Degradation kinetics of Quality Factors, Their Verification and Optimization in a Thermoprocessed Simulated Food System

by

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ABSTRACT

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DEGRADATION KINETICS OF QUALITY FACTORS, THEIR VERIFICATION AND OPTIMIZATION IN A THERMOPROCESSED SIMULATED FOOD SYSTEM

A novel simulated food model (ascorbic acid, thiamine and a mixture of glucose and glycine) incorporating celite was developed. Basic kinetic parameters were established and the analysis of this data led to a reconsideration of the fundamental aspects relating the TDT and Arrhenius systems of evaluating kinetic parameters and their meaning. Heat penetration data was obtained for both conduction and convection systems, with the conduction system being characterized by parameters calculated from the heat penetration data. Stainless steel micro-capsules were used to isolate and obtain centerpoint nutrient destruction and compared it to the predictions of two computer models. Computer models were tested and verified for the conduction system and an optimization technique based on a multi-factor objective function evaluated.

Celite simulated a typical conduction system and the kinetics of quality factor degradation varied depending on composition. Centerpoint capsules worked well in evaluating nutrient destruction and provided a means for verifying computer simulations. Predictions from the Teixeira and Ball models indicated that the Teixeira model was a better process predictor. Multi-factor objective functions for maximizing nutrient retention were shown to work well in defining optimal conditions using the Teixeira program, while those based on the Ball model were indeterminate.

RESUME

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La cinétique de dégradation de certains indices de qualité, leur vérification et optimisation dans des systèm alimentaires simulés ayant été traités thermiquement.

Un système alimentaire inédit (acide ascorbique, thiamine et un mélange de glucose et glycine) incorporant de la terre diatomée (celite) a été élaboré. Les paramètres cinétiques de base ont été mesurés. L'analyse des données obtenues a conduit à la reconsidération des aspects fondamentaux reliant les systèmes TDT et d'Arrhénius pour l'évaluation des paramètres cinétiques, et de leur signification. Les données de pénétration thermique ont été obtenues à la fois pour un système en conduction et un système en convection, le premier étant caractérisé à l'aide de paramètres calculés à partir des données de pénétration thermique. Des micro-capsules d'acier inoxydable ont servi à isoler les éléments nutritifs du centre des boîtes de conserve afin de déterminer leur degré de destruction et de comparer ces données avec ce qui avait été prédit par deux modèles informatiques. Les modèles informatiques ont pu être testés et vérifiés pour des systèmes en conduction. Une technique d'optimisation basée sur une fonction objective multifactorielle a été évaluée.

La terre diatomée (celite) a bien réussi à simuler le comportement en conduction d'un système type. On a observé que la cinétique de dégradation des indices de qualité dépendait de la composition du mélange. La méthode des capsules, pour déterminer le degré de destruction des éléments nutritifs au centre des boîtes de conserve, semble avoir bien fonctionné et a permis de vérifier les modèles de simulation. On a comparé les données expérimentales à l'aide des modèles de Teixeira et de Ball. Les prévisions faites grâce au modèle de Teixeira sont les meilleures. Pour l'optimisation de la rétention des éléments nutritifs, les fonctions objectives multifactorielles utilisées avec le programme de Teixeira ont bien fonctionné pour définir les conditions optimales de transformation. Par contre, celles basées sur le modèle de Ball étaient indéterminées.

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CONTRIBUTIONS TO KNOWLEDGE

In the thermal processing of foods, the most relevant criteria are the product's microbiological safety, shelf-life, retention of nutrients and maintenance of organoleptic properties. Although thermal processing is beneficial, it is major factor causing changes in the nutritional value of foods and consideration has to be given to the loss of these quality attributes.

Previously, most research has been directed toward developing means of predicting the thermal effects of processing on microorganisms and with some quality factors being considered, largely based on mathematical models with little verification. Verification of the adequacy of models and/or simulations is of critical importance to the design of an optimal process, if it is to be practical, however, few attempts have been made to obtain correlations between model predictions and experimental results. This research was initiated with these thoughts in mind, specifically to gather basic data, analyze, interpret and make use of the data in a fashion which would confirm predictive processes from developed computer models. As is the case with most research, the initial direction often diverges as new information comes to light and as a consequence additional concepts and developments have been included.

