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Title: Quality Variability in Institutional Size Canned Foods: Conduction-Heated Pea

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The kinetic parameters for the heat inactivation of thiamine in conduction-heated

canned food (pea puree) were evaluated using an optimization procedure and a

numerical technique for heat transfer calculations and quality retention prediction. The

$D_{121.1^\circ C}$ and z values obtained were 304 ± 32 minutes and $30\pm3^\circ C$ respectively. The

quality variability of canned pea puree in institutional size cans (603x700) with

thiamine retention as a quality indicator showed a much greater variability than pea

puree in retail size containers (303x406). An optimization procedure and the numeric

technique for heat transfer, lethality and quality calculations showed that a search for

time-dependent process temperatures reducing quality variation yields only minor

improvements over constant temperature processes.

Quality Variability in Institutional Size Canned Foods:

Conduction-Heated Pea Puree

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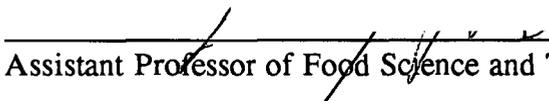
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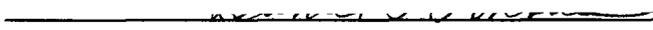
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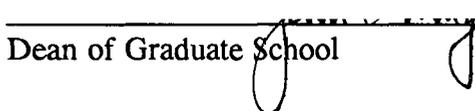
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Dean of Graduate School

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INTRODUCTION

General considerations

Thermal processing is one method by which fresh foods, limited in both time and space, are preserved and made available out of season or remote from growing areas. The purposes of thermal processing are to destroy pathogenic and/or spoilage-causing microorganisms and inactivate heat-labile toxins and enzyme systems that cause degradation in the food. However, while thermal destruction of the detrimental elements is occurring, nutrients and other desirable attributes are being simultaneously destroyed at varying rates. The rate of destruction depends primarily upon the susceptibility of the microorganisms, enzymes, or nutrients to heat. In general, the susceptibility of the microorganisms to thermal destruction is much greater than that of enzymes or nutrients. This difference in susceptibility, combined with the heating characteristics of foods, has led to the development of a variety of various methods aimed at achieving safety while optimizing quality.

Kinetic parameters

The first step in optimizing any process for retention of nutrients is to examine the reaction rates for thermal destruction and, more importantly, to consider the

temperature dependence of reaction rate constants. Ball (1923) proposed the first mathematical model to calculate the thermal processing effect of any time/temperature treatment applied to a food. These calculations were based on the definition of D- and z-values. D-values are defined as the time at a constant given temperature for a tenfold reduction in the concentration of a given quality factor (e.g. microbial load or nutrient concentration). Values are usually reported at a reference temperature (T_r) of 121.1 °C (250 °F). z-values are defined as the temperature increase required for a tenfold reduction of D-values. Today, models are available which use more conventional reaction kinetic parameters. In chemical kinetics the reaction rate constant (k) and the Arrhenius energy of activation concept are used to express the time and temperature dependence of chemical and biological reactions occurring during thermal processing. Reaction rates and their dependence on the thermal history of the product are used to calculate the inactivation of the components used as the basis for the evaluation of a process. Since most deteriorative reactions in foods are first order or pseudo first order, quality factor changes follow a linear relation on a semilogarithmic plot of quality versus time. The relationship between the D-value and k is given by the following expression:

$$D = 2.303/k \tag{1}$$

The temperature dependence of the reaction rate constant is given by the Arrhenius activation energy (E_a) model. The relationship between z and E_a at a temperature T

is given by (Lenz and Lund 1977b):

$$E_a = (9/5) \times (2.303 \ R \ T \ T_r)/z \qquad (2)$$

where R = universal gas constant. Eq. (2) is dependent on temperature even though both z and E_a are independent of temperature. This dependence results from the fact that the temperature effect model used by Ball (1923) is not consistent with that used by the chemical kinetic model. E_a-values are defined as the slope of the linear relationship of the semilogarithmic representation of the kinetic constant versus the inverse absolute temperature.

Optimization of thermal processes for conduction-heating foods

The greater temperature dependence of destruction rates for spores as compared to nutrients and other quality factors suggests that high temperature processes should optimize the nutrient retention of thermal processes. High temperature short time (HTST) processes are used for several foods. However, this procedure is only applicable when all food locations receive approximately the same lethal treatment. This is a good assumption for products which heat very rapidly and thus most of the thermal destruction occurs at the steam or heating medium temperature (such as in plate heat exchangers used for liquid foods). However, it cannot be applied to conduction-heating foods where much of the lethality occurs during the heating-up and the cooling-down operations. Consequently each volume element of the food is

exposed to a different thermal history.

It is often possible to assume that the center point of conduction-heating canned foods receives the least lethality. The lethality of a process is therefore defined as the time at the reference temperature with a lethality equivalent for the temperature history of the geometric can center. However, recent investigations have shown that the location of the least-lethal point, the critical point, depends on the geometry of the container and the boundary conditions of the process. Therefore, it would be more convenient to design thermal processing using an overall lethality-value, F_s. F_s-values are defined as the mass-average lethality obtained by integrating the effect of the heat treatment at every point in the container over the volume of the container. F_s results in the same lethality criteria independent on geometry and displacement of the least-lethal point.

Several investigators have developed methods for calculating the average destruction of nutrients and microorganisms in foods heated by conduction. Most of these methods require computer implementations. Using D and z-values for nutrients and spores, various thermal processes at constant temperature processes, all equivalent in spore lethality, were compared for retention of nutrients. These studies showed that HTST is not the best thermal process for nutrient retention in conduction-heating foods, and, moreover, each process must be individually optimized.

Until recently, only few investigators have considered variable heating medium temperature because of the impractical experimental trial and error evaluations that would be involved. However, recent advances in optimization methods and numerical

techniques combined with the increased availability of fast computers have facilitated the evaluation of retort processes with time-dependent temperatures (microbial inactivation and nutrient retention calculations).

Research justification

The purposes of thermal processing are to destroy pathogenic and spoilage-causing microorganisms and inactivate toxins and enzyme systems causing food degradation. However, concomitant with the destruction of the detrimental elements, nutrients and other desirable attributes are destroyed at varying rates. High temperature short time (HTST) processes have been shown to optimize the quality of convection-heated foods whereas they were not adequate for conduction-heated foods. Preliminary investigations showed that quality retention distribution in the content of conduction-heated foods processed at constant retort temperature depends on the size of the can. An interesting question to be answered is if there is an optimum time-dependent retort temperature profile maximizing quality retention and improving distribution of the quality retention in the content of institutional size cans. The answer for this question can be investigated using optimization methods. Fortunately, several mathematical models and optimization methods have been developed and are available in the literature. However, the use of these models rely on the availability of thermophysical data for the food and the kinetic parameters of the destruction for the quality indicator under consideration.

Research goal

The purpose of this research was the identification of time-dependent retort temperatures that reduce quality variability in the content of institutional size cans when used for conduction-heated foods. Experimental tests and computer-supported calculations used pea puree as an example of conduction-heated foods. Thiamine retention was used as a quality retention indicator.

Research objectives

The following objectives were completed:

1. Determination of the thermal diffusivity of pea puree.

2. Determination of the kinetic parameters for the thermal destruction of thiamine using an optimization procedure and simple retort processing experiments.

3. Experimental validation of a mathematical model to estimate the thiamine retention distribution in the content of cans with conduction-heated foods.

4. Analysis of quality variability inside institutional size cans with conduction-heated foods using thiamine retention as a quality indicator.

5. Identification of time-dependent process temperatures that reduce quality variation in the content of institutional size cans.

LITERATURE REVIEW

Thermal diffusivity

Bacteriological safety recommendations require identification of a thermal history resulting in a required lethality. This history is dependent on the type of food and its container, container geometry, and the boundary conditions during thermal processing. Many foods have physical characteristics that make conduction the primary mode of heat transfer during thermal processing. The temperature-time relationship of a given conduction-heated food may be calculated if the thermal diffusivity of the product is known. Thermal diffusivity (α) determines how fast heat propagates through a material under transient heating conditions.

There are two general approaches to the problem of measuring thermal diffusivity: (1) it may be calculated from the relation $\alpha = k/\rho\, c_p$; or, (2) it may be measured directly from unsteady-state heating experiments. In the first approach, thermal conductivity (k), density (ρ), and specific heat (c_p) have to be evaluated independently. Although density can be easily measured and specific heat can be estimated quite accurately from food composition information, reliable values for thermal conductivity are often not available in the literature and are sometimes difficult to determine experimentally (Gaffney *et al.*, 1986).

