reducing agent such as ascorbate or cysteine although the kinetics with the two are quite different. The flavin-NADH system in isolated systems is markedly inhibited by oxygen. The iron-reducing agent system on the other hand is not affected by the amount of $O_2$ present in the system.

In the experiments described here we have evaluated the effect of both these cofactor systems in red hake tissue. We have utilized both minced muscle and minced muscle from which the soluble low molecular weight components have been largely removed while maintaining the high molecular weight soluble components, i.e., reconstituted muscle.

## MATERIALS AND METHODS

### Materials

Fresh red hake (*Urophycis chuss*) were purchased from a local fish distributor in Gloucester, Massachusetts. They were kept on ice during transport to the laboratory and while being prepared for subsequent storage.

The fish were skinned and filleted with as little damage to the muscle as possible. They were packaged in 10x14 inch polyethylene bags and stored at −80°C. Appropriate amounts of fish fillets were withdrawn periodically for mincing.

Flavin mononucleotide (FMN), phospholipase $A_2$, ascorbate oxidase, NAD nucleosidase (NADase), and glucose oxidase were purchased from Sigma Chemical Company. The glucose oxidase as purchased contained a level of catalase sufficient to degrade all of the $H_2O_2$ formed by the glucose oxidase. Ascorbic acid and cysteine were obtained from Fisher, NADH from Boehringer-Mannheim, and TMAO from Eastman Kodak. All other chemicals were the purest available commercially.

## Methods

**Preparation of Minced Muscle.** Whole fish fillets were minced in a Rival electric meat grinder. The minced muscle was mixed thoroughly to insure a homogeneous batch. Mixing of the additive solution into the minced muscle was done manually with 150 circular strokes. A dye solution was used initially to determine that good homogeneity was achieved in the minced muscle. The concentrations of the additives are expressed on the basis of the water content of the samples. Additives in solution were incorporated into portions of the minced tissue while an amount of deionized, distilled water equal in volume to that added to the experimental sample was added to serve as a control. After thorough mixing, 6 50-g samples were withdrawn, packed in Whirl-pak bags, and stored frozen until analysis. For each experimental run, all samples were taken from the same batch of minced muscle.

**Preparation of Reconstituted Muscle.** Minced tissue was centrifuged for 16 h at 35,000 rpm using a 40-rotor in a Beckman L6-65B preparative ultracentrifuge. The "press juice" was decanted, while the particulate fraction was homogenized and washed twice by centrifugation in 0.15 M KCl in a 10:1 (v/w) ratio (ca 4 liters) based on the initial weight of the muscle (i.e., ca 400 g). The original fraction ("press juice") was dialyzed in Spectrapor membrane tubing (MW cut-off at 6,000-8,000) to remove smaller molecular weight compounds from the larger molecular weight solubles (mostly proteins). Dialysis was performed with at least two changes of deionized, distilled water for 16 h at 6-8°C. Dialysates were discarded.

The washed solid and dialyzed liquid fractions were combined, giving rise to a minced red hake muscle minus the small molecular weight solubles. Aliquots of this mixture were divided into two batches, to one of which was added the metabolite, while to the other was added an equal volume of distilled water, thus serving as the control. TMAO was added to both since it was expected to have been removed during the washing treatment. A flow diagram for the preparation is given in Fig. 1.

The samples were then handled in a manner similar to that for the minced muscle.

**Analysis for DMA and Formaldehyde.** A 50 g sample was homogenized in 100 ml of 10% trichloroacetic acid and 50 ml of deionized, distilled water for 1 min. The sample was then filtered, and aliquots taken for assay for DMA and formaldehyde. The modified (Dowden 1930) copper-dimethyldithiocarbamate colorimetric procedure of Dyer and Mounsey (1945) was used to assay for DMA. Free formaldehyde was determined by the procedure described by Castell and Smith (1973) involving the Nash reagent (Nash 1953). Based on the premise that DMA and formaldehyde are produced on an equimolar basis from the breakdown of TMAO, bound formaldehyde was

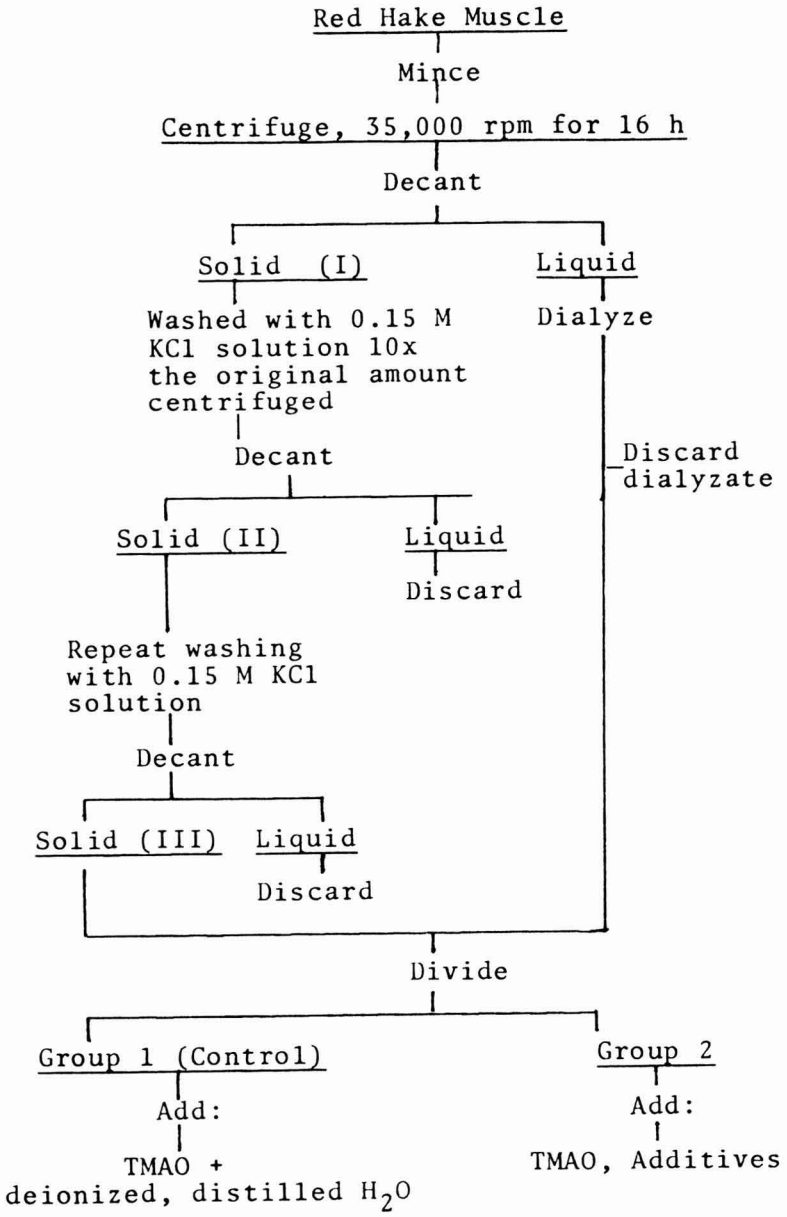


FIG. 1. FLOWSHEET FOR THE PREPARATION OF RECONSTITUTED MUSCLE

calculated as the difference between the determined values for DMA and free formaldehyde.

**Analysis for Water.** Water was determined by air-drying in an oven at 100°C until a constant weight was reached.

**Statistical Analysis.** The absolute values for DMA content were analyzed for each batch using the two-way analysis of variance with the additives and weeks of storage as variables. The DMA values in each batch were tested for normality at the 5% level using the Kolmogorov-Smirnov Statistic prior to performing analysis of variance. Where normal distribution was not apparent, the absolute values were transformed by taking their natural logarithms and testing these values instead. Whenever normality was shown at the 5% level after transformation of the DMA values, subsequent analysis of variance was done on the transformed values. The additives in each batch were compared to the control to determine whether they showed significant effects (Dwass 1970).

## RESULTS

Table 1 shows the effect of the iron-reducing system on the production of DMA in frozen minced red hake muscle with both $Fe^{+2}$ and $Fe^{+3}$ The addition of $Fe^{+2}$ by itself caused an increase in production of DMA while the addition of $Fe^{+3}$ did not. Ascorbate significantly increased the effectiveness of the iron in either the ferrous or ferric state while cysteine had a minimal accelerating effect on DMA production. There was no improvement when ascorbate and cysteine were added together with the iron compared to that of the ascorbate-Fe alone. Results of similar experiments with reconstituted muscle, i.e., that from which the low molecular weight substances had been removed, are shown in Table 2. An accelerating effect of $Fe^{+2}$ was small but was consistently observed. As in the case with the minced muscle, $Fe^{+3}$ did not have any effect on the formation of DMA. The presence of ascorbate again accelerated the formation of DMA in the presence of $Fe^{+2}$ and $Fe^{+3}$. Although the change in absolute values was greater with $Fe^{+3}$, the percentage increase was greater with $Fe^{+2}$. It was never possible between given sets of experiments to get control samples which showed exactly the same rate of DMA production. There appeared to be a greater effect of cysteine with both $Fe^{+2}$ and $Fe^{+3}$ in the frozen, reconstituted red hake muscle than there had been in the frozen minced red hake muscle (Table 1). Again, there was little or no increase in DMA formation on adding cysteine to the Fe-ascorbate system. The effect of cysteine with $Fe^{+2}$ was greater than with $Fe^{+3}$.

Table 1. DMA formation in frozen minced red hake muscle in the presence of ascorbic acid, cysteine and iron

| Additions | DMA, μmoles per 100 g original tissue | | |
|---|---|---|---|
| | $Fe^{+2}$ | $Fe^{+3}$ | |
| | 1 week | 1 week | 2 weeks |
| None (control) | 203 | 313 | 422 |
| Fe | 573 | 305 | 418 |
| Fe, ascorbic acid | 1257 | 1005 | 1550 |
| Fe, cysteine | 657 | 305 | 752 |
| Fe, ascorbic acid, cysteine | 897 | 835 | 2017 |

The following concentrations were used: $FeCl_2$ or $FeCl_3$, 1mM; ascorbic acid, 0.5 mM; cysteine, 0.5 mM. Storage was at −7°C. The DMA contents of the "zero time" samples were 143 and 140 μmoles per 100 g sample for the $Fe^{+2}$ and $Fe^{+3}$ experiments, respectively.

All treatments were significantly different from the control ($p < 0.05$) over the total time period evaluated with the exception of that involving the addition of $Fe^{+3}$ only. The data from the experiments using $Fe^{+2}$ were from a normal population and were analyzed directly. The data from the experiments using $Fe^{+3}$ were from a normal population after transformation to the logarithmic values.

The data in Table 3 were obtained from similar experiments as that in Table 2 except that glucose oxidase and glucose were added to the samples. This was done to reduce the oxygen content of the tissue. As mentioned above, the glucose oxidase preparation contained more than sufficient catalase to remove the hydrogen peroxide produced by the glucose oxidase reaction. The accelerating effect of $Fe^{+2}$ on the rate of DMA production was enhanced under the anaerobic conditions of this experiment compared to those described in Table 2, while there was still no effect on DMA formation by $Fe^{+3}$ alone. Ascorbate again accelerated the reaction with both $Fe^{+2}$ and $Fe^{+3}$. On both an absolute basis as well as a percentage change basis, the effect of ascorbate under anaerobic conditions was greater with $Fe^{+3}$ than it was with $Fe^{+2}$. There was no enhancing effect of cysteine on the $Fe^{+2}$ system com-

Table 2. DMA formation in frozen reconstituted red hake muscle in the presence of ascorbic acid, cysteine and iron

| Additions | DMA, μmoles per 100 g original tissue | | | |
|---|---|---|---|---|
| | $Fe^{+2}$ | | $Fe^{+3}$ | |
| | 1 week | 2 weeks | 1 week | 2 weeks |
| TMAO (control) | 15 | 29 | 53 | 96 |
| TMAO, Fe | 21 | 37 | 56 | 94 |
| TMAO, Fe, ascorbic acid | 130 | 285 | 255 | 518 |
| TMAO, Fe, cysteine | 125 | 162 | 81 | 148 |
| TMAO, Fe, ascorbic acid, cysteine | 120 | 170 | 288 | 628 |

Conditions used were the same as described in the footnote to Table 1. TMAO was added at a level of 70 mM to replace that removed by extraction and dialysis. The DMA contents of the "zero time" samples were 10 and 30 μmoles per 100 g original tissue for the $Fe^{+2}$ and $Fe^{+3}$ experiments, respectively.

The data in this table were not from a normal population either directly or after transformation to logarithmic values. Thus, it was not possible to perform analysis of variance on the data.

pared with the $Fe^{+2}$ alone, whereas there was an enhancing effect with $Fe^{+3}$. The activity in the latter case was brought up to that of the $Fe^{+2}$ when used by itself.

The effect of adding the FMN-NADH system in the formation of DMA in frozen minced red hake muscle tissue is shown in Table 4. Since it has been demonstrated in vitro that this system is strongly inhibited by the presence of oxygen (Parkin 1983; Phillippy 1983), the effectiveness of the flavin-NADH combination was evaluated in the presence and absence of glucose oxidase/glucose which presumably would function to reduce and/or eliminate the oxygen content of the tissue. DMA production was stimulated with no additives other than glucose and glucose oxidase. The effect of FMN and NADH in the absence of the oxygen utilizing system was slight. On the

Table 3. DMA formation in frozen reconstituted red hake muscle in the presence of ascorbic acid, cysteine and iron with glucose oxidase/glucose

| Additions | DMA, μmoles per 100 g original tissue | | | |
|---|---|---|---|---|
| | $Fe^{+2}$ | | $Fe^{+3}$ | |
| | 1 week | 2 weeks | 1 week | 2 weeks |
| TMAO (control) | 36 | 46 | 33 | 36 |
| TMAO, Fe | 106 | 120 | 32 | 39 |
| TMAO, Fe, ascorbic acid | 178 | 362 | 340 | 510 |
| TMAO, Fe, cysteine | 79 | 115 | 84 | 125 |
| TMAO, Fe, ascorbic acid, cysteine | 165 | 292 | - | - |

Conditions used were the same as described in the footnote to Table 2. In addition glucose was added to a final concentration of 13 mM, and 9 units of glucose oxidase were added per ml of retentate from the dialysis procedure. The DMA contents of the "zero time" samples were 21 and 24 μmoles per 100 g original tissue for the $Fe^{+2}$ and $Fe^{+3}$ experiments, respectively.

The data in this table were not from a normal population either directly or after transformation to logarithmic values. Thus, it was not possible to perform analysis of variance on the data.

other hand when the FMN-NADH system was made anaerobic, the formation of DMA was markedly stimulated. When $Fe^{+2}$ was added to the mixture in addition to the FMN-NADH in an anaerobic environment, the production of DMA was stimulated even more to about 10 times that of the control. Although not included in the table, the effect of $Fe^{+3}$ on the FMN-NADH system anaerobically was very minimal, if there was any stimulation at all, compared to the FMN-NADH anaerobic system by itself.

Table 4. DMA formation in frozen minced red hake muscle in the presence of FMN, NADH and iron

| Additions | DMA, μmoles per 100 g original tissue | |
|---|---|---|
| | 1 week | 2 weeks |
| None (control) | 250 | 560 |
| Glucose/Glucose oxidase | 380 | 997 |
| FMN, NADH | 210 | 661 |
| FMN, NADH, Glucose/Glucose oxidase | 660 | 1310 |
| FMN, NADH, $Fe^{+2}$, Glucose/ Glucose oxidase | 2510 | 4790 |

The following concentrations were used: flavin mononucleotide (FMN), 0.1 mM; NADH, 0.1 mM; $FeCl_2$, 1.0 mM; glucose, 13 mM; glucose oxidase, 9 units per ml. Storage was at $-7°C$. The DMA content of the "zero time" sample was 50 μmoles per 100 g original tissue.