The following list summarizes the principal contributions to knowledge that have resulted from this work:

(1) Celite was introduced and shown to work as a conduction heating model for studying the effects of thermal processing on nutrient degradation and color formation. The heat penetration parameters determined were shown to be applicable to the study of quality factors in conduction media with thermal properties close to purees.

(2) A new approach for conversion of the kinetic parameters between TDT and Arrhenius methods was developed, assessed theoretically and verified experimentally.

(3) Centerpoint capsule concept was introduced, tested and verified for nutrient destruction evaluation.

(4) Two thermal processing computer models, those of Teixeira and Ball were tested against experimental data for accuracy in predicting changes in quality factors and it was determined that Teixeira's model is better.

(5) Multi-factor response optimization based on an objective function was used, evaluated and shown to be a useful technique for selecting an optimal process condition in relation to the quality factors one wishes to consider.

In summary, most of these contributions are unique, even controversial, and will provide a platform for further advances to be made in thermal processing.

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I. INTRODUCTION

There has been increasing consumer pressure for the overall quality of conventionally canned foods to be improved, specifically in regard to reducing the nutritional losses associated with the process. This concern has prompted studies into means of minimizing nutrient degradation during thermal processing and to predict losses as a function of process conditions. The amount of thermal processing required in the canning process depends on the chemical and physical characteristics of the food, the rate of heat penetration and the thermal resistance of the contaminating organisms involved. The objectives of the process are to eliminate public health and spoilage organisms, extend the shelf-life of the product and to maintain to the best extent possible the nutrient and organoleptic properties of the food product.

1.1 The Present Status

As noted, the canning industry has to begin minimizing quality (i.e., color, flavor, texture, and nutritive value) losses in foods associated with thermal processing, and in order to advance process evaluation techniques, mathematical modeling must be developed further, must be able to make realistic predictions and to optimize quality factors while assuring public safety. To do this, it is necessary to obtain consistent, reliable and comparable data based on reaction kinetics and heat penetration parameters. Confusion still exists relating the two basic thermal processing kinetic approaches, the Arrhenius and Thermal Death Time (TDT) methods, making it difficult to decide which concept is better in terms of assessing processes. In addition, more detailed knowledge is required about the heat penetration parameters associated with specific food systems. Beyond these factors, much of the published data is not standardized and is limited because it was obtained prior to the advent of more modern and accurate analytical techniques. Process calculation results based on kinetic data for nutrients do not necessarily correlate with the actual destruction taking place in a given food system and improvements are required.

Published information relating predictions from computer models with experimental results is rather limited for conduction systems. This is partly due to the lack of an appropriate heat stable, chemically inert model being available for heat penetration studies in which nutrients can be dispersed and recovered. Several mathematical models, either based on established theories or derived empirically, have yet to be applied to simulate the effects of processing on quality factors. These models may be incorporated into simulations in order to predict the effects of processing on quality factors and must utilize the concept of heat transfer, its subsequent effects on microorganisms and quality related components. Optimization procedures have not been applied to nutrient or quality factor retention to a large extent, and should be expanded and incorporated into computer models.

Although computer models are available for the simulation and modeling of batch processes, these simulations require verification with data obtained under actual experimental conditions in order to be meaningful. Conduction heating foods are more complex to study as is; however the conduction heating process is much more easier to deal with if theoretical heat transfer equations can be used. The complexity arises from the fact that each point in the cross section of a container receives a totally unique thermal process due to the resulting temperature distribution. Presently, all legal thermal processes are based on the slowest heating point (geometric center) rather than making use of the integrated temperature effect throughout the can. During the early part of the cooling cycle, after the holding period, the temperature at the center can will continue to rise and results in over processing, a major cause of quality factor degradation. Hence determining the overall integrated lethal/destruction effect over all points in the container is the key to assuring effective safety standards while simultaneously minimizing reduction in the quality attributes of the product. Hence the proper combination of kinetic parameters for the desired quality factors with accurate heat penetration data and its associated parameters are required for obtaining useful predictions from computer models in the conduction system. This type of data is scarce at present and detailed studies of quality factor changes in conduction heating systems have been limited.