The second and most common approach for determining thermal diffusivity involves temperature versus time measurements on a sample of specified geometrical shape undergoing transient heat exchange. Fourier, who developed the theoretical basis of heat conduction in solids, recognized the possibility of using transient

temperature data to determine thermal properties as early as 1822 (Fourier, 1822). Thompson (1919) developed a transient heat transfer procedure to determine the thermal diffusivity of foods processed in cylindrical cans. Olson and Jackson (1942) and Ball and Olson (1957) were responsible for the widespread use of this procedure in the food processing industry.

The transient method has been used in many ways to determine thermal diffusivity. For our purpose we will review the most used method, namely the slope method. The slope method, developed theoretically by Olson and Jackson (1942) and then applied by many other researchers (Dickerson, 1965; Hayakawa and Bakal, 1973), has been recently reviewed by Gaffney et al. (1986). The slope method involves placing a product sample, initially at a uniform temperature, into a surroundings maintained at a constant temperature different from the initial sample temperature for the duration of the test. The determination of thermal diffusivity involves temperature measurements, as a function of time, at one or more points within the object. Temperature measurements are fitted to an analytical solution for heat transfer in solids.

The analytical solution to the governing heat transfer equation imposes several assumptions that need to be fulfilled for the slope method to be valid. This can be summarized as follows (Gaffney et al., 1986): (1) the food material must be homogenous; (2) an analytical solution must exist for the object shape under consideration; (3) the initial food temperature must be uniform; (4) the temperature of the surroundings must be constant with time; (5) the surface heat transfer coefficient,

h, must be constant with time; and, (6) the thermal properties of the material must be constant with time and temperature. If these assumptions are met, the time temperature response at any position within a solid object undergoing transient heat exchange can be described by infinite series solution of the conduction heating equation. The generalized form of these series solutions are given by Eqs. (3) and (4).

$$T_x = (t_x - t_\infty)/(t_i - t_\infty) = \sum_{n=1}^{\infty} C_n(x)\, EXP[-(\lambda_n)^2\, \alpha\theta/l^2] \qquad (3)$$

$$Bi = \lambda_n\, J_1(\lambda_n)/J_o(\lambda_n) \qquad \text{infinite cylinder} \qquad (4a)$$

$$Bi = \lambda_n\, \tan \lambda_n \qquad \text{infinite slab} \qquad (4b)$$

where

$\alpha\theta/l^2$ = Fourier number (dimensionless) = Fo

T_x = dimensionless temperature ratio, function of time and position within the solid

t_x = temperature as a function of time and position within the solid

t_∞ = constant surrounding environment temperature

t_i = initial solid temperature (uniform)

λ_n = nth root of the transcendental Eq.4 appropriate for the given geometry

$C_n(x)$ = a function of λ_n, geometry, and position within the solid but not dependent on time nor temperature

α = thermal diffusivity

θ = time

Bi = Biot number, hl/k

l = solid characteristic length (cylinder radius and slab half thickness)

h = surface heat transfer coefficient

k = solid conductivity

$J_i(\lambda_n)$ = first order Bessel function of the first kind

$J_o(\lambda_n)$ = zero order Bessel function of the first kind

The slope procedure is based on the observation that the temperature progression becomes purely logarithmic after a sufficient time has elapsed (Fo > 0.2). In this region, the temperature ratio can be described by using only the first term of the series solution.

$$T_x = C_i(x) \, EXP[-(\lambda_n)^2 \, \alpha\theta/l^2] \tag{5}$$

or,

$$\ln(T_x) = -(\lambda_i/l)^2 \, \alpha\theta + \ln C_i(x) \tag{6}$$

A semi-log plot of time-temperature data yields therefore a straight line with a slope given by $-(\lambda_i/l)^2\alpha$. Further, the slope of the straight line portion of the time-temperature curve is the same for any location within the object, since $-(\lambda_i/l)^2\alpha$ is

independent of the position parameter contained in $C_i(x)$. Therefore, all of the information necessary to determine thermal diffusivity is contained in the slope (m) of the straight line portion of the time-temperature curve for any position within the object. The exact location of the temperature probe needs not to be known. The slope is used to evaluate α as follows:

$$\alpha = -m(1/\lambda_i)^2 \tag{7}$$

The use of Eq.(7) for the determination of thermal diffusivity, requires that the product be in the shape of a sphere, an infinite cylinder or an infinite slab. Williamson and Adams (1919) developed an approach for finite geometries which has been utilized by several researchers (Olson and Jackson, 1942; Ball and Olson, 1957; Smith et al., 1967; Crumpton and Threadgill, 1977). This approach consists of using a sample in the form of a short cylinder or a brick shape. Solutions for finite cylinders and slabs are available from the concept of product solutions, that is the temperature ratio for the finite cylinder has been shown to be the product of T_r for the infinite cylinder multiplied by T_x for the infinite slab of a thickness that defines the length of the finite cylinder. Similarly, T_x for a brick shape (finite slab) can be determined with the same concept.

The thermal diffusivity of a product sample in the form of a finite cylinder can therefore be determined from the slope (m) of the straight line portion of a semi-log plot of time-temperature data for any position within the object as:

$$\alpha = -m/[(\lambda_1/l)^2{}_{cyl} + (\lambda_1/l)^2{}_{slab}] \tag{8}$$

In order to compute thermal diffusivity from Eq.(8), the value of λ_1 for the given experiment must be known. The value of λ_1 for the cylinder and the slab are directly related to Bi, which, in turn, is a function of the h, l and k values for the sample. It is common practice, when measuring thermal diffusivity by the slope method, to provide sufficient agitation in the bath, i.e. the value of Bi will be very high. When Bi$\rightarrow \infty$, λ_1 approaches a constant limiting value and the exact value of Bi (or h) needs not to be known or maintained constant during the experiment as long as it is large. When Bi $\rightarrow \infty$, the values for λ_1 are 2.4048 and $\pi/2$ for the two regular geometries of interest, infinite cylinder and infinite slab, respectively (Gaffney et al., 1986).

Thermal processes

Blanching, pasteurization and commercial sterilization are thermal processes used extensively alone and in combination with other preservation techniques to extend the storage life of foods. A thermal process can be defined as the process wherein the product temperature is elevated above ambient temperature. The objective of thermal processes is to eliminate or reduce microorganisms and/or enzymes that would, upon storage, result in food deterioration or would endanger the health of the consumer. Concomitant with these desirable changes essential nutrients are also destroyed (Lund, 1975). Since the purpose of a thermal process is to extend the storage life of the food

to insure a nutritious food supply, a corollary objective of the thermal process must be to maximize the retention of nutrients (Lund, 1977). The destruction of quality factors usually follows a first order reaction kinetics and the temperature effect on the rate constant usually follows the Arrhenius model (Clark, 1978).

Blanching is frequently applied to tissue systems prior to freezing, drying, or canning. The objectives of the blanching process depend on the subsequent treatment of food stuffs (Lund, 1977). For example, blanching prior to freezing or drying is used primarily to inactivate enzymes which would contribute to undesirable changes in color, flavor, or nutritive value during dehydration and storage. Blanching prior to canning serves several different functions including wilting the tissue to facilitate packing, removing tissue gases prior to container filling, increasing the temperature of the tissue prior to container closing, and inactivation of enzymes (Lund, 1977). Blanching is usually accomplished by heating the product in steam or hot water at temperatures below 100°C. Microbial destruction is not the primary objective of the blanching process for canning, but is a key factor in reducing the microbial load in frozen products (Lund, 1977).

Pasteurization is a thermal process designed to inactivate part but not all of the vegetative microorganisms present in foods. Pasteurization must be used in conjunction with other preservation techniques such as fermentation (e.g., pickles), refrigeration (e.g., milk) and maintenance of anaerobic conditions (e.g., beer). A pasteurization process is designed with reference to a spoilage microorganisms (e.g., yeast in beer, yeast and molds in high acid fruit juices) or a health-hazard organism

(e.g., *Coxiella burnetti* in milk).

Sterilization processes are those which inactivate microorganisms, or their spores, which would grow and produce spoilage or health hazards under the condition of food storage (Lund, 1977). Most commercially sterile foods are packaged under conditions which insure anaerobic conditions because spores of anaerobic organisms are generally less heat resistant than spores of aerobic organisms resulting in less severe thermal processes. Finally, it is relatively easy to maintain an uncontaminated anaerobic condition, and oxidative reactions which could occur during heating are minimized.

Mathematical models for heat sterilization processes

One purpose of mathematical modelling is to execute calculations that improve our understanding of an actual process. Experimentation with mathematical models offers practical and economic advantages over the physical system which is often inconvenient to test (Clark, 1978).