All treatments were significantly different from the control ($p < 0.05$) over the total time period evaluated. The data had to be transformed to their logarithmic values to permit analysis of variance.

In Table 5 the rate of DMA formation in frozen, reconstituted red hake muscle is given in the presence of the FMN-NADH system and Fe both aerobically and anaerobically. In the aerobic system there was some stimulation of DMA production in the presence of FMN and NADH, but it was less than that observed with the anaerobic system. There was a marked stimulation by the FMN-NADH system in the presence of $Fe^{+2}$ both aerobically and anaerobically. The total activity was higher in the anaerobic system, but the

Table 5. DMA formation in frozen reconstituted red hake muscle in the presence of FMN, NADH and iron

| Additions | DMA, μmoles per 100 g original tissue | | | |
|---|---|---|---|---|
| | without glucose oxidase/ glucose | | with glucose oxidase/ glucose | |
| | 1 week | 2 weeks | 1 week | 2 weeks |
| TMAO (control) | 36 | 46 | * | * |
| TMAO, FMN, NADH | 64 | 92 | 160 | 227 |
| TMAO, FMN, NADH, $Fe^{+2}$ | 202 | 290 | 305 | 357 |
| TMAO, FMN, NADH, $Fe^{+3}$ | 60 | 85 | 278 | 347 |

The following concentrations were used: TMAO, 70 mM; FMN, 0.1 mM; NADH, 0.1 mM; $FeCl_2$ or $FeCl_3$, 1 mM; glucose, 13 mM; glucose oxidase, 9 units were added per ml of retentate from the dialysis procedure. Storage was at −7°C. The DMA content of the "zero time" sample was 21 μmoles per 100 g tissue.

All treatments were significantly different from the control ($p < 0.05$) over the total time period evaluated. The data had to be transformed to their logarithmic values to permit analysis of variance.

*The data with glucose oxidase/glucose was from the same experiment as the data without glucose oxidase/glucose, i.e., the same control was used.

percentage stimulation compared to the system in the absence of iron was less in the anaerobic than in the aerobic system. $Fe^{+3}$ did not stimulate DMA production over that of the FMN-NADH combination by itself when the experiments were done aerobically but did remarkably stimulate the activity in the anaerobic system. In fact the activity was essentially similar to that obtained with $Fe^{+2}$ addition to the FMN-NADH combination.

The effect of adding the enzymes ascorbate oxidase, NADase, and phospholipase to frozen, minced red hake was evaluated (Table 6). In one experiment, ascorbate oxidase markedly reduced the rate of formation of DMA compared to a control of frozen minced red hake muscle that did not contain the enzyme. In a repeat of this experiment there was indication of a de-

Table 6. DMA formation in frozen minced red hake muscle in the presence of enzymes

| Additions | DMA, μmoles per 100 g original tissue | | | |
|---|---|---|---|---|
| | Experiment 1 | | Experiment 2 | |
| | 1 wk | 2 wks | 1 wk | 2 wks |
| None | 170 | 220 | 80 | 90 |
| Ascorbate oxidase | 20 | 100 | 30 | 90 |
| NADase | - | - | 40 | 50 |
| Phospholipase $A_2$ | 30 | 130 | 60 | 70 |

The following enzymes were added, ascorbate oxidase, 30 units per 100 g tissue; NADase, 30 units per 100 g tissue; phospholipase $A_2$, 300 units per 100 g tissue. Storage was at −7°C. The DMA contents of the "zero time" samples were 120 and 180 μmoles per 100 g tissue for Experiment 1 and 2, respectively.

The data in this table were not from a normal population either directly or after transformation to logarithmic values. Thus, it was not possible to perform analysis of variance on the data.

creased rate of formation of DMA after one week, but this was not evident after two weeks. In one set of experiments, NADase was shown to be effective and reduced the rate of DMA formation by about one half. Phospholipase $A_2$ in two experiments was also found to be an inhibitor of DMA production in minced red hake muscle, although the extent of the reduction in activity was much greater in the first set of experiments than in the second.

Formaldehyde concentrations in the stored muscle were routinely determined and were always found to be less than the amount of DMA. The difference between the amount of DMA formed and that of the determined formaldehyde, was taken as the amount of formaldehyde bound to the cellu-

lar constituents such that it does not give a reaction with the Nash reagent. There is usually considerable scatter in the percentage of formaldehyde which is bound in any group of experiments. Nevertheless it became clear that there was a difference in the minced muscle samples compared to the reconstituted samples. The range of percentage of formaldehyde bound in minced muscle samples was between 55 and 99%. In the reconstituted muscle samples this range was from 4 to 50%. Since the major difference between the samples was in the presence or absence of the low molecular weight soluble compounds, our conclusion is that in muscle in which the low molecular weight fraction is present, a large percentage of the formaldehyde which is produced in the breakdown of TMAO reacts with these small molecular weight compounds. It is not possible to put an exact figure on this because of the variation in the data and the difficulty in reproducing free formaldehyde values between muscle samples. We do not at this time have a very good idea of what causes this variation. Nevertheless, the differences were obvious.

## DISCUSSION

The experiments reported here provide direct proof that the "cofactors" (iron, ascorbate, cysteine, FMN, NADH) in some combinations are rate-limiting in the production of DMA from TMAO in minced red hake muscle. The work with the reconstituted muscle system in which most of the low molecular weight compounds have been removed would indicate that the cofactors tested are sufficient to aid in the catalysis of TMAO breakdown. The small amount of DMA formation which is observed in control samples in the reconstituted muscle, i.e., with only TMAO added, would indicate that either the procedure used was not able to remove all of the small molecular weight compounds, or that a small amount of TMAO breakdown can be catalyzed by the high molecular weight components with cofactors which might be bound to them. In our laboratory we have shown, for example, that the great majority of the iron in the soluble fraction of the muscle is associated with the high molecular weight fraction (Phillippy 1983). The binding of compounds such as flavins and NADH to proteins is extensively documented in the literature (Singer 1966; Sols and Marco 1970).

The reason for utilizing the reconstituted muscle system instead of the mince is that the cofactors are normal constituents of the muscle. It may be difficult to determine the necessity of a particular compound if it is already present in the tissue. This fact notwithstanding, for the most part the results observed with the minced muscle and the reconstituted muscle were similar, at least qualitatively. This may be because the concentrations of the cofactors added were all sufficiently high to have made a significant impact

on the total concentration that was present in the mince. For example, the total iron in muscle tissue has been observed to be around 0.1 mM, including bound iron. We have determined the ascorbate concentration in red hake muscle to be of the order of 50μM. The amount we added was 10 times that. There is an advantage in using reconstituted muscle in that it allows the comparison of two systems of cofactors, i.e., the iron-reducing agent system versus the flavin-NADH system. The concentrations of flavin and NADH that were used were comparable to those which are found *in situ* in muscle tissue.

$Fe^{+2}$ had a positive effect on DMA production in both minced tissue and in reconstituted muscle tissue under aerobic and anaerobic conditions; the effect was least with reconstituted muscle under aerobic conditions. $Fe^{+3}$ by itself had no effect on the rate of TMAO breakdown in any of the samples observed. This work confirmed our previous observations with minced tissue (Parkin and Hultin 1982b), and is consistent with the hypothesis that $Fe^{+2}$ is the active form of the metal in the catalysis. Ascorbate, when added to the system containing iron, caused an increased production of DMA in all cases. There was a greater effect of ascorbate in reconstituted muscle with $Fe^{+2}$ under aerobic conditions and with $Fe^{+3}$ under anaerobic conditions. This could be interpreted to indicate that iron is involved in a cyclic oxidation-reduction during the breakdown of TMAO. This suggestion is consistent with the proposed mechanism of TMAO breakdown (Ferris *et al.* 1967). In the minced muscle, the addition of cysteine with iron had little effect, which could be due to the fact that cysteine, and/or related and comparable compounds such as reduced glutathione, are already there in sufficient quantity. Cysteine had a greater effect in the reconstituted muscle than in minced, but it was not as great as the effect of ascorbate. This is consistent with results which have been observed in the isolated membrane system where at low concentrations ascorbate is a much more effective reducing agent than is cysteine. Under anaerobic conditions, cysteine was not effective with $Fe^{+2}$ but did have some effect with $Fe^{+3}$, although in the latter case it was only to bring the activity up to what was already present in the system with $Fe^{+2}$. This again would indicate that a cyclic oxidation-reduction of iron is required for the reaction.

The work with the flavin-NADH system showed that in the case of minced muscle, simply making the system anaerobic increased production of DMA from TMAO. This presumably is due to the fact that there is flavin and NADH present in the muscle tissue initially. The presence of the FMN-NADH cofactor combination increased the rate of DMA in the absence of glucose oxidase/glucose (aerobic system) only in reconstituted muscle. The reason for this is not clear. There may be a low molecular weight inhibitor which is removed in making the reconstituted muscle, or it may be that even in the absence of glucose oxidase/glucose, anaerobic conditions are partially

met in the reconstituted muscle. It is not clear, however, why this latter would occur in reconstituted muscle and not in minced.

The effectiveness of ascorbate oxidase and NADase in reducing the rate of DMA production in frozen minced red hake muscle is an added indication that these cofactor systems represent the rate-limiting factor in the production of DMA from TMAO (Landolt and Hultin 1981). There is a loss in ascorbate content of red hake muscle on frozen storage (Phillippy 1983). This may explain why the ascorbate oxidase loses much of its effectiveness after 2 weeks of storage, e.g., the ascorbate may be naturally oxidized by this time such that the presence of the enzyme would have little added effect. Since we know that both the ascorbate and flavin-NADH systems can operate independently, it would be useful to examine the effect of ascorbate oxidase and NADase in combination to see whether there is an additive effect of the two. Phospholipase $A_2$ was tested because it has been observed that there is a membrane-associated enzymic system capable of converting TMAO to DMA in a microsomal fraction from red hake muscle (Parkin and Hultin 1982a). The effectiveness of this enzyme in decreasing DMA production indicates that the membrane-associated enzymic system is a significant factor *in situ*.

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# INFLUENCE OF HOMOGENIZATION ON THE HEAT STABILITY AND SALT BALANCE OF BUFFALO MILK AND ITS 1:2 CONCENTRATE

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## ABSTRACT

*The influence of homogenization (two stage) on heat stability (determined as heat coagulation time at 130°) as well as the salt balance of buffalo milk and its 1:2 concentrate was determined. Homogenization had no significant influence on the heat stability and salt balance (molar ratio of Ca + Mg to P + Cit. in the dissolved phase) of fluid milk. However, during concentration both the heat coagulation time and salt balance of homogenized milk were affected significantly. Homogenization caused a significant decrease in the dissolved phosphate but had no significant effect on calcium and magnesium and this resulted in a significant increase in the molar ratio of Ca + Mg/P + Cit. This disruption in the salt equilibrium caused the destabilization of homogenized concentrated milk.*

## INTRODUCTION

So far no work has been done on the influence of homogenization on heat stability and salt balance of buffalo milk. The studies on the effect of homogenization on the heat stability of bovine milk (Tracy and Ruche 1928; Deysher *et al.* 1929; Webb and Bell 1942; Hunziker 1949; Maxy and Sommer 1950; Sommer 1952; Vaitkurs *et al.* 1974; Sweetsur and Muir 1982a, 1982b, 1983a, 1983b) revealed that the homogenization in general had a destabilizing influence on the milk proteins. The destabilization may be the result of the increased adsorption of proteins, especially casein, on the disrupted fat globules (Ortwijn and Walstra 1979). Thus forming centers of high protein concentration favorable to coagulation (Ortwijn *et al.* 1977). Studies by Sweetsur and Muir (1982a) established that seasonal variations in milk constituents had an influence on the destabilization of milk proteins caused as a result of homogenization. They also observed that milk serum rather than milk fat is the major determinent in the heat stability of concentrated homogenized milk and such milks are very sensitive to small changes in

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their level of soluble calcium. Therefore, all the product and process variables which cause alteration in milk proteins and soluble calcium, like seasonal changes; addition of sodium phosphate and citrate (Sweetsur and Muir 1982a); forewarming temperature (Sweetsur and Muir 1982b); addition of β-lactoglobulin, formaldehyde, sulphydryl blocking agents (NEM), oxidizing agents (Cu) and conditions (pressure, temperature and stages) of homogenization (Sweetsur and Muir 1983a) have been found to influence the heat stability of concentrated homogenized milk. However, the nature of changes caused in the mineral equilibrium of milk due to homogenization is still unknown. Sommer (1952) suggested that due to homogenization a disruption is caused in the mineral equilibrium of milk which in turn may have been caused due to the adsorption of either cations or anions on the fat globules membrane surface. To establish such a hypothesis no experimental data were available in the literature. Therefore, an investigation was undertaken to study the influence of homogenization on the heat stability of buffalo milk and its concentrate (1:2) along with its salt balance to have an understanding of the destabilization mechanism.

## MATERIALS AND METHODS

### Milk Samples

Composite milk samples from at least ten buffaloes of the Murrah breed were collected from the Institute farm during morning milking in a clean, dry aluminium container and used for the study.

### Forewarming of Milk

Milk was taken into a pyrex Erlenmeyer flask and heated to 85 ± 1°C for 5 min by dipping in a boiling water bath with constant shaking. The time required for a fixed volume of milk to attend 85°C temperature during such a process was carefully calibrated and was followed thereafter for all the samples. The actual temperature was, however, recorded in each case and heating was continued for 5 min after attaining 85°C. After 5 min the flask was taken out and rapidly cooled to 60°C by circulating cold water over the surface.

### Homogenization of Milk

After cooling the prewarmed milk to 60°C it was homogenized in two stages each at 600 psi in a laboratory homogenizer (Creamac, Mark III Model). After homogenization the milk was cooled to room temperature. The homogenized milk was divided into two portions while the one portion was

kept as such (control) the other portion was concentrated in 1:2 ratio as detailed below.

### Concentration of Milk

Milk samples (both homogenized and unhomogenized) were concentrated in a rotatory type vacuums evaporator at 52 ± 1°C (at an absolute pressure of 0.3 mm Hg). A known quantity of milk was taken in a 2 litre Pyrex round bottom flask which was connected to the evaporator and dipped in a water bath at 52 ± 1°C. The exact concentration was determined gravimetrically, i.e., by taking the weight of milk before and after concentration.

### Separation of the Dissolved and Colloidal Phases

To determine the dissolved proportions of salt constituents in the milk the whey was obtained by centrifuging the fluid milk, homogenized fluid milk and their respective concentrate at 35,000 rpm (105,000x g) for 50 min at 20°C in a preparative ultracentrifuge (Beckman Model L). The proportions of the dissolved minerals in the corresponding milk were calculated by compensating for the volume of fat and casein.

### Determination of Heat Stability and pH of Milk

Heat stability of all the sets of samples (forewarmed, homogenized, concentrated and concentrated after homogenization) was determined as their heat coagulation time (HCT) at 130° ± 1°C. For the determination the method of Davies and White (1966) as modified by Jairam *et al.* (1976) was followed. The pH of milk was determined electrometrically with a mains operated pH meter.

### Analytical Procedures

Determination of all the salt constituents was done as per earlier procedures (Sindhu and Roy 1973).

### Statistical Analysis of the Data

Statistical analysis of the data for the F Test was carried out on a programmable minicomputer (HC1 - Micro 2200).

## RESULTS

Results for the effect of homogenization on the heat stability and salt balance of fluid milk along with the statistically calculated variance ratios (F

values) are presented in Table 1. Results on these parameters of concentrated milk are presented in Table 2. It was observed that homogenization caused a decrease in the heat coagulation time (HCT) of buffalo milk. Due to homogenization of fluid milk its HCT (determined at 130°C) decreased from 26.5 min to 23 min. However, statistical analysis of the data for F test ($P < 0.05$) revealed that the decrease in the HCT caused by the homogenization was not significant ($F = 0.15$).