More information is required to make the process of selecting optimal conditions for conduction processes in general, and more specifically in relation to quality factors. Meaningful evaluation of changes in quality factors requires four basic steps: (1) obtaining representative data and use of meaningful kinetic models, (2) obtaining reliable information on the heat transfer process, (3) the incorporation of the information from steps (1) and (2) into computer based mathematical models and (4) their verification. The models selected should encompass the calculations of temperature-time combinations which would allow the optimization of quality factors while ensuring the minimal lethality to see which one works best in relating predicted values to experimental data.

1.2 The Work Carried Out

In order to meet the basic requirements outlined in steps (1) to (4) the following work was carried out:

(a) A quality factor model was developed composed of two nutrients and temperature sensitive constituents associated with color development.

(b) The basic kinetic parameters for the individual components and mixture of the quality factor model were determined by both the Arrhenius and TDT methods, using capillaries and ampoules. Kinetic parameters were also determined using data from convection heating retort-processed cans.

(c) A conduction heating model using celite was developed to facilitate the study of the quality factors.

(d) The appropriate kinetic data was utilized in conjunction with heat penetration data and incorporated into Ball's and Teixeira's process calculation procedures to predict the losses of quality factors.

(e) The predictions of the models were assessed and compared to the experimental data.

(f) An optimization procedure was incorporated into the Ball's and Teixeira's models and evaluated.

The results associated with the work listed above, its interpretation and discussion are the subject of this thesis.

II. LITERATURE REVIEW

2.1 Introduction

The relevant literature related to batch thermal processing is reviewed to highlight their basic principles, calculations and limitations. Quality factor degradation and formation during thermal processing are discussed to illustrate the need to maximize/minimize relevant components while ensuring commercial sterility of thermoprocessed foods. The Arrhenius and TDT models are discussed and analyzed as they are the kinetic basis for most reactions and processes respectively, and are fundamentally incoherent relative to each other. Computer simulations and modeling are covered at some length, as they are an important part of the work undertaken.

2.2 Quality

Quality can be defined in general as "the degree to which a specific product satisfies the wants of a specific consumer" (Juran, 1962). In terms of a processed food product, the two major quality factors are its organoleptic and nutritional properties. Organoleptic properties of foods indicate a direct impression on sense organs, and include sight, hearing, touch, smell, and taste. These sensory perceptions often determine whether a food product will be acceptable or not. Nutritional properties of food are much more intangible in that one cannot sense them directly, but can be summarized as the amounts of proteins, carbohydrates, fats, vitamins and minerals present in the product relative to the recommended intake of these nutrients. Vitamins are more commonly recognized by the consumer as nutrients and are more important from the standpoint of thermal processing because they are easily affected by heat. Vitamins can be classified into two basic types, water-soluble (example, vitamins C and B1) and fat-soluble (i.e. vitamins A and D). Generally water soluble vitamins are normally heat-labile, readily

leached out and usually destroyed by alkalis and are stabilized by acid. Fat soluble vitamins are relatively more stable to heat and less affected by thermal processing.

Although the term "quality" can be interpreted in many ways (Alli, 1988), it essentially represents that characteristic which imparts to a product or service, "the ability to satisfy certain minimum demands and expectations of the consumer or purchaser". It must be recognized that "absolute quality" does not exist and that judgment of quality often must be made on an individual basis; what is acceptable quality in one situation could be considered poor or unacceptable quality in another (Taylor, 1985). In the case of food system, certain minimum demands and expectations are often related to or concerned with composition, nutritive value, function, color, taste, smell, texture, safety, etc. of the product and the uniformity of these properties from one purchase to another. Hence, both a minimum level of satisfaction and a high degree of consistency are required of the food product. In this study, two vitamins were chosen to represent the influence of thermal processing on nutrient degradation and a mixture of compounds responsible for nonenzymatic color formation was chosen to represent color development which would influence the appearance of the food product. Hence *"quality factors"* used in this thesis are limited to *"vitamin degradation and color formation"* only.

The primary consideration associated with thermal processing has always been microbiological safety, with organoleptic and nutritional quality usually being a secondary consideration. The advent of alternate and competing processes (i.e., sous vide, modified atmosphere packaging and freezing) now provide advantages in both organoleptic and nutritional quality. In addition to these alternatives, the consumer is much more aware of nutrition and is searching for products which meet their perceptions of being a nutritious product and these combined factors are forcing the thermal processing sector to consider nutrient retention more seriously.