The mathematical determination of a sterilization process requires thermal and kinetic information, i.e. microbial lethality and destruction rate of quality factors. Food temperature can be measured directly or predicted theoretically with excellent accuracy (Manson *et al.*, 1974). Microbial lethality is mathematically approximated by the following expressions (Charm, 1971).

$$D_r/D = 10^{(T-Tr)/z} \tag{9}$$

$$F_o = \int_0^t 10^{(T-Tr)/z} \, dt \tag{10}$$

where

D = decimal reduction time, i.e. time required for number or concentration of spores to be reduced by a factor of ten at a given temperature T

D_r = D value at a reference temperature T_r

F_o = sterilizing value of a thermal process, defined as a lethality-equivalent time at the reference temperature

T = food temperature as a function of time

z = temperature increase required for a tenfold reduction of D-values

Several methods have been reported for sterilization calculations and can be classified by Hayakawa (1978) as groups I and II. Group I procedures are based on the evaluation of the lethality at the slowest heating point while those in group II are based on the evaluation of a mass average lethality for the whole container. The latter have the advantage of an easy incorporation of estimates for nutrient retention (or any other quality factor) and can also include energy consumption calculations.

Group I procedures can be divided into general methods and formula methods. General methods usually do not provide a means of predicting the food time-temperature relation. On the other hand, formula methods have built-in means for this prediction. General methods are the most frequently used procedures for estimating the lethality of a process. Experimental heat penetration data are used directly in lethality calculations without any assumptions on the time-temperature relation.

Formula methods may be subdivided into two subgroups depending upon the nature of the formulas used for predicting the temperature history curve of a food undergoing a heat process: those based on the use of empirical formulas and those based on the use of theoretical formulas. In empirical methods, food temperatures collected during heat processing are usually plotted on semi-log paper, on which a log scale represents temperature differences between food and the surrounding heating or cooling medium while a linear scale represents heating or cooling time. The first empirical method was developed by Ball (1923) and is still widely used by many processors. Several modifications have been published to increase its flexibility and accuracy.

Several researchers have developed theoretical formulas to predict the heat transfer process in a can. Most of these methods are applicable only to cylindrical cans. The first method developed assumed an initial uniform food temperature, thermophysical properties independent of location and temperature, food surface temperature identical to the surrounding medium temperature at any time during the process, and finally a can with no headspace (Hayakawa, 1978). Later methods have removed some of these restrictions (e.g. Hayakawa and Ball, 1971).

Group II methods are based on integrated lethality (F_s) and have been adapted to include retention predictions of nutrients. All published procedures are based on theoretical solutions for the heat-conduction equation to estimate transient-state temperature distributions. Mass average concentrations of heat-labile factors were determined by Teixeira *et al.* (1969a,b) using a numerical solution of the heat-conduction equation in cylindrical cans. A finite-difference technique was used to

estimate transient-state temperature distributions. The large number of calculations required by this procedure were possible only by using a digital computer.

Manson *et al.* (1970) developed a method for estimating the mass average sterilizing value of a thermal process applied to solid foods in brick-shaped containers. Their general approach is similar to the one used by Teixeira *et al.* (1969a,b). Manson *et al.* (1974) developed a method for estimating thermal processes applied to solid foods in pear-shaped cans used for packing cured fresh ham. More recently, Simpson *et al.* (1989a,b) described a mathematical model for the sterilization of conduction-heated foods in oval-shaped containers.

HPLC methods for the determination of water-soluble vitamins

HPLC methods offer an attractive alternative to the more time-consuming chemical or microbiological assays for vitamins because of their increased specificity, sensitivity and reduced analysis time.

Sample extraction and clean up. In foods of plant and animal origin the vitamins usually occur in trace amounts as conjugated phosphorylated forms bound to proteins. The extraction procedure involves extensive acid hydrolysis of the food at elevated temperatures producing an extract containing appreciable amounts of potentially interfering substances derived from the hydrolysis of the food matrix (Finglas and Faulks, 1987). Extraction with trichloroacetic (TCA), perchloric, sulfuric or sulphosalicylic (SSA) acid in the 5-10% (w/v) concentration range is usually preferred

to keep the phosphorylated forms intact by chemically denaturing the bound proteins (Vanderslice *et al.*, 1980). If acids are used it is important to ensure that the resulting extract is compatible with the analysis. For example, SSA is strongly fluorescent and it is therefore necessary to remove it from the extract by the use of a suitable pre-column (Gregory and Feldstein, 1985).

Analytical system and quantification. Any chromatographic system used for the determination of vitamins in foods should be robust, rapid, reproducible, sensitive and well-suited to automation (Finglas and Faulks, 1987). The rate determining step of many analytical methods is the sample preparation stage and the time lapsing from extraction of sample to injection onto the column should be kept to a minimum. Quantification of vitamins is usually achieved by reference to standard curves of the vitamin in the free form. Retention times of the sample should not vary as this may make automation difficult (Vanderslice *et al.*, 1980).

Assay validation. Attempts must be made to substantiate the assay procedure not only in terms of precision and accuracy of the procedure but also by comparison to other methods such as chemical or microbiological assays of vitamins (Finglas and Faulks, 1987). One of the most useful criteria used to identify components in a chromatographic run is the retention time of the peak. There is sometimes a problem with retention times when changing from one food sample to another, and these times can differ for each food sample and from values obtained for pure substances. This

may lead to difficulties in automated systems where vitamins are identified by retention times and subsequently quantified by an internal standard (Finglas and Faulks, 1987). Vitamin peaks can be further identified by "spiking" samples either before or after extraction. The analyst should be aware, however, that the form of the vitamin added may be different from that initially present in the food matrix (Finglas and Faulks, 1987).

Determination of thiamin. HPLC methods for thiamin are generally based on reverse-phase columns using either UV or fluorometric detectors. Oxidation of thiamin to thiochrome using alkaline potassium ferricyanide, as required by some HPLC methods, is performed manually prior to injection onto the analytical column or automatically by post-column derivatization. The latter procedure is done by continuously mixing the column eluate with an alkaline potassium ferricyanide solution which eliminates the time-consuming element and variability of the manual conversion to thiochrome (Finglas and Faulks, 1987).

The use of guard-columns to extend the life time of the analytical column has been reported in several cases (Nicolson *et al.*, 1984; Arabshahi and Lund, 1988; Toma and Tabekhia, 1979). Ion-pair reagents in the mobile phases have been used extensively and these are generally sodium salts of pentane-, hexane- or heptane-sulphonic acids at concentrations of approximately 5 mM. The thiamine peak can usually be separated from any interfering substances by the careful addition of one or a combination of ion-pair reagents to the mobile phase (Toma and Tabekhia, 1979; Arabshahi and Lund,

1988). The measurement of thiamine in rice products using UV detection showed recoveries >90% (Toma and Tabekhia, 1979). This form of detection is adequate for samples containing amounts of thiamin in the order of 0.5 mg per 100 g (Finglas and Faulks, 1987).

A comparison of thiamin determination in fortified breakfast cereals by HPLC and the manual thiochrome procedure (AOAC, 1984) found that the HPLC-values were significantly higher than those obtained by the thiochrome method. A reverse-phase system using post-column derivatization and sample purification with Sep-pak" C18 disposable cartridges has been successfully used for 35 foods including meats, dairy produce, cereals, fruits and vegetables. The specificity and sensitivity of the HPLC method with fluorescence detection, together with the use of Sep-pak cartridges for sample preparation, means that the ion-exchange resin clean-up step is no longer required. This would explain why HPLC recoveries were consistently higher (~ 10%) compared to the manual AOAC method, especially in the case of breakfast cereals (Wimalasiri and Wills, 1985). Recovery studies showed that the HPLC method gave >97% recoveries of vitamin when added prior to extraction, the corresponding value for the AOAC procedure was only 87-90%. The difference can be explained on the basis of thiamin losses on the ion-exchange column used in the AOAC procedure.

In conclusion, HPLC has clear advantages over existing chemical or microbiological assays. Selection of a particular procedure should be made only after considering if the sample preparation and clean-up steps are rapid and sufficient to give reasonable column life, the limit of detection and the recovery of added vitamin are

acceptable ($>90\%$), and tests verify the lack of reproducibility and repeatability problems (Finglas and Faulks, 1987).

AN OPTIMIZATION METHOD TO DETERMINE THE KINETIC PARAMETERS

FOR THE HEAT INACTIVATION OF A QUALITY FACTOR:

CONDUCTION-HEATED CANNED FOODS

ABSTRACT

The kinetic parameters ($D_{121.1^\circ C}$ and z values) for the heat inactivation of a quality factor in conduction-heated canned food were evaluated using the Complex optimization procedure and a numerical technique for heat transfer calculations and quality retention prediction. The jackknife method was used to evaluate experimental variability. This methodology was used to determine the $D_{121.1^\circ C}$ and z values for thiamin destruction in pea puree (pH = 6.8, moisture content = 80.8%, and thermal diffusivity, α = 1.8×10^{-7} m^2/sec). Retort processing experiments using 303x406 cans filled with thiamin-enriched pea puree yielded a wide range of thiamin retention values (29-70%). The $D_{121.1^\circ C}$ and z values obtained were 304$\pm$32 minutes and 30$\pm$3°C, respectively.