The salt constituents of milk were also affected due to its homogenization. While there was a decrease in the dissolved proportions of calcium, magnesium and phosphate, the dissolved citrate was found to be higher in the homogenized milk. Further, the decrease caused in the dissolved calcium due to a shift in it from the dissolved to the colloidal phase in the homogenized milk was comparatively lower than the same in phosphate which was indicated by the increase in the ratio of Ca/P in the dissolved phase. However, such unproportionate shift of calcium and phosphate was compensated by a decrease in another cation (magnesium) but no decrease in another anion (citrate). Consequently, the net effect of homogenization on the mineral balance was found to be statistically nonsignificant (which was indicated by the nonsignificant F value of Ca + Mg/P + Cit., 0.93).

Study on the concentrated milk (Table 2) revealed that the HCT of concentrated milk which was prepared from homogenized milk was significantly lower to that which was prepared from unhomogenized milk ($F = 4.28$ at $P < 0.05$). In the homogenized concentrated milk the proportion of dissolved phosphorus was significantly lower ($F = 7.81$ at $P < 0.01$) than the unhomogenized concentrated milk. On the other hand, homogenization had a nonsignificant influence on the dissolved calcium, magnesium and citrate. Due to this unproportionate alteration in the cationic and anionic salt constituents during concentration a significant increase was observed in the molar ratios of Ca/P and (Ca + Mg)/(P + Cit) in the dissolved phase of homogenized concentrated milk ($F = 17.51$ and 4.28).

## DISCUSSION

The findings from the present study in general were in agreement with earlier findings reported on bovine milk (Tracy and Ruche 1928; Deysher *et al.* 1929; Webb and Holm 1942; Hunziker 1949; Maxy and Sommer 1952; Sweetsur and Muir 1982a, 1982b, 1983a, 1983b). All these workers observed that homogenization of milk caused a destabilization of milk proteins. However, the results for the effect of homogenization on the heat stability of milk were not analyzed statistically by any of these workers. Therefore, it is not possible to ascertain whether the decrease in the heat stability caused by the homogenization was significant or not.

Table 1. Influence of homogenization on salt constituents (concentrations and molar ratios in dissolved phase) and HCT of fluid buffalo milk.[a]

| Sr. No. | Parameters | | Types of milk: Unhomogenized milk | Types of milk: Homogenized milk | F value |
|---|---|---|---|---|---|
| 1. | Calcium | Total (mg/100 ml) | 194.1 | 194.1 | 6.6 ** |
| | | Dissolved (mg/100 ml) | 41.1 | 39.1 | |
| | | Percent of total | 21.0 | 20.1 | |
| 2. | Magnesium | Total (mg/100 ml) | 18.7 | 18.7 | 4.3 * |
| | | Dissolved (mg/100 ml) | 9.9 | 9.6 | |
| | | Percent of total | 53.0 | 51.0 | |
| 3. | Phosphorus | Total (mg/100 ml) | 81.0 | 81.0 | |
| | | Dissolved (mg/100 ml) | 28.3 | 25.9 | 7.8 ** |
| | | Percent of total | 35.5 | 32.0 | |
| 4. | Citric acid | Total (mg/100 ml) | 211.1 | 211.1 | |
| | | Dissolved (mg/100 ml) | 174.4 | 179.2 | 1.6 NS |
| | | Percent of total | 82.6 | 84.9 | |
| 5. | Ca/P | | 1.10 | 1.17 | 12.1 ** |
| 6. | (Ca+Mg)/(P+Cit) | | 0.78 | 0.77 | 0.94 NS |
| 7. | HCT at 130°C | | 26.5 | 23.0 | 0.15 NS |
| 8. | pH | | 6.7 | 6.7 | 0.17 NS |

a = Results represent the average of 5 samples

* = Significant at $P < 0.01$

** = Significant at $P < 0.05$

NS = Not significant.

Table 2. Influence of homogenization of salt constituents (concentrations and molar ratios) in dissolved phase and HCT of buffalo 1:2 concentrated milk [a]

| Sr. No. | Parameters | | Type of milk | | F value |
|---|---|---|---|---|---|
| | | | Unhomogenized milk | Homogenized milk | |
| 1. | Calcium | Total (mg/100 ml) | 388.2 | 388.2 | 1.5 NS |
| | | Dissolved (mg/100 ml) | 67.6 | 69.7 | |
| | | Percent of total | 17.4 | 18.0 | |
| 2. | Magnesium | Total (mg/100 ml) | 37.4 | 37.4 | |
| | | Dissolved (mg/100 ml) | 18.4 | 17.8 | 1.0 NS |
| | | Percent of total | 49.1 | 47.5 | |
| 3. | Phosphorus | Total (mg/100 ml) | 162.0 | 162.0 | |
| | | Dissolved (mg/100 ml) | 50.4 | 46.6 | 8.7 ** |
| | | Percent of total | 31.1 | 28.7 | |
| 4. | Citric acid | Total (mg/100 ml) | 422.2 | 422.2 | |
| | | Dissolved (mg/100 ml) | 315.7 | 321.8 | 0.40 NS |
| | | Percent of total | 74.7 | 76.2 | |
| 5. | Ca/P | | 1.04 | 1.16 | 17.5 ** |
| 6. | (Ca+Mg)/(P+Cit) | | 0.75 | 0.78 | 21.3 ** |
| 7. | HCT at 130°C | | 3.6 | 2.50 | 4.0 * |
| 8. | pH | | 6.55 | 6.60 | 2.3 NS |

a = Results represent the average of 5 samples.

** = Significant at $P \leq 0.01$

* = Significant at $P \leq 0.05$

NS = Not significant

With regards to the influence of homogenization on the mineral equilibrium the present findings were in agreement with the hypothesis of Sommer (1952) who suggested that homogenization causes a disruption of ionic equilibrium in the system which in turn may be caused due to the adsorption of either cations or anions on the fat globule membrane surface. Our findings confirmed this hypothesis because in the case of concentrated milk which was homogenized prior to concentration a significant decrease was observed in the dissolved phosphate (anion) which may have been adsorbed either on the fat globule membrane surface or on the surface of casein micelles. On the other hand, no significant decrease was observed in the dissolved cations (calcium and magnesium) in the homogenized concentrated milk. On the contrary, there was a slight increase in the dissolved calcium in the homogenized concentrated milk. Consequently, a disruption was caused in the salt balance of the concentrated milk due to an unproportionate decrease of cations and anions in the dissolved phase. The disruption in the salt balance of homogenized concentrated milk was evident from the significant increase in the molar ratios of Ca/P ($F = 17.5$) and Ca + Mg/P + Cit. ($F = 4.02$). This disruption in the salt balance resulted in an increased concentration of calcium ions compared to that of phosphate in the dissolved phase.

This increase in the concentration of calcium ions in the dissolved phase of milk as a result of homogenization may be one of the reasons for the decreased heat stability of the concentrated homogenized milk. Findings from the studies of Sweetsur and Muir (1982a, 1982b, 1983a) were also in support of the above conclusion. Although these workers found that many factors like sulphydryl blocking agents, oxidizing agents, β-lactoglobulin, formaldehyde, forewarming temperature and conditions (pressure, number of stages and temperature) of homogenization etc. affected the extent of destabilization of concentrated homogenized milk, these milks were found to be very sensitive to small changes in their level of soluble calcium. Further, they found that winter milks were more sensitive to homogenization and addition of stabilizing salts such as sodium phosphate and sodium citrate stabilized such milks. These workers were unable to offer any explanation for this behaviour of winter and summer milks. But it was clear from their results that winter milks contained greater proportions of cations (calcium and magnesium) than anions (phosphate and citrate) in the dissolved phase compared to summer milks. This was indicated by a higher molar ratio (0.6) of (Ca + Mg)/(P + Cit.) in winter milk compared to 0.58 in summer milk (These ratios were calculated from their results). Stabilizing influence of anionic salts (sodium phosphate and sodium citrate) may also be attributed to the same effect i.e., the decrease in soluble calcium in the homogenized concentrated milk which they caused as has been suggested by Evenhuis (1957) that it is the maintenance of high calcium ion concentration during

heating rather than the existence of high initial calcium concentration which causes the destablization. So any factor which alters the calcium ion concentration will influence the destabilization.

As indicated in Table 1 in case of fluid milk also there was a decrease in the dissolved phosphate. However, such decrease in the dissolved phosphate was compensated by a similar decrease in the dissolved calcium and magnesium, consequently a very little and statistically nonsignificant change was caused in the mineral balance (molar ratio of Ca + Mg/P + Cit. in the dissolved phase) of fluid milk due to homogenization. Therefore, the homogenization had no significant influence on the heat stability of fluid milk.

## CONCLUSION

It can be concluded from the results obtained during the present investigation that homogenization causes a disruption in the salt balance of milk due to an unproportionate decrease in the dissolved phosphate and calcium which in turn was the result of a greater adsorption of phosphorus compared to calcium either on the surface of fat globules membrane surface or on the surface of casein micelles. This disruption in the salt balance resulted in an increased concentration of calcium in the dissolved phase. However, this increase in the dissolved calcium was compensated by a simultaneous increase in the dissolved magnesium during the homogenization of fluid milk. Therefore, the net result of homogenization on the salt balance (molar ratio of Ca + Mg/P + Cit. in the dissolved phase) was found to be nonsignificant in case of fluid milk. On the other hand, in case of homogenized milk which was subsequently concentrated the increase in dissolved calcium was not compensated by a simultaneous decrease in the dissolved magnesium and this resulted in a disruption in the salt balance of homogenized concentrated milk. This disruption in the salt balance if not the only factor is one of the important factors causing the destabilization of homogenized concentrated milk.

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# THE ROLE OF HEAT EXCHANGER FOULING IN THE FORMATION OF SEDIMENT IN ASEPTICALLY PROCESSED AND PACKAGED MILK[1]

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## ABSTRACT

*Sedimentation rates in stored aseptically processed and packaged lowfat milk were related to the initial thermal treatment of the product. Total thermal treatments were reduced over time due to heat exchanger fouling. Product input and discharge temperatures for the heating section were maintained constant while steam temperature increased as deposits formed. Processing conditions included product entrance temperature of 363.9 and 366.7 K for heater exit temperature of 410.7 and product velocity of 2.70 m/s; 364.6 for 410.7 and 3.25; 378.5 for 427.4 and 3.25 m/s. A model for sedimentation rate was determined for equivalent times and temperatures representing the total thermal treatment at any time of processing. The significance of the amount of the total thermal treatment subject to fouling was discussed in relation to sedimentation rates.*

## INTRODUCTION

For many years researchers have felt that there exists some connection between fouling of product in the heat exchanger and the amount of sediment accumulation in stored aseptic dairy products. Burton (1968) commented on this possible connection when he proposed two separate mechanisms for fouling in the heat exchanger. First, he proposed that the temperature effect produces a condition where milk solids are no longer in true solution. At this stage they either absorb to a surface or aggregate. He suggested that the presence of an available surface would determine whether the solids form de-

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posit in the heat exchanger or sediment in the processed product. However, Burton noted that the literature was conflicting as to the relation of the degree of product deposition during processing to sediment formation during storage.

Having a site available for fouling may depend on any number of process and product variables. Swartzel (1983) reviewed the then-current literature concerning the relationships between process and product variables and the fouling rate. Many of the variables or functions of variables were interrelated. Attempts to reduce contributing variables in statistical models tended to reduce the usefulness of the model. By using an earlier developed method of thermal evaluation (Swartzel 1982) equivalent time ($t_E$) and temperature ($T_E$) values were determined for each run and run time ($t_r$). Since these equivalent time and temperature values were uniquely defined for each process condition and represented a point of process description independent of activation energy values they also represented a description of process reactions. Interestingly only equivalent time and temperature values at run time zero were required to explain 96-97% of the variation in the fouling rate.

With a build-up of deposits in the heat exchanger, the heating curve drops (Fig. 1). As the curve drops through run time the thermal treatment correspondingly is reduced. The manner in which the thermal treatment is reduced depends on many of the same factors that control the fouling rate. Fouling rates have been recognized as one of six relations: linear where deposition rate predominates over the erosion rate; a falling rate where the erosion rate increases with the fouled layer thickness until the rate eventually equals the deposition rate; intermediate falling rate behavior patterns; and corresponding fouling rates with a lag or induction period where no fouling occurs (Epstein 1978 as described by Lund and Sandu 1981).

Sedimentation rates too have been shown to be affected by the total thermal treatment of the process in a nonfouled system (run time less than 15 min, Ramsey *et al.* 1983). As yet no literature is available relating the role of fouling rates in the heat exchanger to sedimentation rates in the stored product.

With the possible inclusion of part of the heating curve as part of the process lethality requirement, minimum thermal treatments as a result of fouling must be known (Swartzel 1983). However, designing for reduced fouling may or may not yield reduced sedimentation rates in the stored package. A balance between added expense and reduced run time due to fouling and reduced consumer acceptance due to sedimentation in the carton must be made. Additionally, the ratio of the contribution of erosion of fouled material to that of mass reaction resulting with sediment may be a major factor to consider in process design.

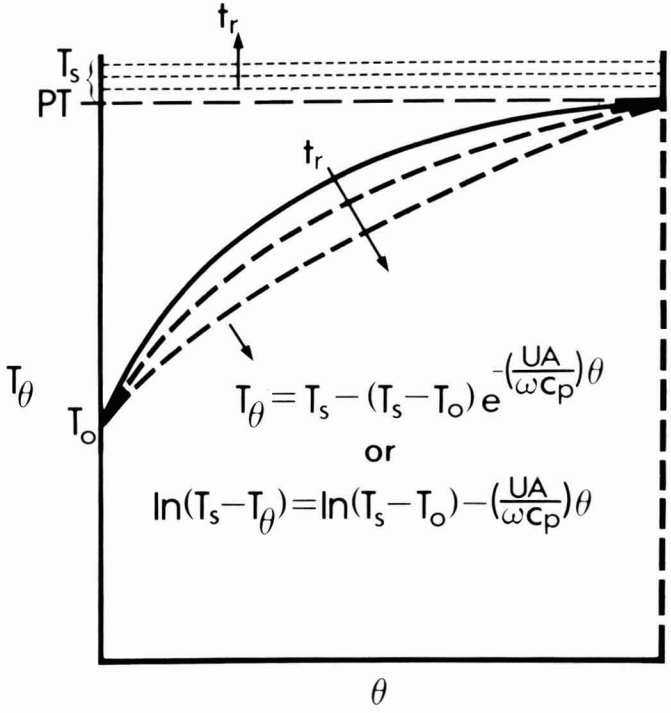


FIG. 1. TYPICAL HEATING TIME-TEMPERATURE CURVES FOR INDIRECT UHT PROCESSING
The arrow direction of $t_r$ indicates the direction that the heating curve moves from time zero (solid line) as run time continues (dashed lines). From Swartzel (1983)

It was the intent of this study to investigate sedimentation rates in stored aseptically processed milk as related to thermal treatment and process run time. Aspects relating to fouling and amount of total thermal treatment given to the product by the heating section were examined as related to sedimentation rates.

## MATERIALS AND METHODS

Winter lowfat milk was processed and aseptically packaged in a tubular heating system as described by Swartzel (1983). Product input and discharge temperature for the heating section were maintained constant while steam temperatures increased as deposits formed. Heater entrance temperatures were 363.9 and 366.7 K for an exit temperature of 410.7 and product velocity of 2.70 m/s; 364.6 for 410.7 and 3.25; 378.5 for 427.4 and 3.25 m/s.

Product testing was reported in an earlier work (Swartzel 1983) as log standard plate count, 3.58-5.94; means of % fat, 2.17%; total solids, 11.0%; pH, 6.66; and dissolved oxygen, 6.08 ppm.