The nutritional quality of thermally processed foods continues to be a subject of controversy among both consumers and processors (Lathrop and Leung, 1980a). The loss of vitamins has to be

balanced against the preservative effect obtained by thermal processing, as the availability of food, which may be slightly less nutritious, may well outweigh a nutritious product available only seasonally. Nutrients are obviously destroyed, lost or altered to some extent due to the effects of heat, reducing their overall biological availability (Bender, 1978). The major question is to what extent nutrient destruction occurs or can be controlled, considering that the destruction process involved could be a very complex phenomenon. Vitamin C has been used as an indicator of the overall quality of thermally processed foods due to its instability (Birch and Parker, 1974) while vitamin B1 has been used as an index of the thermo-chemical changes which take place during processing (Skjoldebrand et al., 1983).

The establishment of kinetic models for food quality factors is an area that still requires substantial development (Villota and Hawkes, 1986). The major reason for this is that many variables affect quality, including the order of reaction, rate constants, activation energies, environmental and compositional parameters. In addition, accurate information on heat and mass transfer for individual processes and products needs to be known in order to minimize discrepancies between experimental and real processes to allow the accurate prediction of quality changes.

2.3 Kinetic Models

2.3.1 Thermal Death Time Approach (TDT)

Most thermally induced reactions occurring in foods obey or can be approximated by well established kinetic models. Microorganisms, most quality factors and enzymes tend to obey first order reaction kinetics where the rate of change is proportional to concentration (Lund, 1975), and are frequently referred to as having a "semi-logarithmic order of destruction". In such a situation, regardless of the initial concentration, a constant fraction of the remaining substrate reacts per unit time and is this semi-logarithmic destruction behavior used extensively in sterilization modeling (Burton, 1977). The first order reaction rate with reference to destruction of nutrients/microorganisms at constant temperature can be expressed mathematically (Charm, 1966; Lund, 1975; Stumbo, 1973) as:

$$- dc/dt = kc \qquad [1]$$

where:

-dc/dt is the rate of decrease of concentration/microbial numbers

c is the concentration of nutrients/microorganisms at time t

k is the first order reaction rate constant

Rearrangement and integration of equation [1] between limits c_1 at time t_1 and c_2 at time t_2, and conversion of the natural logarithm to base 10 leads to:

$$\log c_2 = \log c_1 - k(t_2-t_1)/2.303 \qquad [2]$$

Equation [2] suggests that if the logarithm of concentration is plotted against time on a linear scale, the slope of the resulting straight line will be -k/2.303. The D value or decimal reduction time (i.e. the time required to reduce the concentration by 90%) can be obtained from the resulting semi-logarithmic curve as the time taken to traverse one log cycle, and is related to k by:

$$D = 2.303/k \qquad [3]$$

Thus, both D and k values can be obtained from the slope of the logarithm of concentration against time on linear scale (Figure 1).