INTRODUCTION

The effect of the heat sterilization process on the quality and nutrient retention of foods has been a major concern of processors since the beginning of the canning industry. This concern prompted studies into ways to reduce nutrient and quality destruction in the sterilization process, and into different means to predict these losses. The main approach to solving this problem has been the formulation of mathematical models that predict bacterial destruction and loss of nutrients. These mathematical models are based on experimental kinetic studies (Feliciotti and Esselen, 1957; Lund, 1973; Mulley *et al.*, 1975a,b; Teixeira *et al.*, 1969a,b; Ohlsson, 1980; Ghazala *et al.*, 1989, Simpson *et al.*, 1989a,b, 1990a). Two approaches are used to determine the kinetic model for destruction of a food component during heating (Lenz and Lund, 1980). In the steady-state approach, the experimental design is based on a series of tests in which only one variable is changed at a time, usually over a wide range of values (Mizrahi and Karel, 1977; Saguy *et al.*, 1978). Each sample is analyzed to determine the concentration of the desired factor after a given time at a constant temperature (Feliciotti and Esselen, 1957; Mulley *et al.*, 1975a). The data at each temperature are compared to a kinetic model; when the data matches the model, a rate constant is calculated for that processing temperature. The Arrhenius equation is then used to calculate an activation energy (E_a) for the reaction (Hill and Grieger-Block, 1980). In the unsteady-state approach, the raw data consists of the desired component concentration for samples with known time-temperature histories. The determination

of the kinetic parameters is facilitated by average-retention predicting methods. For instance, Hayakawa (1969) described an unsteady-state-method based on a programmed heating of samples which heat very rapidly. Lenz (1977) used a trial-and-error procedure to determine the kinetic model for the destruction of thiamin in pea puree. Saguy *et al.* (1978) developed an accelerated method to determine the kinetic model of ascorbic acid loss during a simulated air drying process.

A major shortcoming of steady-state methods is the relatively long time and large number of samples required to evaluate the kinetic model of deterioration. The application of numerical methods supported by faster computers has allowed the application of unsteady-state methods to problems with mathematical complexity and large number of calculations. The choice of which procedure to use, steady-state or unsteady-state, depends to some degree on the availability of equipment and mathematical models (Lenz and Lund, 1980).

The aim of this study was to develop a new unsteady-state method to determine the kinetic parameters for the heat destruction of thiamin in conduction-heating foods. A homogeneous and conduction-heated food was required to use the model previously developed in our laboratory (Almonacid *et al.*, 1990). This model incorporates an optimization technique based on the "Complex" search method (Beveridge and Schechter, 1970) and a numeric method for heat transfer, lethality and quality retention calculations. Experimental variability was evaluated using the jackknife procedure (Efron and Tibshirani, 1986). Retort processing experiments were used to determine thiamin retention data in pea puree thermally processed in 303x406 cans. This

approach has the advantage of exposing thiamin to thermal histories similar to commercial processes.

MATERIALS AND METHODS

Sample preparation

Pea puree (with 0.26 g thiamine/100 g puree) was prepared from 1500 g of frozen peas (Norpac, Lake Oswego, OR) rapidly thawed in boiling water (2 minutes). After draining off the water, peas were passed through a food grinder and then blended in a food processor. Thiamin hydrochloride (4 g, Sigma, St. Louis, MO), mixed with a small amount of pea juice (ca. 20 ml) collected from the food grinder, was added to the pea puree and mixed thoroughly in a stainless steel bowl. Control samples with no added thiamin contained approximately 0.25 mg thiamine/100 g sample is consistent with reported values (Duckworth, 1966).

Thermal processing

Electrolytic tinplate cans (303x406) with enameled body and ends were filled with pea puree (500 g) prepared as above and sealed under vacuum (13 inches) (CanCo Model 6 Sealer, American National Can Co., Chicago, IL).

Determination of thermal diffusivity.

Three cans were fitted with needle copper-constantan thermocouples (Type CNS, O.F.

Ecklund Inc., Cape Coral, FL) located in the geometric center of the can. These thermocouples were connected to an electronic Campbell 21X datalogger (Logan, UT) through 36 gauge thermocouple wires (Omega Engineering Inc., Stamford, CT) and programmed to record temperature every 1 minute. The cans were placed in a constant temperature water bath (KS-20D, Brinkmann, Westbury, NY) until the center temperature equilibrated with the water bath temperature ($46\pm0.05\,^\circ$C). The cans were then heated in boiling water in a steam-jacketed kettle. Kettle water temperature was monitored by a thermocouple (Catalog No.NB2-CPSS-14Q-12, Omega Engineering, Inc., Stamford, CT) also connected to the datalogger. The time-temperature data was used to determine the thermal diffusivity as described by Simpson *et al.* (1990b).

Thermal processing experiments.

Triplicate cans, filled with pea puree as described above and then kept for two hours in a 37.5°C constant temperature bath (KS-20D, Brinkmann), were processed in a Dixie No. 3 vertical steel retort (RDSW-3, Dixie Canner, Athens, GA). Six different retort processes with equivalent lethality were specified (F_r = 10 min, Table 1). Retort temperatures and corresponding process times were calculated by the numerical method described by Teixeira *et al.* (1975). Two thermocouples (Catalog No.NB2-CPSS-14Q-12, Omega Engineering, Inc.), placed in the retort in close proximity to the cans, were connected to the datalogger to record retort temperature every minute during heating and cooling. Cans were cooled to 17-21°C using tap water (13°C) and then stored at -12°C. Thiamin analysis was conducted within a week. For each

blended in a stainless steel container. Two 5 g-samples were extracted and assessed for thiamin content by HPLC as described below. The thiamin content of a sample taken before heating was similarly determined.

Optimization technique for determination of kinetic parameters

The kinetic model for thiamin destruction in pea puree was assumed to be first order (Feliciotti and Esselen, 1957) and the product to be solid and homogeneous. Heat transfer and thiamin retention were predicted as a function of retort temperature using the numerical method described by Simpson *et al.* (1990a). Reported $D_{121.1°C}$ and z values for thiamine in pea puree (Feliciotti and Esselen, 1957) were used as a first guess to evaluate for each process the average retention predicted by the model. The search procedure used the Complex method (Beveridge and Schechter, 1970) taking as variables $D_{121.1°C}$ and z-values and as objective function the following expression:

$$\text{Minimize} \quad \sum_{i=1}^{k} (R_i^{\alpha} - R_i^{pr})^2 \qquad (11)$$

where

R_i^{α} = experimental overall thiamine retention for process i (triplicates, average)

R_i^{pr} = predicted overall thiamine retention in process i

k = number of thermal processes considered

To evaluate experimental error by the jackknife statistical method (Efron and Tibshirani, 1986; Thomas, 1990) the above procedure was repeated six times using as

experimental data the six subsets generated by considering each time only five (k = 5) of the six thermal processing experiments. The procedure was also repeated using all six (k = 6) determinations. This allowed the following calculations:

$$E_i \quad = n\,E_o - (n-1)\,E_{-i} \quad = \quad E_o + (n-1)\,(E - E_{-i}) \tag{12}$$

$$E_{avg} \quad = 1/n\, \sum E_{-i}; \quad i = 1, \ldots, n \tag{13}$$

$$\hat{E} \quad = 1/n\, \Sigma E_i \tag{14}$$

$$SE(\hat{E}) = \sqrt{\frac{\Sigma\,[\hat{E}_i - \hat{E}_{avg}]^2}{n(n-1)}} \quad ; i = 1, \ldots, n \tag{15}$$

where:

E_{-i} $\quad = \quad$ $D_{121°C}$- and z-values calculated by the optimization procedure ignoring experiment i

E_{avg} $\quad = \quad$ average of all $D_{121°C}$- and z-values calculated ignoring one experiment

E_o $\quad = \quad$ $D_{121°C}$- and z-values calculated using all n experiments

E_i $\quad = \quad$ $D_{121°C}$- and z-values corrected using Eq. (12)

$\hat{E}$ $\quad = \quad$ estimated $D_{121°C}$ or z-value

$SE(\hat{E})$ $\quad = \quad$ error estimate for parameter $\hat{E}$

Thiamin assay by HPLC

Sample extraction. The methodology for thiamin extraction from pea puree was a modification of the methods used by Toma and Tabekhia (1979) and Arabshahi and

Lund (1988). Five-gram pea samples and 50 ml 0.1N sulfuric acid were thoroughly mixed in a 250 ml Erlenmeyer. The mixture was autoclaved for 30 minutes at 121°C, cooled to room temperature and the pH adjusted to 4.6 by addition of 2 M sodium acetate. The sample was then diluted to 100 ml with distilled deionized water and filtered through Whatman No. 42 filter paper. Before injection into the HPLC, an aliquot was filtered through a 0.2 μm membrane (Acro LC13, Gelman Sciences, Ann Arbor, MI).