Each run was operated with a single pass of product operating with a maximum of 5300 liters of product available or to the limit of the steam supply (450 K). Product was packaged in 250 ml Brik Pak cartons (Brik Pak, Inc., Dallas, Texas) at hourly intervals for each run. Container dimensions were 10.6 x 6.2 x 4.0 cm. Sedimentation was determined by the method of Ramsey (1983) at weekly intervals for five weeks of storage at ambient temperature then biweekly intervals through the 26 week storage period. Fouling rates were monitored for the heating section and reported in an earlier work (Swartzel 1983).

## RESULTS AND DISCUSSION

The heat treatment during heating was defined for each run and $t_r$ from the heating curve (Fig. 1) as

$$\text{Ln}\,(T_s - T_\theta) = \text{Ln}\,(T_s - T_o) - \left(\frac{UA}{c_p}\right)\theta$$

The heating curve may rise rapidly and level off at or near PT (Curve A, Fig. 2). This would constitute a high heat treatment. For a low heat treatment the curve may rise gradually from $T_o$ and not reach PT until just before the end of the heat exchanger (Curve B, Fig. 2). For given $T_o$ and PT this would correspond with a lower fouling rate. Increased product velocities decreased the slope of the curve. Changing product velocities changes $\Theta$. Increasing

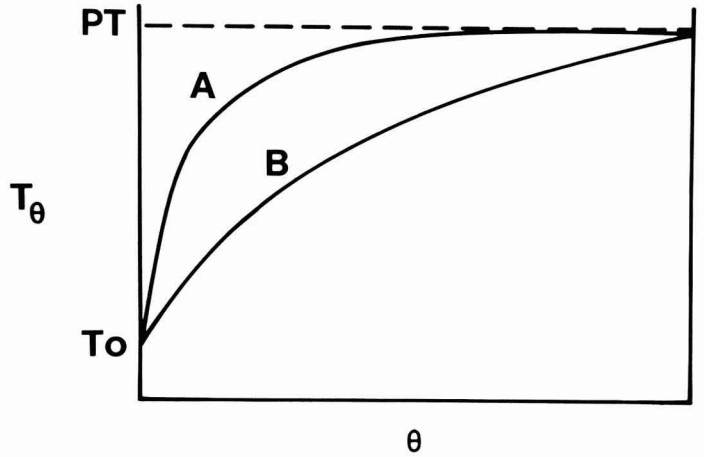


FIG. 2. HEATING TIME-TEMPERATURE CURVES FOR INDIRECT UHT PROCESSING Curve A represents a high heat treatment; Curve B, a low heat treatment

product velocities (increased Reynolds Numbers) have been associated with increasing shear at the wall, resulting with decreased deposition rate and/or increased erosion rate (Lund and Bixby 1975).

Swartzel (1982) used Arrhenius kinetic modeling to describe the thermal process treatments for the product bulk mass. This method develops one set of equivalent time and temperature values for each heating section curve and totally defines the thermal process for changes with constituent concentrations. This is true since the values represent a description of the process which is independent of activation energy.

Equivalent time and temperature values for the heating section alone as related to the fouling rate have been reported earlier in detail (Swartzel 1983). Ramsey and Swartzel (1983) related total thermal treatment to sedimentation rate. The runs in that study were of such short duration (less than 15 min) that fouling and run time effects were not considered. The total thermal treatment through run time, which decreases with increase deposition in the heat exchanger, should represent the role of fouling in formation of sediment. This would be true only where the fouling rate is controlled by depositional rate. For fouling with falling rates through time, erosion may become a more important factor with sediment than the mass reaction caused by the thermal treatment. For this study, all fouling rates were linear through $t_r$. Deposition rates were always greater than erosion rates (Swartzel 1983).

Assuming no sediment at zero storage time, models were developed for sediment in the form of gsed = $a(t_{st})$. Models were determined for product packaged at each hour and for each run. Results are shown in Table 1. Sedimentation rates (gsed/wk) were calculated from the models. Thermal levels of the heating section were totaled with the thermal treatment given to the product by the holding section. Total equivalent time and temperature values were then developed (Swartzel 1982). To establish a relationship between the total thermal treatment and the sedimentation rate the model

$$d(gsed)/d(t_{st}) = -0.145\,(t_E) + 1.40 \times 10^{-5}\,(T_E) + 3.571 \times 10^{-5}\,(t_E)\,(T_E)$$

was established by multiple regression where

$d(gsed)/d(t_{st})$ represents the rate of sedimentation in grams/week, and

$t_E$ and $T_E$ represent the total equivalent time (sec) and temperature (°K) of each process curve for each run and $t_r$. Standard error for the first term coefficient is 0.00118; for the second, $3.8 \times 10^{-6}$ and for the third $2.89 \times 10^{-6}$ with $r^2 = .99$.

Table 1. Model constant, standard error, C.V., and $r^2$ values for model gsed = $a(t_s)$ where gsed = grams of sediment and $t_s$ = storage time in weeks

| RUN | v (m/s) | PT (K) | $t_r$(HR) | a(gm/wk) | Std Err | C.V. | $r^2$ |
|---|---|---|---|---|---|---|---|
| | 2.70 | 410.7 | 0 | .0067 | .00039 | 44.02 | 0.85 |
| | 2.70 | 410.7 | 1 | .0072 | .00039 | 40.42 | 0.87 |
| 1 | 2.70 | 410.7 | 2 | .0068 | .00039 | 41.80 | 0.85 |
| | 2.70 | 410.7 | 3 | .0059 | .00038 | 46.54 | 0.82 |
| | 2.70 | 410.7 | 4 | .0060 | .00038 | 45.36 | 0.83 |
| | 2.70 | 427.4 | 0 | .0157 | .00031 | 17.84 | 0.98 |
| | 2.70 | 427.4 | 1 | .0139 | .00028 | 17.57 | 0.98 |
| 2 | 2.70 | 427.4 | 2 | .0139 | .00030 | 19.56 | 0.97 |
| | 2.70 | 427.4 | 3 | .0138 | .00029 | 19.04 | 0.97 |
| | 2.70 | 427.4 | 4 | .0137 | .00033 | 21.75 | 0.97 |
| | 3.25 | 410.7 | 0 | .0063 | .00055 | 58.90 | 0.73 |
| | 3.25 | 410.7 | 1 | .0072 | .00047 | 48.13 | 0.81 |
| 3 | 3.25 | 410.7 | 2 | .0076 | .00052 | 49.81 | 0.81 |
| | 3.25 | 410.7 | 3 | .0072 | .00051 | 51.30 | 0.79 |
| | 3.25 | 410.7 | 4 | .0075 | .00055 | 52.77 | 0.78 |
| | 3.25 | 410.7 | 5 | .0084 | .00063 | 50.56 | 0.80 |
| | 3.25 | 427.4 | 0 | .0132 | .00069 | 39.94 | 0.88 |
| 4 | 3.25 | 427.4 | 1 | .0092 | .00064 | 48.73 | 0.81 |
| | 3.25 | 427.4 | 2 | .0073 | .00062 | 54.57 | 0.75 |
| | 2.70 | 410.7 | 0 | .0080 | .00100 | 60.16 | 0.68 |
| | 2.70 | 410.7 | 1 | .0079 | .00090 | 56.94 | 0.71 |
| 5 | 2.70 | 410.7 | 2 | .0069 | .00090 | 60.26 | 0.66 |
| | 2.70 | 410.7 | 3 | .0070 | .00090 | 63.10 | 0.64 |
| | 2.70 | 410.7 | 4 | .0068 | .00110 | 67.30 | 0.59 |

Equation 2 is shown graphically in Fig. 3 with sedimentation rate as mg/wk. For constant $T_E$ sedimentation rate increases linearly with increases of $t_E$. The greater $T_E$ the greater the sedimentation rate with increases in $t_E$. With increases in $t_r$ the heating curve drops and the effect on the thermal treatment in the heating section is one of reduction (Fig. 1). This would mean a decrease in $T_E$, $t_E$ or both. $T_E$ may decrease and $t_E$ increase, $T_E$ increase $t_E$ decrease but the net effect would be a reduction in the total thermal treatment given to the product in the heating section. Two systems may have equal $t_E$ and $T_E$ but have totally different process curves with different fractions making up heating and holding (Fig. 4).

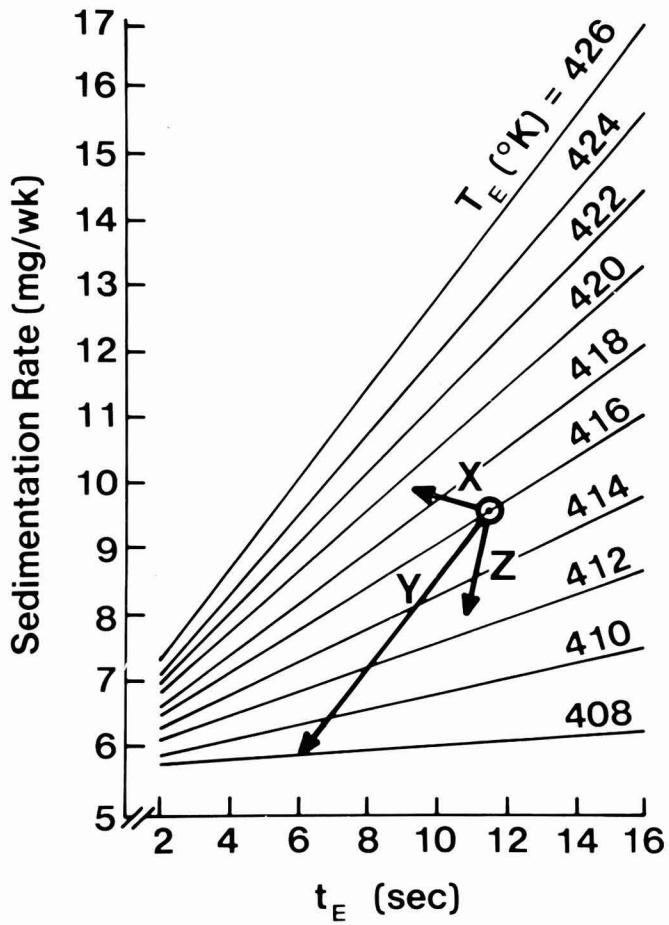


FIG. 3. SEDIMENTATION RATE (mg/wk) DURING STORAGE AS RELATED TO $T_E$ AND $t_E$ REPRESENTING THE TOTAL THERMAL TREATMENT Vectors X, Y, Z indicate the direction and magnitude of change to $T_E$ and $t_E$ after 5 hours of processing with different heating and holding configurations. Corresponding sedimentation rate changes are indicated

Upon examining the relationship between thermal treatment and sediment in the stored product various effects are observed. The circled point (Fig. 3) represents one initial total thermal treatment. As fouling occurs in the heating portion the thermal level will decrease as indicated by the vectors X, Y and Z. Vectors Y and Z decrease in both $T_E$ and $t_E$ and therefore the sedimentation rates decrease through $t_r$. Vector Y represents a process with much fouling in the heating portion with a large part of the initial total thermal treatment being made up in the heating section. The large decline in overall thermal treatment substantially reduced the sedimentation

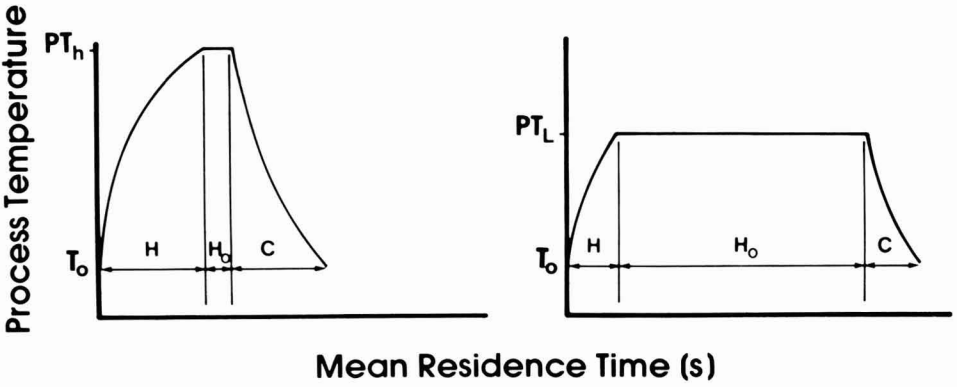


FIG. 4. PROCESS TIME-TEMPERATURE CURVES REPRESENTING HOW TWO PROCESS SYSTEMS HAVE DIFFERENT PROCESS CURVES WITH EQUAL $t_E$ AND $T_E$ VALUES

rate. Since the fouling rate was linear (Swartzel 1983) throughout $t_r$, a constant influence of erosive material in the stored product on sedimentation rate was assumed. Vector Z represents a process with either minor fouling or with a large portion of the thermal treatment being made up by the holding section. A small decline in the thermal treatment means a small decline in the sedimentation rate. Vector X represents a process that declines in $t_E$ and increases in $T_E$. In this case the sedimentation rate would be increased from the zero to the fifth hour of operation, indicating a falling fouling rate. An increased sedimentation rate through $t_r$ with decrease in the thermal treatment would indicate an increased influence of erosion. Although falling fouling rates were not observed with this study, vector X is shown to demonstrate the possible effect on sedimentation rates due to increased influence of erosion. Present studies are being made to determine the effect of fat levels, storage temperatures and erosion on sedimentation rates as related to changes in the thermal level of the heat exchanger. To reduce fouling (Swartzel 1983), the process curve through the heat exchanger should resemble curve B of Fig. 2. To reduce sedimentation in the package, a linear fouling rate should exist through $t_r$ with the major heating contribution to the product being carried out in the heat exchanger. If consumer acceptance based on sedimentation is the primary design factor, then minimum heat treatment should be realized in the holding sections. Additional studies are needed to identify the level of consumer acceptance.

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## NOMENCLATURE

| Symbol | Quantity Represented | Units |
|---|---|---|
| A | Heat transfer surface area | $m^2$ |
| c | Specific heat | J/kg K |
| gsed | Amount of sediment | g |
| PT | Process temperature (desired temperature at the end of the heat exchanger) | °K |
| t | Time | units of s or h |
| T | Temperature | °K |
| U | Overall heat transfer coefficient | $J/m^2$ h K |
| v | Product velocity | m/s |
| $\omega$ | Mass of flowing product in heat exchanger | kg |
| $\theta$ | Mean residence time through the heat exchanger, also used as a subscript | s |

## Subscripts

| Symbol | Quantity Represented |
|---|---|
| E | Equivalent |
| o | Initial condition (t = o) |
| p | Product |
| h | Represents high PT |
| L | Represents low PT |
| r | Run ( when used with t refers to the time at some point into the run) |
| s | Steam |
| st | Storage |

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# TRANSIENT COOLING OF CONDUCTION HEATING PRODUCTS DURING STERILIZATION: TEMPERATURE HISTORIES

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## ABSTRACT

*Temperature histories at the geometric center of containers filled with conduction heating products exhibit a rise after steamoff under certain conditions. This temperature rise (called overshooting), is quantified for cylindrical containers subjected to air and water cooling. Results of computer simulations using the Finite Element method suggest that the extent of overshooting is greater during air cooling than during water cooling. Heat penetration tests in laboratory and industrial retorts indicate that the overshooting phenomenon during water cooling is especially pronounced when conduction heating products are packaged in large metal containers and glass jars (e.g., a temperature rise of 2.5°C for 30 min was measured in a No. 10 can).*

## INTRODUCTION

The initial time temperature pattern that occurs after steamoff is an important but problematic phase in the sterilization cycle. It is important because product temperatures early in the cooling period are high so the sterilization value of this period can be a significant part of the total sterilization value delivered during the whole process. It is problematic because it is difficult to accurately predict temperatures at the slowest heating zone during this period (Ball and Olson 1957).