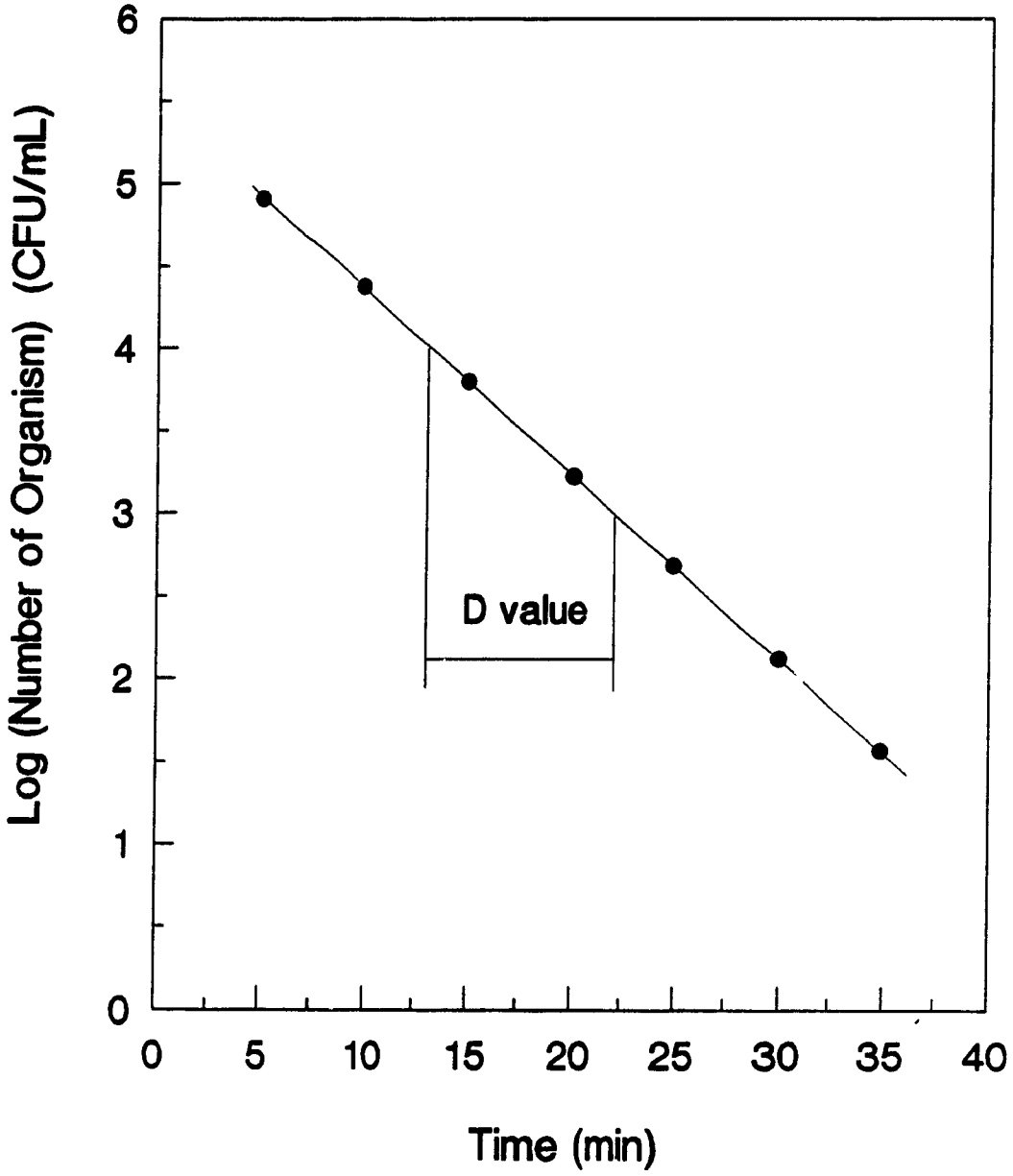


Figure 1. Typical Thermal Death Time (TDT) curve, illustrating the decimal reduction time (D).

The reaction rate constants, k and D, for the thermal destruction of nutrients/spores are temperature dependent, a fact which has to be considered as food products require time and undergo temperature change as they heat up, are held and cool down. Therefore, the reaction rate constants as a function of temperature plus the time-temperature profile of the product must be known. The two principal methods used to describe the dependence of the reaction rate constants on temperature are the thermal death time (TDT) and the Arrhenius models.

In TDT method, D values are described as a direct exponential function of temperature with a z value (negative reciprocal slope of the log-D value versus temperature curve) representing the slope index. In the Arrhenius technique, the logarithm of the reaction rate constant is related to the reciprocal of the absolute temperature with the activation energy (E_a) representing the slope index of the semi-logarithmic curve. Both methods are based on and assume first order kinetics, although deviations from the first order kinetics have been recognized for the thermal destruction of both microorganisms and nutrients (Pflug, 1982; Stumbo, 1973).

The TDT concept was first introduced by Bigelow and Esty (1920) based on an empirical approach to the temperature dependence of the first order destruction of microorganisms, was studied extensively, and has since led to its widespread application to thermal process calculations. The assumption that the logarithm of D value is directly proportional to temperature is a distinct advantage of the TDT approach, as it allows the expression of thermal process data in understandable terms as opposed to the Arrhenius approach which uses activation energy and the reciprocal of absolute temperature, which are not easily comprehensible. Over the years, a variety of mathematical, nomographic and computer models have been developed for process calculations based on the TDT approach (Stumbo, 1973).

2.3.2 Arrhenius Approach

The Arrhenius method is based on a thermodynamic approach and has been widely used for studying chemical kinetics. The concept is relatively simple, but yet not widely used in the food processing sector as the TDT method. The esthetic limitation of ln(k) vs reciprocal temperature is slowly being obviated as process calculations are getting more computerized and data can be retrieved in the form desired by the analyst. The Arrhenius method for process calculations has been advocated by some researchers (Deindoerfer and Humphrey, 1959; Lenz and Lund, 1977a; Sadeghi et al., 1986; Swartzel, 1982) largely because of its sound theoretical foundations.