Apparatus and operating conditions. The HPLC system consisted of a Spectra-Physics SP8700 solvent control delivery system (Spectra-Physics, San Jose, CA), a Spectra-Physics SP8750 pump, a variable wavelength UV/Vis detector (Model UV 50, Varian Instrument Division, Palo Alto, CA) set at 254 mm, and a linear recorder (Model 355/MM, Linear Instruments Corp., Irvine, CA). The chromatography column was an Adsorbosphere HSC18, 7μ, 150x4.6 mm (Alltech, Deerfield, IL). The mobile phase (1.5 ml/min) was a mixture of 60% buffer (0.035M KH_2PO_4, pH 3.0) (Mallinckrodt, Paris, KY), 28% HPLC grade methanol (J.T. Baker Chemical Co., Phillipsburg, NJ), and 12% 0.05M sodium heptane sulfonate (Sigma, St. Louis, MO) filtered through a 0.45 μm membrane filter (Filinert PTFE (FN), Nuclepore Corp., Pleasanton, CA) and degassed under vacuum. The mobile phase was kept refrigerated before use the next day.

Calibration and calculations. Chromatographic peak heights were plotted against

concentrations (7.5 to 20 mg/100 ml) of standard solutions of thiamin in distilled deionized water. A linear response was observed (r = 0.9977) confirming published work (Arabshahi and Lund, 1988). Recovery studies were conducted by adding 15 mg thiamin to 5 g of pea puree prior to the sample preparation described above. The acid extraction used in this study resulted in a 95-96% recovery.

RESULTS AND DISCUSSION

Determination of the pea puree thermal diffusivity

The time-temperature data used to determine the thermal diffusivity (α) for pea puree is shown in Figure 1. The value obtained, 1.8×10^{-7} m^2/sec, is at the high end of values reported for conduction-heated foods (Singh, 1982). This is related to the high moisture content of the pea puree (80.8%).

Thermal processing experiments

Retort temperature recorded during thermal processing varied less than 1°C. Measured thiamin retention values are reported in Table 1. The large difference in thiamin retention confirms the need to identify optimum process conditions to retain product quality while achieving the same process lethality.
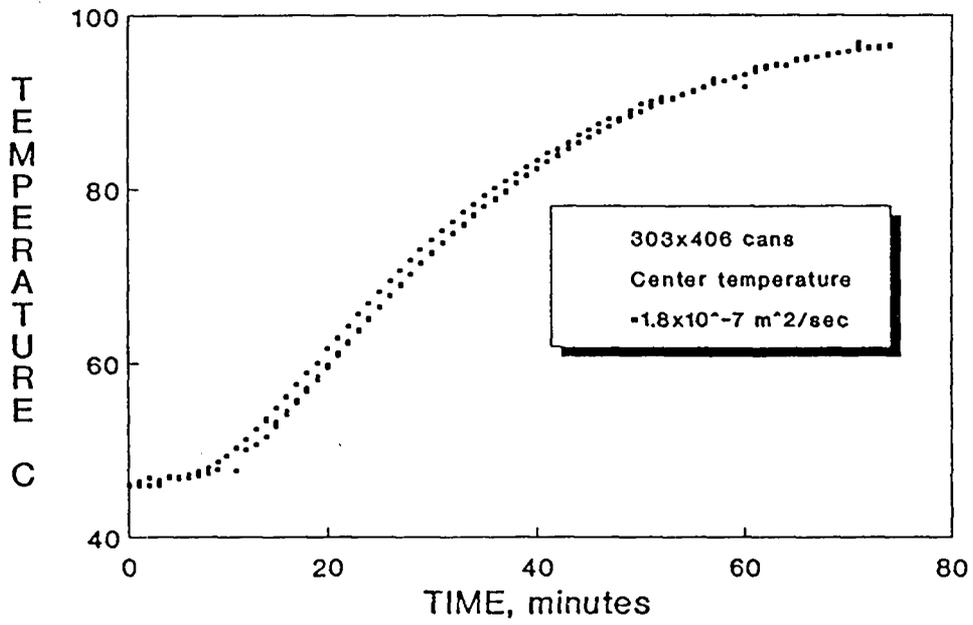
FIGURE 1

Determination of the thermal diffusivity of pea puree
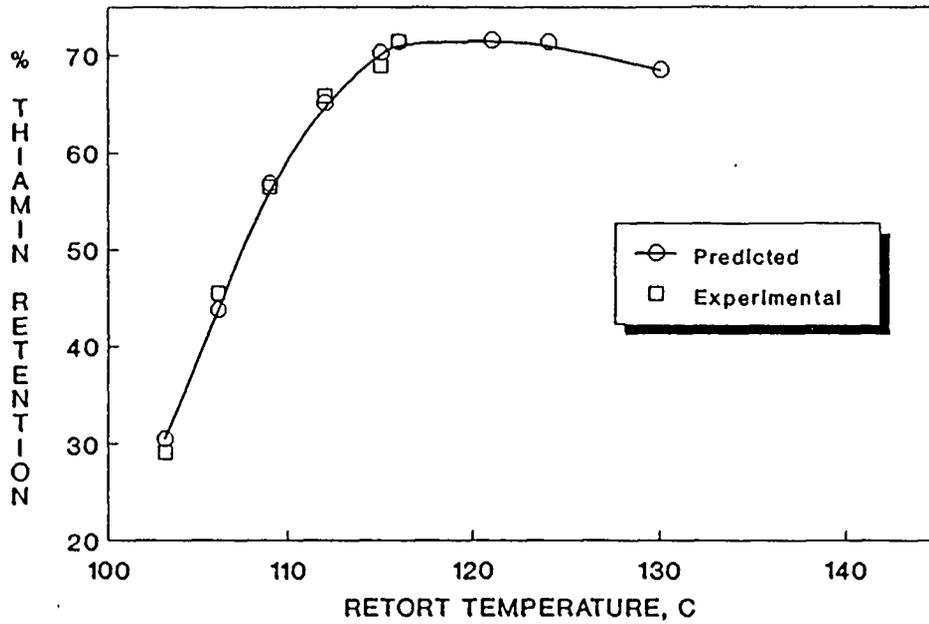
FIGURE 2

· Thiamine retention in conduction-heated pea puree for

equivalent lethality processes (F, = 10 minutes)

Limitations of the experimental retort (maximum operating temperature = 116°C) prevented experiments at higher temperature to experimentally determine the optimum retort temperature for thiamin retention in pea puree (Teixeira *et al.*, 1975; Simpson *et al.*, 1989a,b). The curvature around the maximum retention point depends upon the thermal diffusivity value for the food involved. High values will result in a flat curve as in our case (Figure 2).

Determination of kinetic parameters

Table 3 summarizes the jackknife statistical calculations used to evaluate the kinetic parameters for the heat inactivation of thiamine in pea puree. The z-value, 30 ± 3°C, is higher than other published values (Table 2). The $D_{121.1°C}$-value, 304 ± 32 minutes, is similar to the one obtained by Mulley *et al.* (1975a,b) but differs significantly from the values published by Feliciotti and Esselen (1957) and Lenz and Lund (1977a,b). Pea puree preparation differences were noted (Table 3) but may only partially account for the observed discrepancies. Feliciotti and Esselen (1957) and Mulley *et al.* (1975c) have studied the thermal destruction rates of thiamin in phosphate buffers and concluded that its destruction in foods is pH dependent (Table 3). Unfortunately, some authors have not reported the pH and moisture content of their samples. Finally, some investigators have attempted to explain the increased stability of thiamin in biological systems with reference to the existence of a "free" and "combined" (pyrophosphate ester) form of the vitamin (Greenwood *et al.*, 1943). However, Farrer (1948, 1955) and Mulley *et al.* (1975c) have shown that this does not

seem to be the case. Differences in methods of determination of kinetic parameters also exist. Feliciotti and Esselen (1957) and Mulley *et al.* (1975a,b,c) used a steady-state method to determine kinetic parameters. On the other hand, the study of Lenz and Lund (1977a,b), and this work are based on unsteady-state methods.

CONCLUSIONS

The optimization method described here is based on a numerical method for nutrient retention prediction and uses simple experimental procedures available in most food processing pilot plants. The food is exposed to conditions similar to those found during actual processing. Also, temperature deviations that occur during experimentation do not affect the procedure since actual retort temperature is used to calculate the canned food temperature and to predict nutrient retention. Estimated $D_{121.1°C}$ and z values were used to predict the retort temperature for optimum thiamin retention (about 121°C, Figure 2). Experimentally measured retention values are also shown to indicate the degree of fit of the experimental values to the predicted values and curve fitted line.