Hicks (1951); Gillespy (1951); Lund (1975); Kopelman *et al.* (1982), and others, have recognized that since a temperature distribution exists in a conduction heating product at steamoff, temperatures at the cold zone will continue to rise even after steamoff. This continued temperature rise that occurs during early cooling has been named overshooting (Kopelman *et al.* 1982). In certain cases, more specifically in conduction heating products packaged in large containers, the temperature at the slowest heating zone

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can rise by several degrees after steamoff (Hicks 1951). Recognizing the significance of overshooting, Flambert and Deltour (1972) used the model developed by Texeira *et al.* (1969), to calculate its effect on the location of the critical (least lethality) zone in the container. They calculated a displacement of the critical zone from the geometric center of the container, for various container geometries (length to diameter ratio). This displacement was attributed to the overshooting of temperatures after steamoff, but no attempt was made to quantify the overshooting of temperatures themselves as a function of processing, or heat transfer parameters. Thus, although awareness to the existence of the overshooting phenomena has existed and it is sometimes taken into account in commercial practice (NCA, 1982), the contribution of overshooting has not been incorporated in the mathematical methods for process design in use today (Ball 1923, 1957; Hayakawa 1970; Stumbo 1973; and others).

This study was undertaken in an attempt to quantify the overshooting of temperatures in cylindrical containers analytically, and demonstrate the phenomena experimentally. This is a first step towards the construction of a new mathematical method of thermal process design and evaluation that will include the lethality contribution of the overshooting phenomenon.

## EXPERIMENTAL

### Laboratory

Containers: 603 x 700 (No. 10), 603 x 408, 307 x 409 (No. 2), 307 x 200.25 (Salmon, ½ lb.) metal cans and 309 x 508 (23 oz), 214 x 309 (12 oz) glass jars.

Food Products: Cream style corn (Miss Daisy brand), cream style corn with 1% xanthan (Hercules) and 1% avicel (FMC, RC591), lean pork meat, and pumpkin puree.

Retort: A laboratory vertical retort (16 in. x 33 in.) that uses steam or water as the heating medium with air agitation. Retort temperature is maintained to within 0.2°C after the retort has come up to temperature (2-4 min). Cooling water is introduced from retort bottom and top at high flow rates. Overriding air pressure can be controlled during cooling.

Temperature Measurements: Premium grade Teflon/Teflon 24 gauge Cu/Co thermocouples were inserted into Bakelite rods as described in Blaisdell (1963). Temperature was monitored by a Kaye Digistrip III Datalogger. Data was transmitted to floppy discs (WTI DMII), and analyzed using a CYBER 172 (CDC) computer, with software described elsewhere (Naveh 1982). Temperature calibration of the data acquisition and measuring system was carried out against 100 ohm platinum RTD's that were in turn calibrated against an NBS standard (#221105).

Heating and Cooling Tests: Empty containers were filled with product and the Bakelite rod containing the TC lead was inserted. The cans were sealed at room temperature, placed in the retort and heated in steam or hot water. When heating medium was steam, typically, less than two minutes elapsed from steamoff until containers were covered with water. Cooling of glass containers heated in water started with warm (60°C) water which was gradually replaced with cold water. Throughout the cooling phase, water was maintained 3-6 in. above container height. During can and jar cooling overriding air pressure of 5 psia above heating retort pressure was maintained.

Data Analysis: Data collected during a run was analyzed by computer with appropriate software (Naveh 1982).

## Computer Simulations

**Governing Equation, Initial, and Boundary Conditions.** Fourier's transient quasi-harmonic equation, for heat conduction in an axisymmetric body where there is no heat generation, in cylindrical coordinates is given by: (1)

$$\frac{\partial}{\partial r}\left(rk_{rr}\frac{\partial T}{\partial r}\right) + k_{rr}\left(\frac{\partial T}{\partial r}\right) + \frac{\partial}{\partial z}\left(rk_{zz}\frac{\partial T}{\partial z}\right) = r\rho C\frac{dT}{dt}$$

where r and z are the coordinate directions,

$k_{rr}$ and $k_{zz}$ are the conductivities in these directions,
T is temperature, $\rho$ is density, C is specific heat, and t is time.
The initial condition assumed was a uniform temperature,
$T_o$ before heating:

$$T(r,z,O) = T_o \tag{2}$$

The temperature distribution at steamoff was used as the initial condition for cooling simulations.

A Cauchy convective boundary condition was assigned to the container surfaces, S:

$$k\frac{\partial T}{\partial n}(r, z, t) = h\,(T - T_1); \qquad r, z \text{ on } S \tag{3}$$

where h is the surface heat transfer coefficient,

$T_1$ is the medium temperature, and
n is the outward normal to the surface.

For heating simulations, the initial temperature $T_o$ was 25°C. A medium temperature $T_1$ of 125°C with a surface heat transfer coefficient (h) of 1135 mW/cm²°C was used to represent condensing steam. Nodal temperatures at the end of heating were used as the initial condition for cooling simulations. Cooling medium was at 25°C, with an h of 100 mW/cm²°C to represent water cooling (Blaisdell 1963), and 1 mW/cm²°C to represent cooling by natural convection in air (Okada 1941). The thermal diffusivity assigned to the product in computer simulations was 0.096 cm²/s representing immobilized water.

**Variational Finite Element Solution.** Solution of Fouriers quasi-harmonic transient conduction equation was carried out by the Finite Element (FE) method. The variational approach (Wilson and Nickell 1966), is based on the minimization of a functional derived through the calculus of variation that is equivalent to the governing equations. For the conduction of heat in an axisymmetric body subjected to convection on the surface S, the functional reads:

$$\chi = \int_v \frac{1}{2}\left[\frac{\partial}{\partial r}\left(rk_{rr}\frac{\partial T}{\partial r}\right) + \frac{\partial}{\partial z}\left(rk_{zz}\frac{\partial T}{\partial z}\right) + 2r\rho C\frac{\partial T}{\partial t}\right]dv + \int_S \frac{1}{2}\left[h(T - T_1)^2\right] ds \quad (4)$$

The integral (Eq. 4) is minimized with respect to the nodal values that characterize each element the cylinder is divided into, to yield element equations. These are solved in the time domain by a Finite Difference scheme, to yield the nodal temperatures at each time. From this data, heating rate parameters (f, j), point and integrated sterilization values are readily obtained.

**Accuracy in Calculations.** The extent of oscillations in calculated values and the degree of accuracy obtained depends on the element size and material properties, as well as on the time step and initial temperature distribution. In the case at hand, when the quarter cylinder analyzed was divided into 40 quadrilateral 6 noded (2nd order) elements with time steps of 5-10 s between iterations, a high degree of accuracy was obtained: a coefficient of variation of less than 0.2% between the $f_h$'s at the 99 nodes, with a maximal difference of 2% between the exact solution and the numerical solution was obtained for the case of a step change in $T_1$ during heating, for which an exact analytical solution exists (Carslaw and Jaeger 1959).

## RESULTS AND DISCUSSION

### Computer Simulations

As the cooling medium contacts the containers, the initial temperature distribution at steamoff (Fig. 1A), is changed due to formation of shoulders (Fig. 1B, 1E). Heat from the hot can periphery (shoulders) is now flowing towards the cooled container walls and towards the center. The temperature at the center will therefore continue to rise (overshoot) until the temperature profile that was seen at steamoff is inverted. By this time the temperature at the slowest heating zone has ascended and "normal" cooling patterns are established (Fig. 1C, 1D).

From time-temperature histories at container center after steamoff (Fig. 2) it is clear that the extent of overshooting is primarily dependent on the magnitude of the gradients at steamoff as represented by the value of g (the temperature difference between the retort and the slowest heating zone at steamoff). For example, for a g of 10°C at steamoff, the extent of overshooting was calculated to be 2.5°C and 2.3°C in a conduction heating product ($\alpha$ = 0.096 $cm^2/s$) packaged in a No. 10 and No. 2 can respectively, cooled in water, only an 8% difference. However, the duration of overshooting (the period of time elapsed from steamoff ($t = B$, $T = T_B$) until the temperature at the slowest heating zone is again $T_B$) depends more strongly on the container dimensions than on the value of g for a given food product, and cooling medium. For the conditions described in the example above, the overshooting lasted 11 min in the No. 2 can, and 42 min in the No. 10 can, a four-fold difference.

It is interesting that the value of $j_c$ is nearly unaffected by the value of g in the range studied ($0.1 < g < 15$°C). Since the value of the temperature response parameter, $f_h$, is also independent of the temperature distribution at steamoff, cooling curves for different g's look nearly identical (Fig. 3) when plotted on cooling graphs. This is because although the overshooting exists, it does not affect total cooling time and it is difficult for the eye to detect it on the semilogarithmic scale (Fig. 4).

The temperature profiles in an air cooled container are less sharp than during water cooling (Fig. 1D, 1E). Also, a three-fold increase in the duration of overshooting and a significant increase in the extent of overshooting is observed (Fig. 5) when comparing to the phenomena during water cooling. Even under these conditions where the overshooting phenomenon is more pronounced than during water cooling (Table 1), from semilogarithmic cooling curves, the overshooting is not clearly visible (Fig. 6).

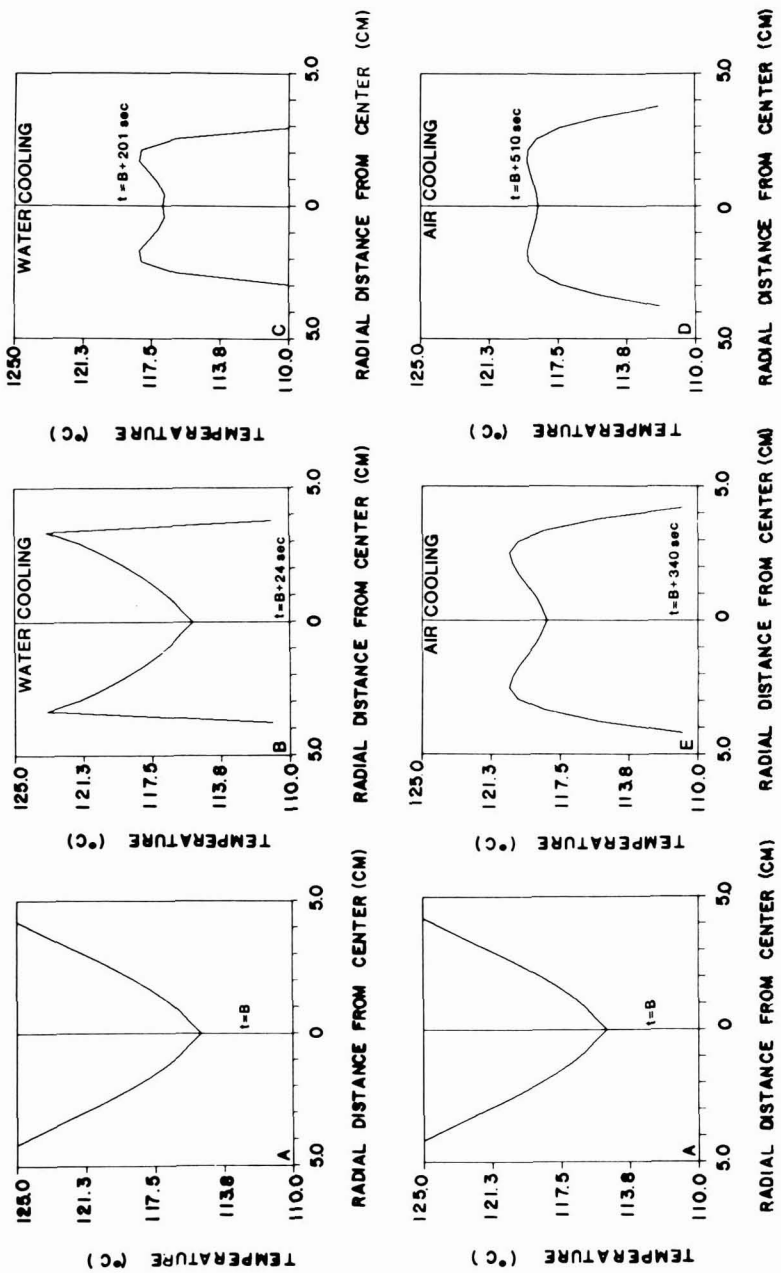


FIG. 1. TEMPERATURE PROFILES AT MIDHEIGHT OF 8 oz (307 x 200.25) CAN AT STEAMOFF (A), AND DURING EARLY COOLING (B-E) IN AIR AND IN WATER (CALCULATED)

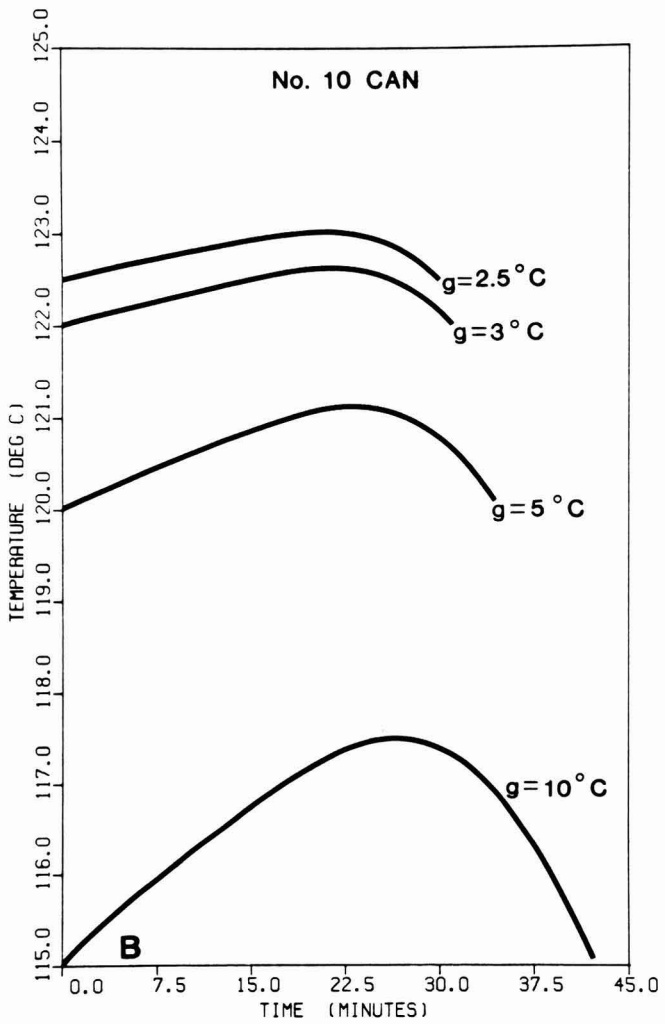


FIG. 2. OVERSHOOTING AT GEOMETRIC CENTER OF A No. 10 (603 x 700) CAN AFTER STEAMOFF DURING WATER COOLING (CALCULATED)

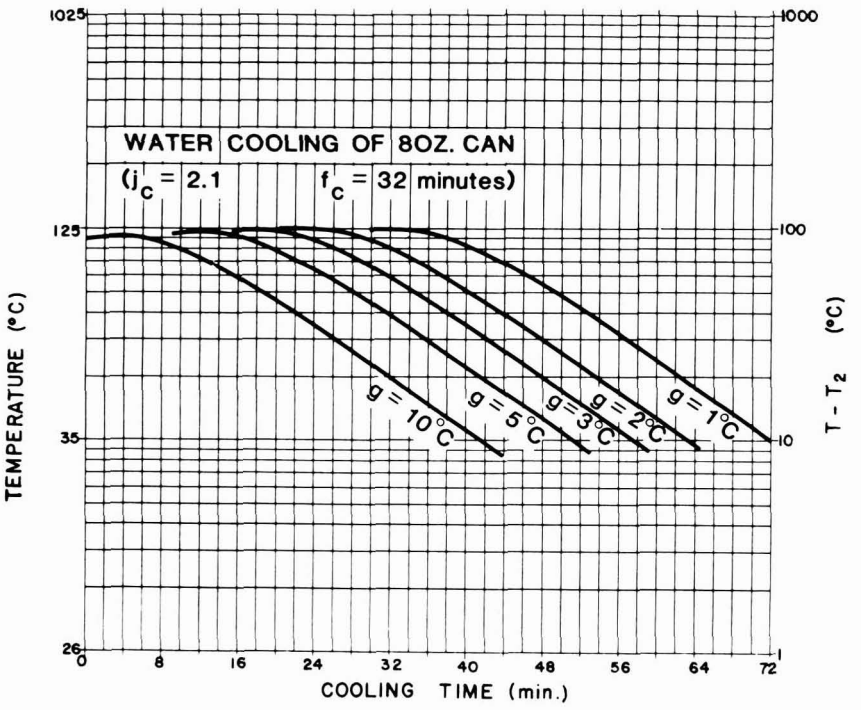


FIG. 3. SEMILOGARITHMIC COOLING CURVES AT CENTER OF 307 x 200.25 CONTAINER DURING WATER COOLING FOR DIFFERENT VALUES OF g (CALCULATED)