The TDT approach is based on the assumption that the decimal reduction time (or D values) of nutrients/microorganisms follows a semi-logarithmic relationship with temperature:

$$\log (D_1 / D_2) = (T_2 - T_1) / z \qquad [4]$$

where:

D_1 is the decimal reduction time at T_1

D_2 is the decimal reduction time at T_2

z is the negative reciprocal slope of the D value curve

Since k and D are related by equation [3], substitution into equation [4] results in:

$$\log (k_2 / k_1) = (T_2 - T_1) / z \qquad [5]$$

or

$$\log (k_1/k_2) = (T_1 - T_2) / z \qquad [6]$$

The Arrhenius equation describes temperature dependence by relating the reaction rate constant k to the reciprocal of absolute temperature:

$$k = s \exp (- E_a / RT) \qquad [7]$$

where:

k is the reaction rate constant

s is a constant, frequency factor

E_a is the activation energy

R is the gas constant

T is the absolute temperature

Using k_1 and k_2 as reaction rate constants at temperatures T_1 and T_2, equation [8] can be derived from equation [7]:

$$\log (k_1/k_2) = [-E_a/(2.303R)][(T_2-T_1)/(T_2T_1)] \qquad [8]$$

From equations [6] and [8], the relationship between E_a and z can be obtained as shown below:

$$E_a = 2.303 \, R \, T_1 \, T_2 / z \qquad [9]$$

Lund (1975) suggested using T_1 as a selected reference temperature and T_2 as a temperature z degrees less than T_1.

Equation [8] states that the logarithm of the reaction rate is inversely proportional to the temperature which is in direct contradiction of equation [6], which states that the logarithm of the reaction rate constant is directly proportional to the temperature. This fundamental discrepancy has concerned scientists for many years (Lund, 1975); however, direct comparisons of the two techniques have been limited (Cleland and Robertson, 1985; Jonsson et al., 1977; Lund, 1975; Manji and van de Voort, 1985). In general, these studies suggest that most experimental kinetic data fit either model reasonably well. After a careful analyses of the utility of the two methods, Pflug (1982) recommended the use of TDT method as an objective tool for experimentation, in plant, and for validating and monitoring sterilization processes. Judgment as to which model better describes the kinetic data is difficult because experimental results obtained for reaction rate constant (k) values generally have significant level of uncertainty associated with them. This may due to the possible inadequacy of the first order kinetic model and/or due to difficulties arising from data collection (Cleland and Robertson, 1985). Both methods have been considered to be satisfactory (Stumbo, 1953), however, the TDT approach has the advantage of providing data based on reaction rates directly as a function of temperature.

Both the TDT and Arrhenius concepts have merit and have been proven to be adequate to study degradation kinetics; however, conversion of kinetic parameters from one system to the other can lead to erroneous results. Lund (1975) reported that over narrow temperature intervals, the two approaches are reconcilable and suggested a relationship which is valid at a specified reference temperature and a small temperature range around it. More recently, Norwig and Thompson (1986) compiled an extensive set of kinetic data in terms of reference k and E_a values for microbial destruction, enzyme and protein denaturation which were obtained in many instances by converting published D and z values; however, no details were provided on how the conversions were made. A clearer understanding is required in terms of how these two approaches are related and more specifically whether the values can be converted from one system into the other and the limitations associated with such conversions.

2.4 Quality Factor Degradation

The nutritional quality of thermally processed foods is of increasing concern to the public in general as there is an increased perception of processed foods generally being inferior in nutritional value and because they constitute a significant part of the diet. This concern has prompted studies to minimize quality degradation in thermally processed foods, particularly, canned foods. The high temperature short time (HTST) processing techniques (Nordsiden et al., 1978; Teixeira et al., 1975) benefit from the differential degradation of microorganisms and quality factors at higher temperatures. Although the nutritional aspects are of considerable concern, the organoleptic properties such as texture, color and flavor also need to be considered. Thermal process optimization for maximizing nutrient retention while minimizing other deteriorative changes during the heat processing of foods requires an understanding of the reaction mechanism and its kinetics. Ascorbic acid is a heat sensitive vitamin which illustrates the complexity which can be associated with the degradation of nutrients.