The thermal process conditions selected in this study correspond to equivalent lethality processes at various retort temperatures. It should be noted that this is not a methodology requirement; any selection of process conditions covering a wide range of temperature and quality factor retention values would be equally suitable. An advantage of the jackknife statistical procedure incorporated in our methodology is that

it allowed an estimation of experimental error. A potential limitation of the computer software utilized in this study is that it assumes that during come up time the can surface temperature is equal to the temperature of the retort. Further experiments will be conducted to quantify the error introduced by this assumption.

Finally, the large difference in the $D_{121.1^{\circ}C}$-values reported in the literature needs further investigation. The comparison of experimental values with literature values was hindered by the lack of precise characterization of experimental samples, e.g. pea source, pH, and moisture content of the puree.

Table 1

Equivalent lethality processes

Process No.	Retort temperature (°C)	Heating time	Cooling time	% Retention
		(minutes)		
1	116	92	24	76.6±3.5
2	115	100	25	68.9±3.4
3	112	137	25	65.8±2.1
4	109	211	25	56.5±5.7
5	106	367	23	45.5±4.1
6	103	675	22	29.1±2.7

Table 2

Kinetic parameters for the heat inactivation of thiamine

Experimental system	$D_{121°C}$	z	Reference
a. Pea puree[a]			
puree adjusted to 84.4% moisture		166	25.6	Feliciotti & Esselen, 1957
pH=6.75			
15% peas in distilled water		247	26.7	Mulley et al., 1975a
"few" ml added distilled water	258	26.7	Mulley et al., 1975b
	100	24.7[b]	Lenz and Lund, 1977b
80.8% moisture, pH=6.8 (no water added)	304±32	30±3	This study
b. Thiamin buffered solution			
pH = 5	285	25	Feliciotti & Esselen, 1957
	231	25	Mulley et al., 1975c
pH = 6	149	25	Feliciotti & Esselen, 1957
	157	25	Mulley et al., 1975a
pH = 6.5	57	25	Feliciotti & Esselen, 1957
	78	25	Mulley et al., 1975c
pH = 7	12.5	25	Feliciotti & Esselen, 1957

(a) Prepared from frozen peas except Lenz and Lund (1977b) who used canned peas
(b) E_a=27 kcal/gmole converted to a z-value using T_r=121.1°C (Lenz & Lund, 1977a)

Table 3

Estimation of kinetic parameters for the heat inactivation of thiamin in pea puree

Experimental data	D_j minutes	z_j °C	D_i minutes	z_i °C
subset[a] 1	288.0	28.5	308.5	30.3
subset 2	285.6	28.4	320.4	30.8
subset 3	292.1	28.8	287.9	28.8
subset 4	296.8	29.8	264.4	23.8
subset 5	261.9	25.7	438.9	44.3
subset 6	308.6	30.1	205.4	22.3
all[b]	$D_o = 291.4$ minutes			
	$z_o = 28.8$ °C			

(a) Values calculated using five of the six thermal processes
(b) Values calculated using all six thermal processes

NOMENCLATURE

D_{-i} = D value calculated by the optimization method ignoring experiment i

D_i = D value corrected using Eq.(12)

D_o = D value calculated using all n (six) thermal processes

$\hat{E}$ = estimated $D_{121°C}$ or z-value

E_{-i} = value calculated by the optimization method ignoring experiment i

E_{avg} = average of values calculated ignoring one experiment

E_i = values corrected using Eq.(12)

E_o = value calculated using all n (six) thermal processes

k = number of thermal processes considered

n = total number of thermal processing experiments = 6

R_i^{ex} = experimental overall thiamine retention, process i (average of 3 replicates)

R_i^{pr} = predicted overall thiamine retention in process i

$SE(\hat{E})$ = error estimate for parameter $\hat{E}$

z_{-i} = calculated z-value ignoring experiment i

z_i = z-value corrected using Eq.(12)

z_o = z-value calculated using all n (six) thermal processes

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QUALITY VARIABILITY IN INSTITUTIONAL SIZE CANS:
CONDUCTION-HEATED FOODS

ABSTRACT

Canning has been and continues to be one of the most widely used methods of food preservation and plays a major role in the implementation of nutrition improvement efforts, particularly in third world countries. A mathematical model for the retention distribution of thiamine was experimentally validated and then used to examine quality variability inside institutional size cans with thiamine retention as a quality indicator. A search for time-dependent process temperatures reducing quality variation yielded only minor improvements over constant retort temperature processes.

INTRODUCTION

The annual production of canned food in the U.S. is about 33 billion pounds for which the food industry purchases more than 35 billions cans (Lopez, 1987; Brewbaker and Henderson, 1988; Fernandez *et al.*, 1988). This production with a 25 billion dollars FOB value, involves more than 1,400 different food items in about 1,500 plants (Lopez, 1987). In developing countries, canned foods play a major role in the implementation of nutrition improvement efforts, particularly in school feeding programs.

Retort processing times are dependent on initial product temperature, retort temperature, product type and container size. For example, beans (initial temperature, TI, 21.1°C) in 303x406 cans require 115 minutes at a retort temperature (RT) of 115.5°C (240°F) and only 95 minutes at 121.1°C (250°F). In institutional size cans (603x700) the heating times are 325 and 275 minutes, respectively (Anonymous, 1982). Computer supported calculations have been used to examine the effect of container geometry at constant volume on process time and nutrient (thiamine) retention (Teixeira *et al.*, 1975; Barreiro *et al.*, 1979).

A large volume of information is available on experimental determination and mathematical modelling of the heat inactivation of microorganisms and enzymes, as well as the loss of several product quality factors (nutritional value, color, texture, aroma and flavor) (Feliciotti and Esselen, 1957; Hayakawa, 1969; Teixeira *et al.*, 1975; Lund, 1982; Ghazala *et al.*, 1989; Banga *et al.*, 1990; Nasri *et al.*, 1990). On

the other hand, a literature search shows limited information on the quality distribution within a container. Quality distribution is particularly important in the case of institutional size cans since these quality differences mean that consumers in schools and other mass feeding institutions receive servings with differing sensory quality and varying nutritional value.

Mathematical models exist to find the effect of processing on nutrient retention, energy consumption and food safety of constant and time-dependent process temperatures (Teixeira et al., 1969a; Saguy and Karel, 1979; Ohlsson, 1980a,b; Simpson et al., 1989a,b). Almonacid et al. (1990) developed mathematical models to verify the physical feasibility of a process with time-dependent retort temperature. The inclusion of a transient energy balance equation allowed the identification of physically feasible time-dependent process temperatures without direct experimentation. Physically feasible processes were defined as those retort processes that do not include temperature drops resulting in negative steam consumption. Almonacid et al. (1990) combined the transient energy with an optimization technique to identify physically feasible temperatures that minimize energy consumption or total process time while maintaining a specified quality and process lethality (F_s-value).

Automatic thermal sterilizer systems facilitate the operation of retorts, particularly when implementing processes with time-dependent temperatures. Computer control allows on-line corrections for temperature deviations from the pre-established process and also allows the implementation of optimum processes (Saguy and Karel, 1979; Ohlsson, 1980a,b; Van Boxtel and De Fielliettaz Goethart, 1982; Mulvaney et al.,

1990) identified by mathematical modelling. Datta *et al.* (1986) developed a control algorithm for the retort processing of conduction-heated foods. They used an F_o-value evaluated at the slowest heating point in the product. Simpson *et al.* (1990a) noted that control strategies based on center temperature conditions can be inaccurate when dealing with processes at high temperature or products with low thermal diffusivities. Their model used an integrated F_o value (F_s) taking into account the cumulative lethality of the heating and subsequent cooling period.

In this paper we present and validate a mathematical model for quality retention during the thermal processing of conduction-heated foods. It was used to examine quality variability in the content of institutional size cans. This model was also used to search for processes with time-dependent temperatures reducing this quality variation. Such temperature profiles were restricted to those physically feasible without retort modifications. Thiamine destruction was used as a quality loss indicator.