## Laboratory Heat Penetration Tests

Temperatures monitored at the center of No. 10 cans and 309 × 508 glass jars filled with conduction heating products show the strong effect of g value on the extent of overshooting (Fig. 7, 8). Magnitudes of predicted and experimentally determined extent and duration of the overshooting phenomenon are comparable though in most cases the predicted values were greater than those measured (Table 2). Several possible sources of differences between assumptions used in computer simulations and experimental conditions may explain these results. First, even a small error in thermocouple (TC) location will dramatically (consistently) reduce the extent and duration of overshooting observed (e.g., a displacement of 4 mm away from the geometric center of the container will result in a 30% reduction in the extent and in a 20% shortening of the overshooting measured). Accurate TC location is problematic especially when considering the possible movement of the product (or TC) in the container when the external pressure is released and con-

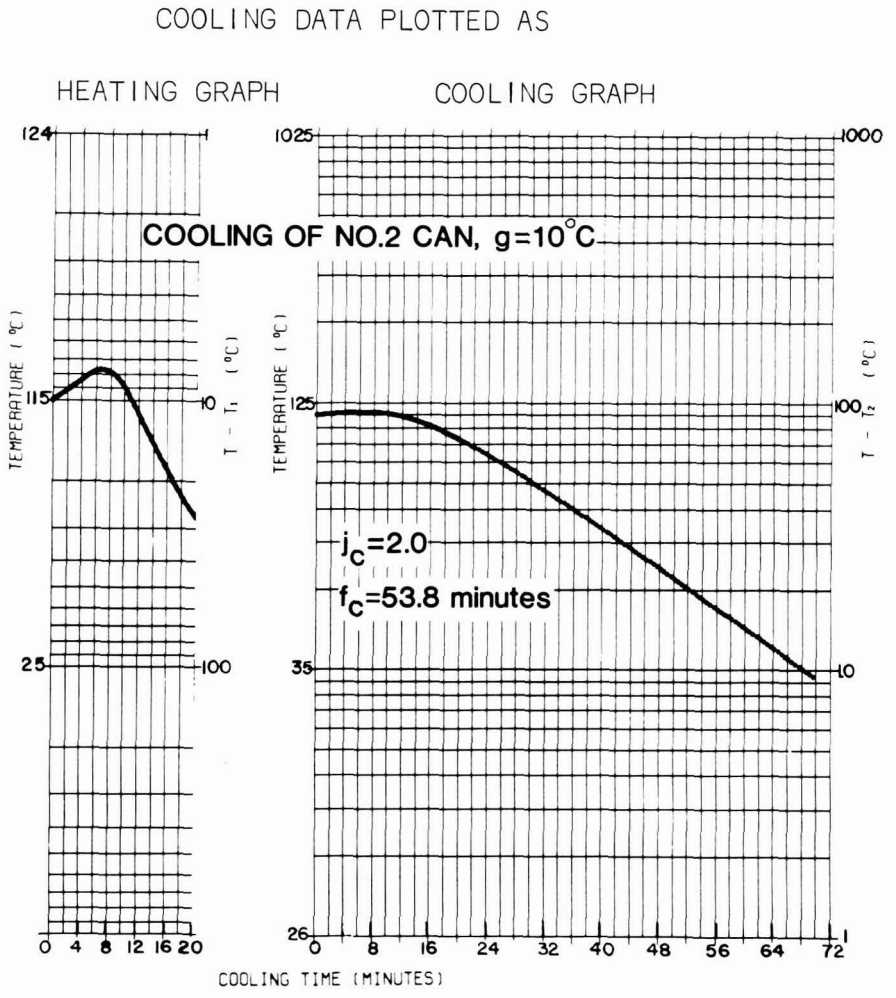


FIG. 4. TEMPERATURES AFTER STEAMOFF DURING WATER COOLING AT GEOMETRIC CENTER OF A No. 2 CAN FILLED WITH A CONDUCTION HEATING WATER-LIKE PRODUCT ON A HEATING AND ON A COOLING GRAPH (CALCULATED)

tainer ends bulge, at steamoff. These effects are not included in the computer model. Second, the formation of large temperature gradients (especially in small containers) during initial cooling, when product viscosity and yield stress values are minimal may promote natural convection even in products that heat by conduction. In contrast, the computer model assumes that heat is transferred by conduction only.

However, replacement of hot water with cold water during the processing

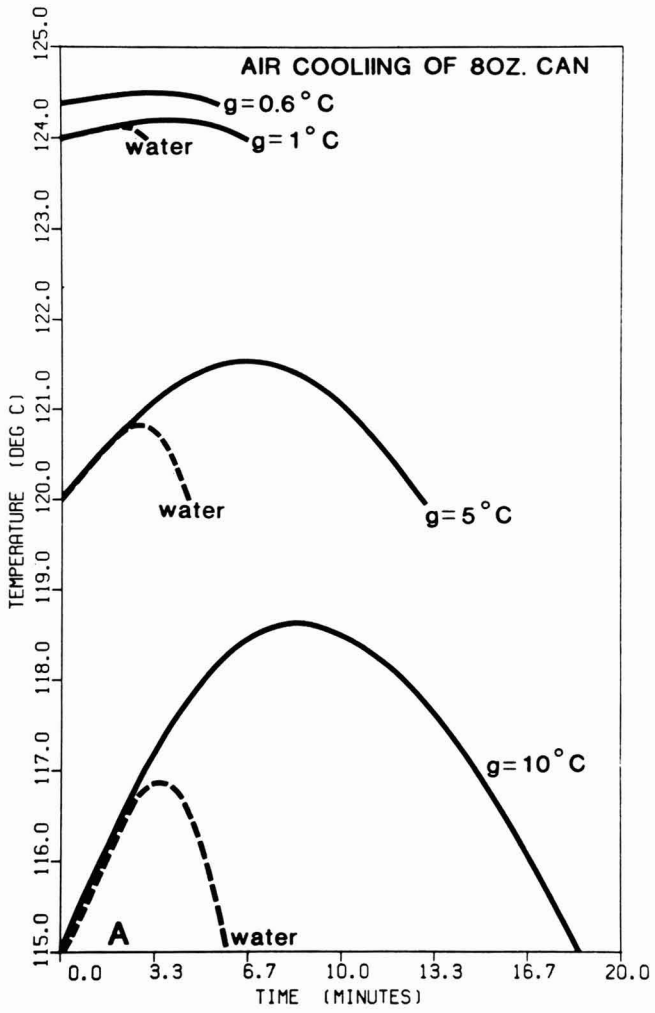


FIG. 5. OVERSHOOTING AT GEOMETRIC CENTER OF 8 oz CAN DURING AIR AND WATER COOLING FOR DIFFERENT VALUES OF g (CALCULATED)

Table 1. Effect on overshooting of external heat transfer coefficient (htc) of cooling medium used in computer simulation for a 8 oz (307 x 202.25) salmon can.

| g °C | External htc mW/cm$^2$ °C | Overshooting extent °C |
|---|---|---|
| 10 | 0.5 | 4.16 |
| 10 | 1.0 | 3.61 |
| 10 | 1.5 | 3.31 |
| 10 | 2.0 | 3.12 |
| 10 | 50.0 | 1.89 |
| 10 | 100.0 | 1.88 |
| 1.0 | 0.5 | 0.25 |
| 1.0 | 50.0 | 0.13 |
| 1.0 | 100.0 | 0.13 |

of foods in glass jars, for example, lasts over 10 min in most commercial retorts, and the replacement of steam with cooling water lasts over 5 min. This effect will tend to increase the overshooting of temperatures after steamoff under industrial processing conditions.

## Concluding Remarks

When the mechanism of heat transfer in a food container is conduction after steamoff, the overshooting can be significant, especially in large containers which have sterilization cycles that are designed for large values of g. The magnitude of the overshooting phenomena may differ under commercial processing conditions from data reported here depending on the rate of cooling water flow, retort pressure during cooling, container headspace and composition (i.e., seal temperature), and other factors which affect initial cooling rate. However, from the results reported it is evident that the possible effect of the overshooting on sterilization value delivered in a thermal process may be significant. This will be discussed in a following paper.

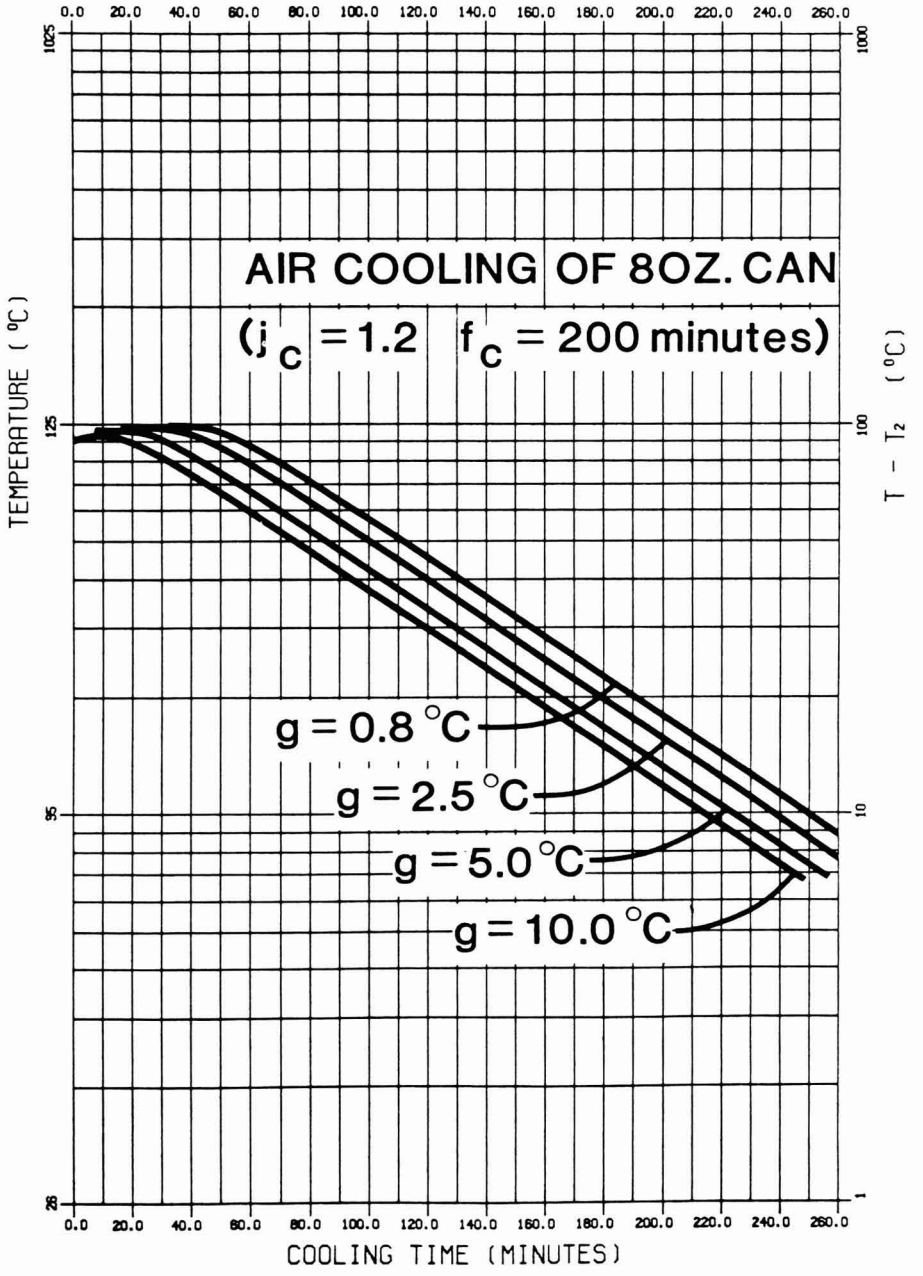


FIG. 6. SEMILOGARITHMIC COOLING CURVES AT CENTER OF 8 oz CONTAINER DURING AIR COOLING FOR DIFFERENT VALUES OF g (CALCULATED)

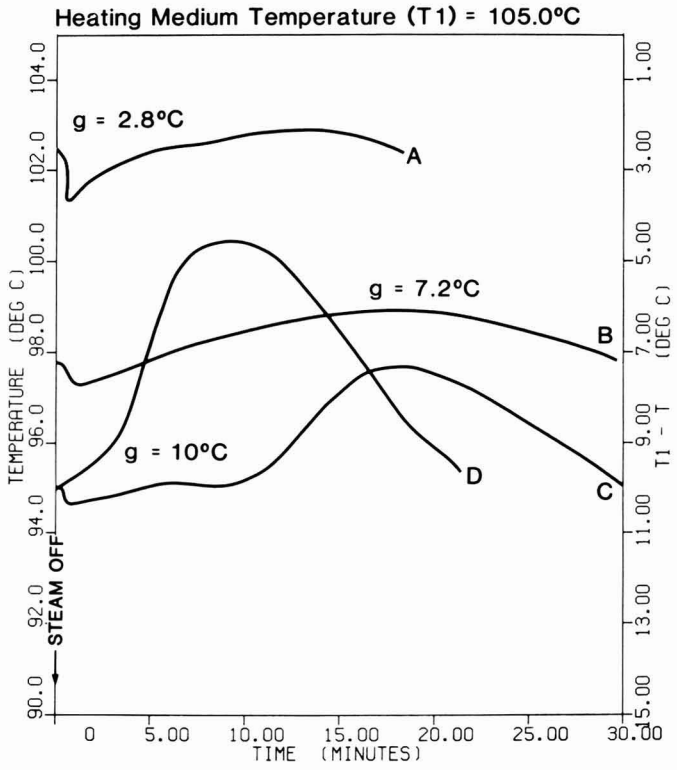


FIG. 7. TEMPERATURES MONITORED AT THE GEOMETRIC CENTER OF No. 10 (603 x 700) CAN FILLED WITH CREAM STYLE CORN (LINES A AND C) AND CREAM STYLE CORN WITH 1% AVICEL AND 1% XANTHAN (LINES B AND D) AFTER STEAMOFF DURING WATER COOLING