MATERIALS AND METHODS

Model development

The general model for commercial sterilization utilized was developed on the basis of the following phenomena and their governing equations (Teixeira *et al.*, 1969, 1975; Simpson at al., 1989a,b, 1990; Almonacid *et al.*, 1990):

- Unsteady-state conduction heat transfer with temperature independent thermophysical properties

$$\frac{1}{\alpha}\frac{\partial T}{\partial \theta} = \frac{1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} + \frac{\partial^2 T}{\partial Z^2} \tag{9}$$

- Kinetics of cell destruction to achieve a given integrated F_s-value

$$\frac{dN}{d\theta} = - kN; \tag{10}$$

$$k = k(T)$$

(c) Kinetics of destruction for a quality factor (thiamine)

$$\frac{dC}{d\theta} = - k_c C; \tag{11}$$

with $k_c = k_c(T)$

(d) Transient energy balance for a batch retort (Simpson *et al.*, 1990a; Almonacid *et al.*, 1990):

CONVECTION LOSSES Q'_c

RADIATION LOSSES Q'_r

PRODUCT HEATING Q'_p

STEAM INPUT

M1 = retort mass

M2 = empty metal cans

M3 = steam and accumulated condensate

M = M1 + M2 + M3

BLEEDER STEAM LOSSES
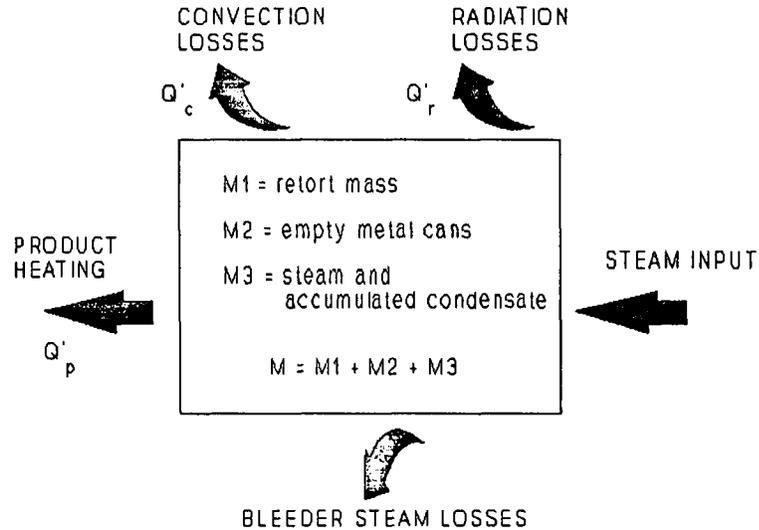
$$\left[\sum_{i=1}^{n} m_i' \hat{H}_i \right]_{in} - \left[\sum_{j=1}^{m} m_j' \hat{H}_j \right]_{out} + Q_p' + Q_r' + Q_c' = d(\hat{E}\, M)_{system}/d\theta \tag{12}$$

Energy calculations were included to ascertain the physical feasibility of processes with time-dependent temperatures that reduce product variability within the can. For this reason the calculation procedure does not include the energy consumption during the venting time. The derivation of Eq.(12) and the characteristics of the retort assumed in these calculations are summarized in the Appendix. Information on other modeling parameters (thermophysical properties and thiamine destruction kinetics) was obtained from Nasri *et al.* (1990).

Experimental validation of thiamine retention prediction

Two cans containing pea puree prepared and processed as described by Nasri *et al.* (1990) (heating time = 92 minutes at 116°C, cooling time = 24 minutes, F, = 10 minutes, can size = 303x406) were stored frozen at -12°C for 4 days and finally dipped in liquid nitrogen for 30 minutes immediately before opening. The frozen content was cut in four equal-size slices and the weight and thickness of each frozen slice were recorded. Thiamine content for each slice was determined by HPLC as described by Nasri *et al.* (1990). Thiamine retention values were expressed as a percentage of initial concentration values.

Thermal process optimization

The objective functions selected were maximization of the thiamine surface retention and reduction of the nutrient concentration variability inside the same can. The optimum processes using a time-dependent retort temperature were compared with

the results obtained for a constant retort temperature process with an equivalent lethality. Can symmetry considerations reduced computation effort by examining only a portion of the can (Figure 3). Thiamine retention variability was assessed by calculating the average retention $(R_{i,j};$ $i = 1\text{-}5;$ $j = 1\text{-}6)$ for each element of the 5x6 matrix view of the can portion under consideration. Retort heating time was divided into six equal time intervals. Preliminary experiments showed that a larger number of intervals yielded equally acceptable optimum solutions.

Surface retention optimization

The search procedure used for optimization was the Complex method (Beveridge and Schechter, 1970) taking as objective function the following expression (Figure 3):

$$\text{Maximize} \quad [\sum_{i=1}^{5} R_{i,6} + \sum_{j=1}^{5} R_{5,j}] \tag{18}$$

subjected to the following restrictions, $105°C \leq RT \leq 135°C$, and $F_s \geq F_s^{desired}$.

Reduction of the nutrient concentration variability

The same search procedure and restrictions were used for the following objective function:

$$\text{Minimize} \, [(A - P)^2 + (B - P)^2 + (C - P)^2] \tag{19}$$

where A, B, and C correspond to the average thiamine retention per slice (Figure 3) and P is the average thiamine retention in the whole container. The minimum value for this objective function will occur when the thiamine concentration of the individual

RADIUS

	5	4	3	2	1
6	$R_{5,6}$	$R_{4,6}$	$R_{3,6}$	$R_{2,6}$	$R_{1,6}$
5	$R_{5,5}$	$R_{4,5}$	$R_{3,5}$	$R_{2,5}$	$R_{1,5}$
4	$R_{5,4}$	$R_{4,4}$	$R_{3,4}$	$R_{2,4}$	$R_{1,4}$
3	$R_{5,3}$	$R_{4,3}$	$R_{3,3}$	$R_{2,3}$	$R_{1,3}$
2	$R_{5,2}$	$R_{4,2}$	$R_{3,2}$	$R_{2,2}$	$R_{1,2}$
1	$R_{5,1}$	$R_{4,1}$	$R_{3,1}$	$R_{2,1}$	$R_{1,1}$

HALF HEIGHT (left axis); LAYERS A B C (right)

Figure 3.

Assessment of nutrient variability: 5x6 matrix

view of the can

layers approaches the average value for the can.

RESULTS AND DISCUSSION

Validation of mathematical model

Predicted and measured average thiamine retention values for the four slices

obtained from each can are reported in Table 4. No significant statistical differences

were detected between measured and predicted thiamine retention values (95%

confidence). It was not possible to confirm experimentally (95% confidence) the small

retention difference (4%) predicted between the middle and the top and bottom slices.

This was probably due to the experimental error (3-5%) (Nasri *et al.*, 1990).

Constant retort temperature processes

Table 5 summarizes predicted average and surface thiamine retention values for

two can sizes processed at constant retort temperature. Small cans (303x406)

processed at 116°C (F_s = 15 minutes) gave an average retention of 64.8% and a

surface retention only slightly lower, 61.3%. On the other hand, institutional size cans

(603x700) processed at 121°C yielded an average thiamine retention of 44.1% and a

significantly lower surface retention, 33.3%. A similar situation is shown for F_s = 10

minutes.

The thiamine retention distribution in institutional size cans (603x700, RT =

121°C, F_s = 15 minutes) ranges from 26.3 to 63.1% (Table 6) suggesting a large quality variation within the can. Surface retention values ranged from 26.3 to 36.8%.

Surface retention optimization

The search for the time-dependent process temperatures achieving the best surface thiamine retention in an institutional size can (F_s = 15 minutes, 603x700 cans) yielded a profile with a surface retention of 34.6% and an average retention of 44.8%. No restrictions were placed on the average retention in the can to enhance the possibility of identifying processes with a larger surface retention of thiamine. These results should be compared with those obtained when using a constant retort temperature of 121°C, 33.3% and 44.1%, respectively. This result seems to differ from the predicted values reported by Banga *et al.* (1990) who found a 20% increase in the surface retention over the best constant retort temperature process. As in this study, their optimization program uses no restrictions on the average retention. It should be noted, that although Banga *et al.* (1990) chose a much wider temperature range (12.2°C - 150°C), the actual optimized temperatures fell in a much narrower range (100°C - 135°C). The more favorable optimization results obtained by these workers can be traced to their surface definition. Banga *et al.* (1990) defined surface as the food in immediate contact with the metal can whereas we defined surface as the external layer formed by considering one fifth of the radius and one sixth of the half height of the can. Consequently, Banga *et al.* (1990) had a much tighter control on the surface temperature; by their definition this temperature is equal to the retort temperature.

Reduction of the nutrient concentration variability

The constant retort temperature of 121 °C gave the following nutrient retention per slice, 35.5%, 46.5% and 50.2% for layers A, B and C (Figure 3), respectively. The average retention was 44.1%. The best time-dependent process temperatures, predicted to minimize the difference in thiamine retention, achieved only a minor improvement. The optimization gave the following thiamine retention values, 36.6%, 47.2% and 50.9% for layers A, B, and C, respectively.

CONCLUSIONS

This paper highlights the need to consider the content variability of institutional size cans containing conduction-heated foods frequently used in institutional feeding programs. An attempt to identify process conditions reducing content variability achieved no significant improvement; thus, it will continue to be important to be aware of the quality variability of the meals provided when using this type of container.