## ACKNOWLEDGMENTS

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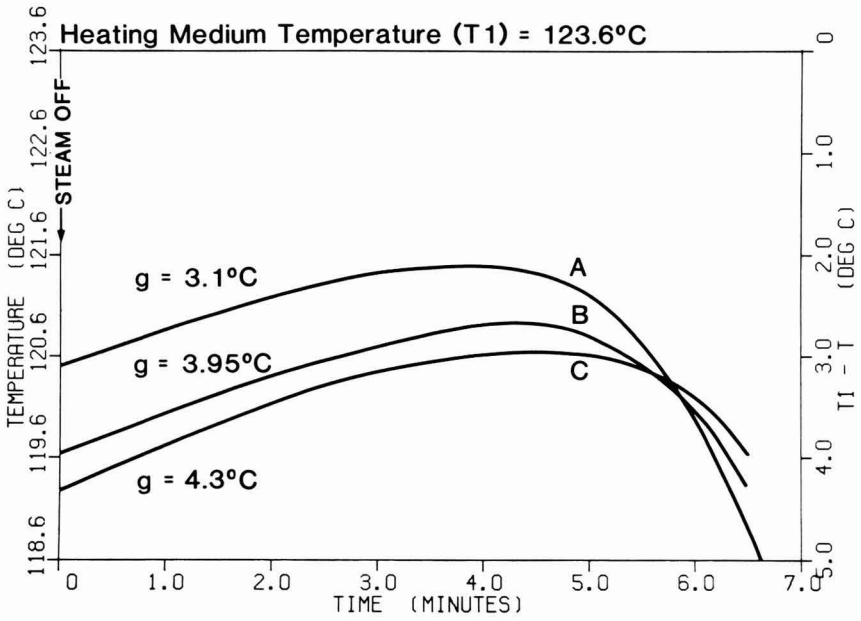


FIG. 8. TEMPERATURES MONITORED AT GEOMETRIC CENTER OF 23 oz GLASS JARS FILLED WITH A HIGH VISCOSITY STARCH PASTE PROCESSED IN A COMMERCIAL AGITATING RETORT AT A REELSPEED OF 18 rpm DURING THE COOLING STAGE

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Table 2. Duration and extent of overshooting (OS) of temperatures after steamoff obtained in laboratory and from computer simulations

| Container | | | | | Laboratory experimental | | Computer simulation | |
|---|---|---|---|---|---|---|---|---|
| size | type | g °C | Product | Heating medium | OS duration minutes | OS extent °C | OS duration minutes | OS extent °C |
| 603 x 700 | Metal | 10.0 | CSC + A (2) | Steam | 30 | 2.6 | 42 | 2.5 |
| 603 x 700 | Metal | 2.8 | CSC | Steam | 18 | 0.55 | 18 | 0.58 |
| 307 x 409 (1) | Metal | 10.0 | Meat | Steam | 10 | 1.7 | 11 | 2.3 |
| 303 x 406 (1) | Metal | 9.9 | CSC + A (2) | Steam | 9.9 | 1.13 | 9 | 2.0 |
| 309 x 508 | Glass | 13.0 | Meat | Water | 12.0 | 2.7 | 11 | 2.6 |
| 309 x 508 | Glass | 5.0 | CSC + A (2) | Water | 11.0 | 1.3 | 8 | 1.1 |
| 309 x 508 | Glass | 9.1 | Pumpkin | Water | 16.5 | 2.4 | 10 | 2.1 |
| 603 x 408 (3) | Metal | 9.6 | CSC | Steam | 39.0 | 2.8 | 35 | 2.3 |
| 603 x 408 (3) | Metal | 5.8 | CSC | Steam | 24.0 | 1.3 | 23 | 1.2 |

(1) Results presented are not average, but highest overshooting values measured for this can size and g value.

(2) 1% Avicel + 1% xanthan were mixed into the product.

(3) Retort was filled with cooling water within 5 minutes after steamoff.

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# TRANSIENT COOLING OF CONDUCTION HEATING PRODUCTS DURING STERILIZATION: STERILIZATION VALUES

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## ABSTRACT

*Significant differences (of 50-150% in some cases) between sterilization value (SV) delivered in a thermal process are calculated using Ball and Olson's (1957) and Hayakawa's (1970) mathematical methods for thermal process design and using a numerical Finite Element solution to Fouriers equation. This is because the contribution of overshooting (OS) to SV which is significant in conduction heating products packaged in large containers is not incorporated into these methods. The value of* ρ *(the ratio of SV during heating to SV during heating and cooling including the OS) is shown to be a unique function of g (the retort to cold zone temperature difference at steamoff) for given cooling conditions and z value. The relationship is validated in a laboratory and can be used for thermal process evaluation for products that heat and cool by conduction.*

## INTRODUCTION

In the previous paper (Naveh *et al.* 1984) we calculated and measured the extent and duration of the long recognized (Hicks 1951; Lund 1975; Kopelman *et al.* 1982 and others) temperature rise at the geometric center of conduction heating products during cooling, called overshooting.

The use of numerical methods to solve for temperature profiles in the product during the sterilization cycle (for example, Teixeira 1969), should yield accurate sterilization values. However, since these methods necessitate use of a computer they have not been widely implemented in the food industry. Of over 6 basic mathematical methods for thermal process design, at the present time only the time proven Formula Method (Ball 1923), over 50 years old, is presently being used.

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Recognizing the overshooting phenomena, and the fact that direct computer simulation of sterilization processes is impractical for routine process design and evaluation, in this paper, we will attempt to: (a) Further establish the need for a new mathematical method by examining the cooling curve approximations used in well accepted methods of thermal process design, (b) demonstrate the significance of overshooting in terms of sterilization value delivered in a thermal process, and (c) develop the basis for a simple mathematical method for process evaluation and design that includes the contribution of overshooting.

## EXPERIMENTAL

### Laboratory Heat Penetration Tests

The retort, metal containers, food products tested, and the procedure for carrying out the heat penetration tests, as well as the data acquisition system are described in the previous paper. (Naveh *et al.* 1984).

### Computer Simulations

The theoretical basis for the variational Finite Element method used and the validation of the accuracy of the Finite Element solution are delineated in the previous paper (Naveh *et al.* 1984). For additional information on the software used and for a stability analysis of the numerical solution see Naveh *et al.* 1983.

The model assumes that heat is transferred by conduction only during cooling and heating, that there is no movement of the product, or deformation of container (wall or lid) at the onset of cooling, and that the value of the surface heat transfer coefficient (htc) is equal on all container surfaces, and has a constant value during heating, and during cooling.

The Values below were used as input parameters unless otherwise stated:

Initial temperature, $T_o$ = 25°C
Steam temperature $T_1$ = 125°C
Cooling water temperature $T_2$ = 25°C
htc during heating, h = 1135 mW/cm²°C
htc during water cooling, h = 100 mW/cm²°C
product thermal diffusivity $\alpha$, = 0.096 cm²/s, and, container dimensions were taken as nominal dimensions minus an 1/8 in. and a 1/4 in. for internal diameter and height, respectively.

## RESULTS AND DISCUSSION

### Cooling Approximations in Thermal Process Design

The data in Fig. 1B show that for large values of g (g is the retort to cold zone temperature difference at steamoff), temperature histories predicted by Ball and Olson (1957) and Hayakawa (1970) during water cooling are significantly lower than those calculated by the Finite Element Method. Neither Ball's or Hayakawa's cooling approximations predict any temperature rise at the slowest heating zone after steamoff. The difference in initial temperature histories obtained from the numerical simulations and from the formulas of Ball and Hayakawa, is somewhat smaller, but exists even for small values of g (Fig. 1A).

The relationship between the initial cooling curves may be different for air cooling than for water cooling. In the Formula Method (Ball and Olson 1957), the initial cooling curve approximation is based on a $j_c$ of 1.41. How-

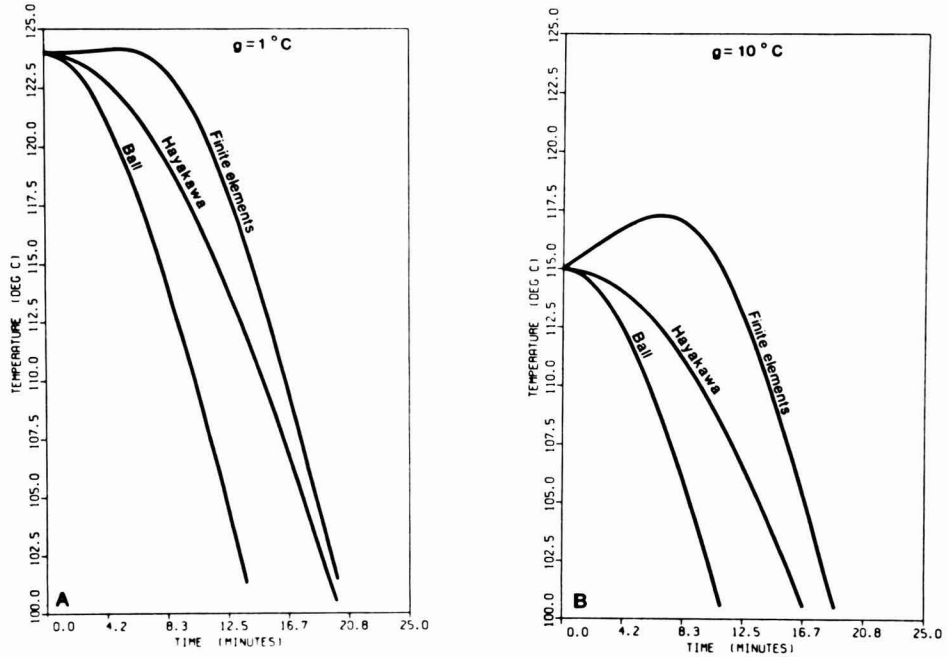



FIG. 1. TIME TEMPERATURE AT CENTER OF NO. 2 (307 x 409) CAN FILLED WITH CONDUCTION HEATING WATER-LIKE PRODUCT DURING EARLY COOLING IN WATER ($h_c$ = 100 mW/cm$^2$°C, $T_2$ = 25°C) FOR g's OF 1° C AND 10°C AT STEAMOFF ($T_1$ = 125°C)

ever, for the film heat transfer coefficient values (h) assigned in the computer simulation (h = 1 mW/cm$^2$°C, Okada 1941), a $j_c$ of approximately 1.2 was obtained. Thus, temperatures predicted by Ball may be slightly higher than those calculated by the numerical solution to Fourier's equation (Fig. 2) for small values of g where the extent of overshooting is small (Fig. 2A). As the value of $j_c$ is adjustable in Hayakawa's (1970) functions, and as in each case presented the value of $j_c$ selected was identical to that obtained by the numeric solution, the cooling approximation of Hayakawa is closer than Ball's to that calculated numerically when the overshooting is small (Fig. 2A). However, both Hayakawa's and Ball's cooling curve approximations predict much lower temperatures than those calculated by the Finite Element method for large values of g, where overshooting is more pronounced. (Fig. 2B).

Since the microbial death rate is an exponential function of temperature, the differences in the cooling curve approximations are magnified when sterilization values are calculated.

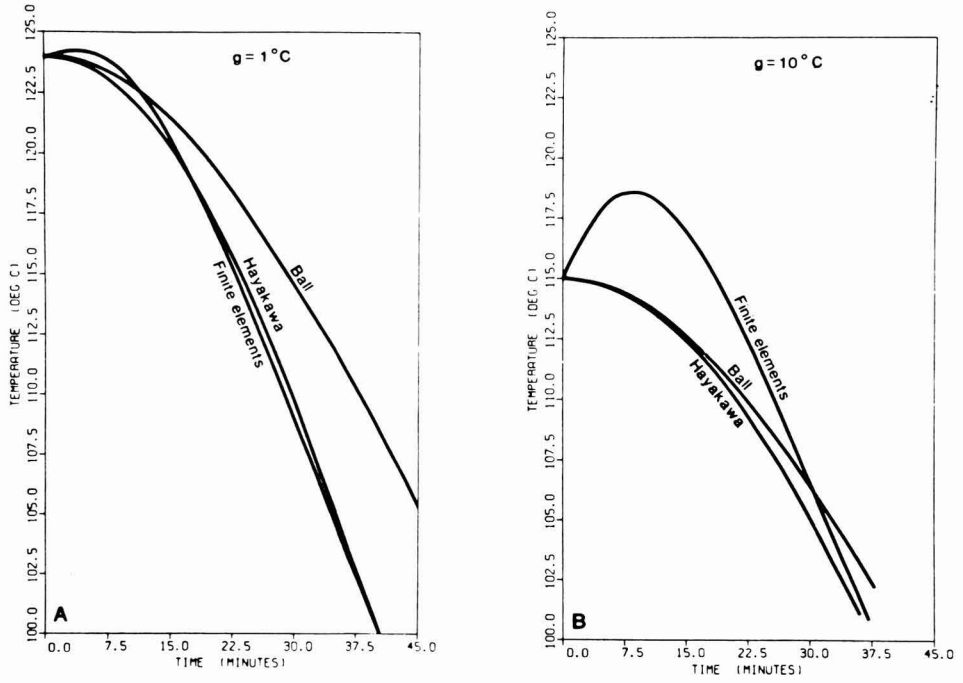



FIG. 2. TIME TEMPERATURE AT CENTER OF 8 oz (307 x 200.25) SALMON CAN FILLED WITH CONDUCTION HEATING WATER-LIKE PRODUCT DURING EARLY COOLING IN AIR ($h_c$ = 1 mW/cm$^2$°C, $T_2$ = 25°C) BASED ON BALL'S AND HAYAKAWA'S FUNCTIONS ($j_c$ = 1.02) AND THE FINITE ELEMENT SOLUTION

The sterilization value calculated using data generated by the Finite Element solution is 63% larger than the sterilization value calculated from Ball's Formula Method for the process depicted in Fig. 3, which is designed for a g of 5°C. This huge difference is typical for large cans (i.e., No. 10) filled with conduction heating products, which are commerically processed with g's of 5-15°C (Bulletin 26L, NCA, 1982). For a g of 10°C, for example, the Finite Element data gave a sterilization value 130% greater than calculated by Ball's Formula method.

From these differences in sterilization values, it is apparent that there is a need to include the contribution of the overshooting into thermal process design.

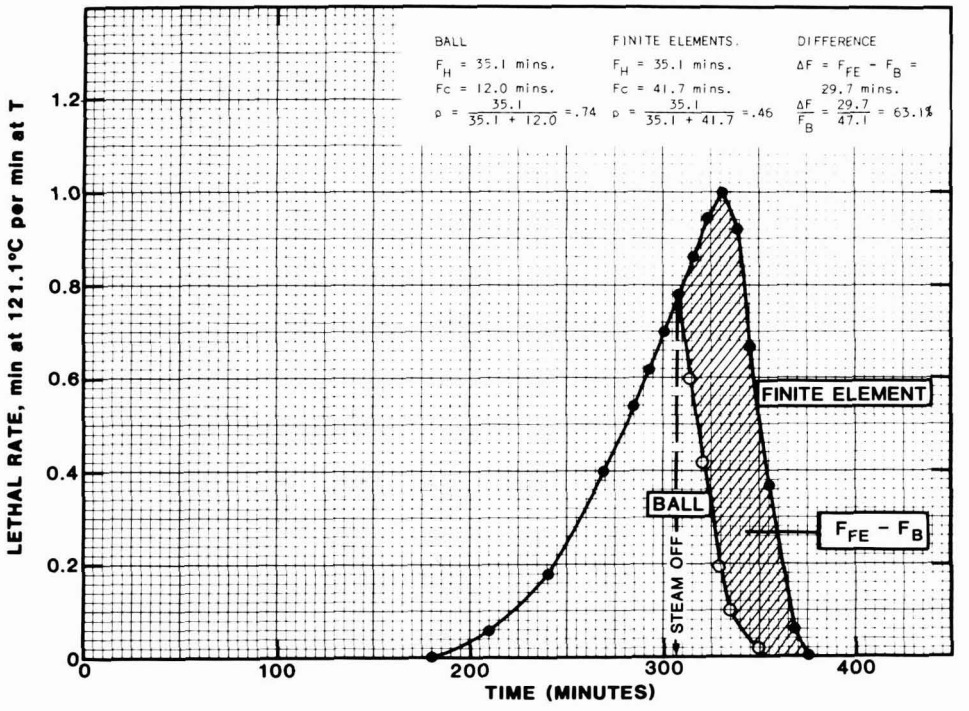



FIG. 3. LETHAL RATE PLOT OF A STERILIZATION CYCLE FOR A 603 x 700 CAN FILLED WITH A CONDUCTION HEATING PRODUCT ( = 0.096 $cm^2$/min) FOR g = 5°C AT STEAMOFF BASED ON BALL'S COOLING APPROXIMATION AND FROM FINITE ELEMENT SOLUTION ($T_1$ = 125°C; $T_2$ = 25°C; $h_c$ = 100 mW/$cm^2$°C)

## Development and Testing of a Calculation System to Include Overshooting

The ratio between sterilization value delivered in the heating phase of the sterilization cycle to the total process lethality, denoted ρ (Ball and Olson 1957), was selected as the basic dimensionless group to be used for process evaluation and design. The selection of ρ and formulation of a method for thermal process evaluation was based on the following observations:

(a) ρ is only slightly affected by container dimensions; for example, for a g of 5°C, a 5% difference in the value of ρ was calculated between a large No. 10 (603 x 700) and a small 8 oz (307 x 200.25) container.