NOMENCLATURE

α	=	thermal diffusivity
θ	=	time
A, B, C	=	average thiamine retention per slice (see Figure 3)
C_i	=	concentration of a quality factor (thiamine)
$\hat{E}_1$	=	energy accumulated by the retort
$\hat{E}_2$	=	energy accumulated by the metal cans
$\hat{E}_3$	=	energy accumulated by the steam condensate
$\hat{E}_{system}$	=	total energy of the system
F_s	=	integrated lethality value
$\hat{H}_{average,1}$	=	average enthalpy of the steam in during the time $d\theta$
$\hat{H}_i$	=	enthalpy in, stream i, i = 1, 1, ..., n
$\hat{H}_j$	=	enthalpy out, stream j, j = 1, 2, ..., m
k	=	rate constant, destruction of cells
k_c	=	rate constant, destruction of a quality factor
M_1	=	retort mass
M_2	=	empty metal cans mass
M_3	=	steam and accumulate condensate
m_i'	=	mass flow rate in, stream i, i = 1, 2, ..., n
m_j'	=	mass flow rate out, stream j, j = 1, 2, ..., m
M_{system}	=	total mass of the system

N	= number of viable cells per unit volume
P	= average thiamine retention in the whole container
Q'_c	= heat convection losses
Q'_p	= heat transferred to the food product by conduction
Q'_r	= heat radiation losses
Q_i	= heat term, i = conduction, convection, radiation
r	= radial axis
$R_{i,j}$	= average retention for element i, j (see Figure 3)
RT	= retort temperature
T	= temperature at any point and time θ
Z	= vertical direction

Table 4

Experimental validation of kinetic parameters[1]

		% Thiamine retention	
	Slice[2]	Measured	Predicted
Can 1	Top	71.7	69.3
	Bottom	71.7	
	Mid-1	71.1	73.3
	Mid-2	72.9	
Can 2	Top	71.1	69.3
	Bottom	70.0	
	Mid-1	71.7	73.3
	Mid-2	71.2	

(1) Heating time = 92 min, retort temperature = 116°C, cooling time = 24 min, F_s = 10 min, can size = 303x406. Thiamine retention values are expressed as a percentage of initial concentration.

(2) Frozen can content was sliced as follows:
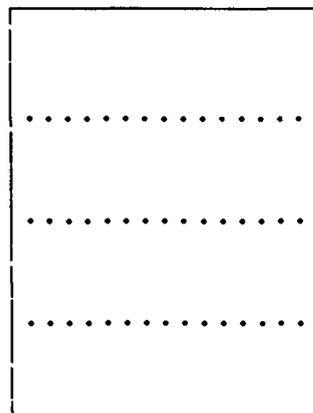
TOP SLICE

MID-1 SLICE

MID-2 SLICE

BOTTOM SLICE

Table 5

Constant retort temperature processes, predicted thiamine retention

Can size	Temperature °C	F_s minutes	% Thiamine retention	
			Average	Surface
603x700	121	15	44.1	33.3
	121	10	49.9	38.4
303x406	116	15	64.8	61.3
	116	10	71.3	67.5

Table 6

Variability in % thiamin retention ($R_{i,j}$) in an institutional size can (603x700), $F_s = 15$ minutes

a. Constant retort temperature = 121°C

j	5	4	i 3	2	1
6	26.3	31.1	34.2	36.2	27.2
5	30.9	40.7	47.1	51.2	53.3
4	33.7	46.5	53.2	57.1	59.0
3	35.4	50.3	57.1	60.0	61.1
2	36.4	52.7	59.6	61.9	62.4
1	36.8	53.8	60.8	62.9	63.1

b. Time-dependent retort temperature (maximum surface retention)[1]

j	5	4	i 3	2	1
6	27.3	32.3	35.5	37.6	38.6
5	32.1	41.3	47.5	51.6	53.7
4	34.9	46.9	53.4	57.3	59.6
3	36.7	50.8	57.3	60.2	61.3
2	37.8	53.2	58.8	62.0	62.5
1	38.2	54.4	61.1	63.0	63.7

c. Time-dependent retort temperature: nutrient concentration variability reduction[2]

j	5	4	i 3	2	1
6	27.7	32.4	34.6	37.7	38.7
5	32.2	41.4	47.6	51.7	53.8
4	35.0	47.0	53.6	57.5	59.3
3	36.8	50.9	57.4	60.3	61.5
2	37.8	53.3	60.0	62.2	62.7
1	38.3	54.5	61.3	63.2	63.4

Process time (184 minutes) divided into 6 equal time intervals, optimum temperature values: [1] Maximum surface retention objective, °C = 128.6, 117.7, 121.4, 123.1, 123.5, 117.7, 105.8; [2] Nutrient concentration variability reduction, °C = 126.6, 117.0, 121.4, 122.5, 123.3, 119.5, 106.7

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RESEARCH CONCLUSIONS

The advantage of the optimization method used to determine the kinetic parameters is its simplicity and versatility. Food is exposed to conditions similar to those found during actual commercial processing, temperature deviations do not affect the predictions and constant process temperature conditions are not assumed. However, the method does not provide a good mean for the evaluation of the experimental variability associated with the determination of D- and z-values. The latter objective was achieved by the jackknife statistical method. The wide difference between the reported D- and z-values, including the high values found in this research, could not be explained due to the poor characterization of the food samples used by previous researchers. This highlights the advantage for kinetic parameter determinations under experimental conditions approaching industrial process conditions and highlights the need to further investigate the difference found between the reported values.

To assure the validity of the D- and z-values for wide range of industrial conditions six process conditions equivalent in their lethality were chosen. The selected process conditions was confirmed by the wide range of quality retention values obtained experimentally. However, the number of experiments chosen was arbitrary and some statistical analysis method needs to be developed to estimate the number of experiments necessary to determine kinetic parameters with a given level of confidence.

Finally, this investigation showed that the use of time-dependent retort temperature over does not reduce the content variability observed in institutional size cans as

compared to constant retort temperature processes. However, it highlights the need to be aware of this variability, particularly in mass feeding institutions where servings with equal nutritional value are critical.

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APPENDIX

Derivation of energy balance equation

The transient-energy balance equation (Eq. 12, page 48) was solved as follows:

$$(m_I'\hat{H}_I)_{in} - (m_I'\hat{H}_I)_{out} + Q_r' + Q_c' + Q_p' = d(\hat{E}\,M)_{system}/\,d\theta \tag{13}$$

where:

$$d(\hat{E}\,M)_{system}/d\theta = d(\hat{E}_I\,M_I + \hat{E}_2\,M_2 + \hat{E}_3\,M_3)/d\theta \tag{14}$$

$$d(\hat{E}\,M)_{system}/d\theta = d(\hat{E}_I\,M_I)/d\theta + d(\hat{E}_2\,M_2)/d\theta + d(\hat{E}_3\,M_3)/d\theta \tag{15}$$

Therefore,

$$(m_I'\,\hat{H}_I)_{in} - (m_I'\,\hat{H}_I)_{out} + Q_r' + Q_c' + Q_p' = d(\hat{E}_I M_I)/d\theta + d(\hat{E}_2 M_2)/d\theta + d(\hat{E}_3 M_3)/d\theta \tag{16}$$

The steam consumption during each time interval ($\Delta\theta = 7.5$ seconds) can be calculated using average properties as follows:

$$m_{vapor} = (m_I')_{in}\,\Delta\theta =$$

$$\frac{\Delta(\hat{E}_I M_I) + \Delta(\hat{E}_2 M_2) + \Delta(\hat{E}_3 M_3) - \int_\theta^{\theta+\Delta\theta} Q'_r\,d\theta - \int_\theta^{\theta+\Delta\theta} Q'_c\,d\theta - \int_\theta^{\theta+\Delta\theta} Q'_p\,d\theta + (m'_I\,\hat{H}_{ave,I})_{out}\,\Delta\theta}{(\hat{H}_{average,I})_{in}} \tag{17}$$

Processing conditions for computer simulation model

Correlations of steam table data (Weast, 1984), valid in the range of interest (105°- 135°C), were used to estimate the thermodynamic properties of steam and condensed water. Steam removed by bleeding $((m_i')_{out})$ was calculated using the methodology described by Barreiro *et al.* (1984) assuming constant conditions in the autoclave and external environment during the time interval $\Delta\theta = 7.5$ seconds.

Retort:

    mass, 163.6 kg

    area, 2.97 m^2

    volume, 0.356 m^3

    c_p, 0.5 kJ/kg °C

    bleeder area, 7.94x10^{-6}m^2

Other:

    initial retort temperature (T_i), 20°C

    initial product temperature, 71.1°C

    environmental temperature, 30°C

    process temperature, variable

    temperature profile limits, 110-135°C