(b) ρ is only slightly affected by product thermal diffusivity (α); as product α increases, a bigger temperature rise (overshooting), with decreased duration is observed (Fig. 4). However, the value of ρ is essentially unchanged (Table 1).

(c) ρ is affected by the heating to cooling medium temperature difference (m + g); Stumbo (1973) has reported that the value of m + g has only a small effect on the sterilization value: A 10°F increase in the value of m + g (colder cooling water), will decrease the sterilization value ob-

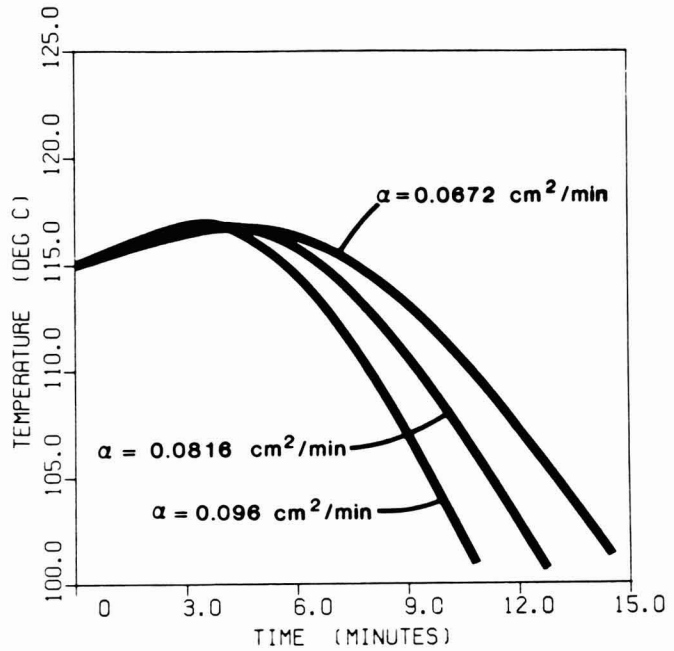



FIG. 4 COOLING CURVES AT CENTER OF 8 oz (307 x 200.25) CAN FOR THREE THERMAL DIFFUSIVITIES ($T_1$ = 125°C; g = 10°C; $h_c$ = 100 mW/cm²°C; $T_2$ = 25°C)

Table 1. Effect of product thermal diffusivity and external heat transfer coefficient (h) on ρ values for different g's calculated from cooling simulations on a 307 x 200.25 (8 oz) salmon can.

| g (°C) | Thermal diffusivity $cm^2/min$ | Cooling medium $h_1$ ($mW/cm^2°C$) | |
|---|---|---|---|
| | | Water (h = 100) | Air (h = 1) |
| 10 | 0.096 | 0.315 | 0.104 |
| | 0.0816 | 0.318 | * |
| | 0.0672 | 0.319 | 0.110 |
| 5 | 0.096 | 0.489 | * |
| | 0.0672 | 0.499 | * |
| 1 | 0.096 | 0.755 | 0.547 |
| | 0.0816 | 0.756 | 0.555 |
| | 0.0672 | 0.758 | 0.573 |

*No simulation was carried out for these parameter values.

tained by only 1%. The effect on the overshooting of temperatures as calculated from the Finite Element generated data, (Fig. 5) and on the value of $\rho$ (Table 2) indicate that Stumbo may have underestimated the importance of this parameter, especially for large values of g, where a 10°F increase in m + g corresponds to a 2-3% decrease in sterilization value.

(d) Calculated ρ values and experimentally determined ρ values were in agreement: Laboratory heat penetration data for several products packaged in metal and glass containers was used to calculate ρ. Results (Table 3), suggest that for conduction heating products packaged in large metal and glass containers, the effect of overshooting on sterilization value delivered is significant, thus decreasing ρ to values that are close to the predicted values. However poorer agreement was obtained for small size cans under the conditions studied.

These factors (a-d) suggest that for the limits of accuracy in which we normally operate in thermal process design, ρ can be considered to be a function of g only for given values of z and m + g during water cooling.

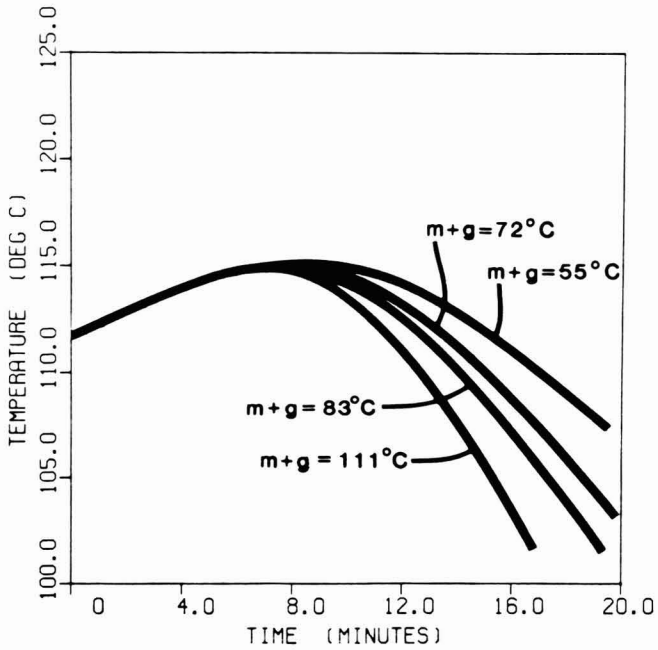



FIG. 5. COOLING CURVES AT CENTER OF NO. 2 (307 x 409) CANS FOR A CONDUCTION HEATING WATER-LIKE PRODUCT FOR VARIOUS VALUES OF m + g ($T_1$ = 125°C; g = 13.35°C; $h_c$ = 100 mW/cm²°C)

Table 2. Values of ρ obtained for different heating to cooling medium temperature difference (m + g) during water cooling.

| g (°C) | m+g, °C (°F) | | | | |
|---|---|---|---|---|---|
| | 55.5 (100) | 72.2 (130) | 83.3 (150) | 100 (180) | 111.1 (200) |
| 13.35 | 0.1584 | 0.1792 | 0.1907 | 0.2076 | 0.2120 |
| 11.0 | 0.2086 | 0.2319 | 0.2441 | 0.2621 | 0.2677 |
| 6.0 | 0.3685 | 0.3939 | 0.4071 | 0.4255 | 0.4315 |
| 1.2 | 0.6774 | 0.6958 | -- | 0.7182 | -- |

Table 3. ρ values determined experimentally for different container types, products and jars (1).

| Container | g (°C) | Product | m+g (°C) | ρ | |
|---|---|---|---|---|---|
| | | | | Experimental | Predicted |
| 603 x 700 | 10.0 | CSC + A (2) | 100 | 0.322 | 0.284 |
| 603 x 700 | 2.3 | CSC | 100 | 0.602 | 0.624 |
| 603 x 408 (3) | 9.6 | CSC | 95 | 0.294 | 0.296 |
| 603 x 408 (3) | 8.2 | CSC | 95 | 0.338 | 0.339 |
| 603 x 408 (3) | 7.0 | CSC + A (2) | 95 | 0.382 | 0.382 |
| 307 x 409 (4) | 10.0 | Meat | 100 | 0.30 | 0.284 |
| 307 x 409 (4) | 8.7 | CSC | 122 | 0.40 | 0.323 |
| 303 x 406 (4) | 9.9 | CSC + A (2) | 100 | 0.26 | 0.287 |
| 303 x 406 (4) | 7.5 | Pumpkin | 95 | 0.30 | 0.36 |
| 23 oz jar | 9.1 | Pumpkin | 95 | 0.26 | 0.310 |

(1) Rho values are calculated for a z of 10°C.

(2) 1% avicel and 1% xanthan gum were mixed into the product.

(3) Retort was filled with cooling water within 5 minutes (vs. 2 minutes usually).

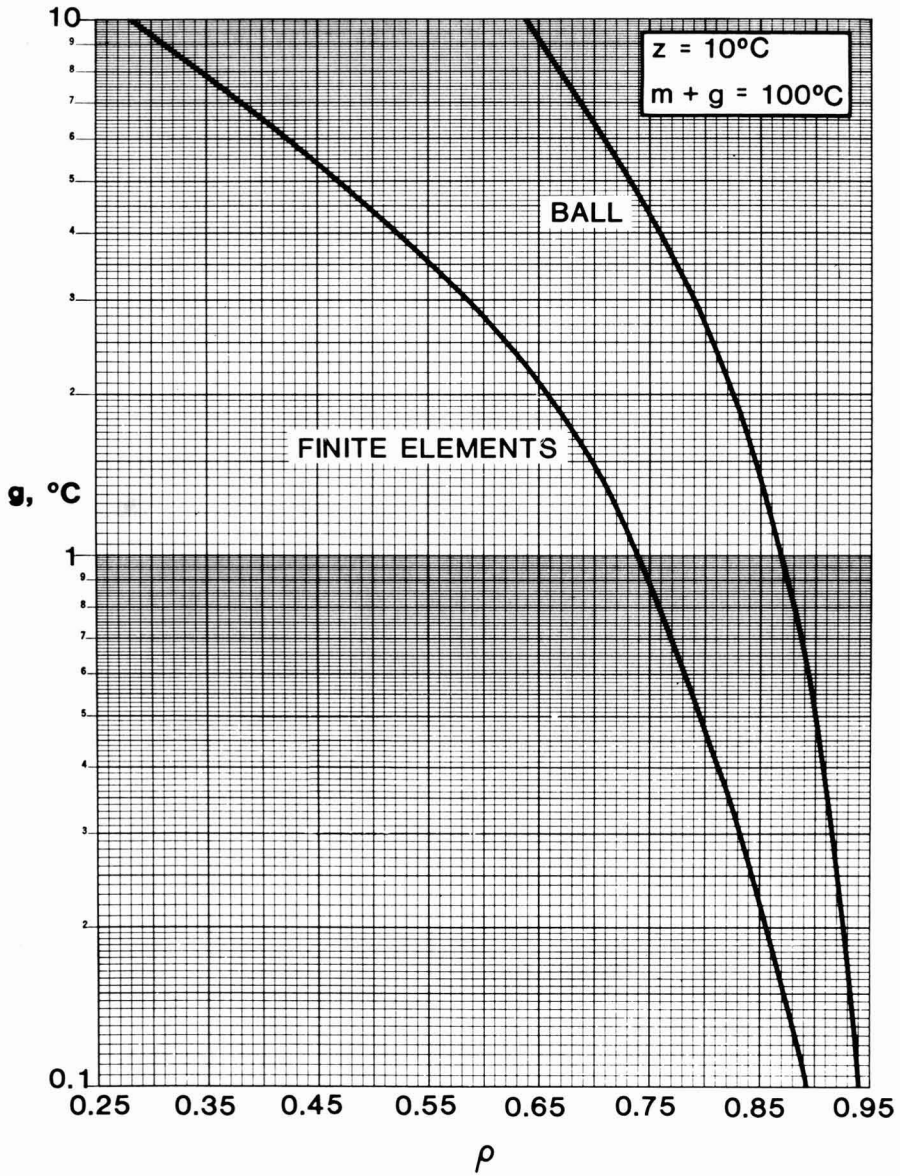
(4) Lowest ρ value obtained for this can size and g is reported.

In Fig. 6 are presented the ρ values obtained from computer simulations for a range of g values. These values are significantly lower than predicted by Ball's formula method. The chart can be used for process evaluation. We are presently developing ρ versus g tables and polynomials that will facilitate process design and evaluation, to be published shortly.

## CONCLUDING REMARKS

The relationship between ρ and g can be used as a basis for a mathematical method for process design and evaluation of thermal processes. It is

FIG. 6. ρ VERSUS g BASED ON BALL'S FORMULA METHOD AND FROM COMPUTER SIMULATIONS FOR WATER COOLING



based on the assumption that the transfer of heat in the container occurs by conduction only during heating and cooling. Therefore, before applying the method to commercial products it must be verified that the mode of heat transfer is indeed conduction. From a limited experimental matrix we have shown good agreement between predicted and experimental value for products packaged in large sized cans and glass jars, and poor agreement for smaller containers.

It is expected that the application of a mathematical method for process design and evaluation based on the $\rho$-g relationship developed, will be primarily directed to conduction heating products processed in large sized containers which are commercially processed to large values of g, where overshooting is significant.

## ACKNOWLEDGMENTS

This research was supported in part by a grant from the U.S.-Israel Binational Agricultural Research and Development Fund (BARD) (J-32-75) and HHS/FDA Contract 223-79-2258. Scientific Journal Series 14,009 Minnesota Agricultural Experiment Station, St. Paul, Minnesota 55108.

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NAVEH, D., KOPELMAN, I. J. and PFLUG, I. J. 1983. The finite element method in thermal processing of foods. J. Food Sci. *48,* 1086.
TEIXEIRA, A., DIXON, J. R., ZAHRADNIK, J. W. and ZINSMASTER, G. E. 1969. Computer determination of spare survival distributions in thermally processed conduction heating foods. Food Tech. *23,* 78.

**The Vanishing Harvest,** a study of food and its conservation, R. K. Robinson, Department of Food Science, University of Reading, Oxford University Press, 1983. $39.95.

In the preface of this book, the author indicates that he wishes to focus attention on the avoidable losses between the farm gate and the consumer. He consequently attempts to cover all aspects of food conservation from current world resources through projections for the next century.

This book would serve well for individuals who are novices in the area of world food supply programs and are far from expert in the area of food science and technology. It serves as an overview of potential. The author suffers as do most individuals writing on this subject from the difficulty of interpreting the diverse facts and figures on agricultural output.

After a brief overview of the world food resources, a chapter is dedicated to composition of foods. Again, this is useful for those individuals who have little or no background in the area. The next chapter studies the causes of post-harvest deterioration ranging from the insects to indigenous biological activities in the food. The chapter on conservation-the first steps emphasizes the use of appropriate techniques and identifies the possible options available for preservation. An entire chapter is dedicated to the drying of foodstuffs. This is appropriate since it has great significance in the developing nations. Again appropriate technologies are emphasized. The chapter on preservation at low temperatures also identifies certain appropriate technologies that are valuable in developing nations. Preservation by heat treatment discusses both pasteurization and commerical sterilization techniques. The role of fermentations discussed in the next chapter of the book seems to be less than comprehensive for the possible treatment of the variety of fermented products that are or could be available worldwide. Miscellaneous techniques for preventing spoilage include the application of chemicals, fumigants, organic acids and preservatives; concentration; intermediate moisture foods; and radiation. They have to be treated briefly. In the concluding chapter on toward the next century, the author treats the attitude to the west and developments in the third world, including limited assistance and free enterprise. In the latter the author discusses the role of multinationals and dedicates five pages to the role of Nestle in milk processing in the tropics. This was anticlimatic as the last item in the book.

This book should serve the purpose of a general overview of food conservation and its role in supplying adequate food in developing countries. It is written at a level that individuals with little or no scientific or technical background can readily appreciate food conservation.

F. BUSTA

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