2.4.1 Ascorbic Acid (AA)

Ascorbic acid is a hexose derivative and is properly classified as a carbohydrate. It is a white crystalline substance, highly soluble in water. The vitamin is quite stable in the dry state but is easily oxidized when in solution. It is stable in acid solutions below pH 4.0 but the instability of ascorbic acid in solution increases markedly as the alkalinity of the solution increases. Ascorbic acid is unstable in the presence of certain metals such as iron and copper (Pike and Brown, 1975). Reduced ascorbic acid is easily oxidized to form dehydroascorbic acid which is just easily reduced back to the original form. The simplicity with which the two active forms of the vitamin are inter-converted is related to some of the physiological properties of the vitamin. Further oxidation of dehydroascorbic acid results in formation of diketogulonic acid and loss of vitamin activity.

A number of studies have focused on degradation of ascorbic acid in thermoprocessed foods (Abou-Fadel and Miller, 1983; Chen and George, 1981; Elkins, 1979; Lathrop and Leung, 1980a,b; Lund, 1977; Kirk et al., 1977; Klein, 1982; Vojnovich and Pfeifer, 1970); however, only a few have focused on the *kinetics* of the thermal destruction of ascorbic acid. Some studies have shown that the degradation reaction follows a zero-order reaction with respect to ascorbic acid concentration (Barron et al., 1936; Karel and Nickerson, 1964; Laing et al., 1978) while most others indicate it to be degraded by a first order reaction. Sakai et al. (1987) presented a model combining an initial zero-order and a subsequent first order reaction rate for the destruction of ascorbic acid.

Saguy et al. (1978b) found the ascorbic acid retention in grapefruit juice during both thermal and concentration processes to be dependent on the solids content and temperature. Using first order Arrhenius kinetics they reported an activation energy range of 21 to 48 kJ/mole. Using the TDT method, Lathrop and Leung (1980a) found that the total ascorbic acid content in peas and brine followed first order destruction over a temperature range of 110-132^{o}C with an associated E_a of 171 kJ/mole. For canned sweet peas over the temperature range of 99-127^{o}C, Rao et al. (1981) reported a much lower E_a value of 55 kJ/mole. In a buffer of pH 5.6, Blaug and Hajratwala (1972) reported an E_a of 75 kJ/mole for the aerobic destruction of ascorbic acid over 60-85^{o}C, while at pH 6.0 over a broader temperature range (30-100^{o}C), Huelin (1953) reported an E_a value of 94 kJ/mole for anaerobic decomposition. Kinetic data complied by Thompson (1982) and Villota and Hawkes (1986) indicate a wide E_a range of 14 to 171 kJ/mole for ascorbic acid degradation during processing and storage.

Most studies on ascorbic acid degradation kinetics were based on actual food products subjected to common unit operations such as thermal processing, concentration, freezing and drying as well as storage at varying conditions of temperature, moisture and water activity. Optimization of thermal processes to maximize nutrient retention requires kinetic data obtained under controllable conditions. Because this was not the case in most of the studies noted above, the results are of limited value for comparative purposes unless applied under the specific conditions mentioned because of the large

numbers of variables associated with them. The net result is that although substantial research has been done on ascorbic acid destruction, only a few studies have systematically evaluated thermal destruction of ascorbic acid in aqueous systems and more basic information is needed.

2.4.2 Thiamine (B1)

Thiamine is a relatively simple chemical compound composed of a pyrimidine and a thiazole ring; it is available commercially both in the hydrochloride and the mononitrate forms. Thiamine hydrochloride is a white crystalline solid and is stable when in dry form. It is highly soluble in water. Although somewhat more stable in acid solutions, the vitamin decomposes rapidly in alkaline solutions and the decomposition is hastened by heat (Pike and Brown, 1975).

Thiamine is a relatively heat-labile vitamin that has been used as a chemical index of sterility (Guzman-Tello and Cheftel, 1987; Mulley et al., 1975a,b,c) and a number of studies on its thermal destruction kinetics have been carried out (Bendix et al., 1951; Cameron, 1955; Dennison et al., 1977; Everson et al. 1964; Feliciotti and Esselen, 1957; Fernandez et al., 1986; Greenwood et al., 1944; Lenz and Lund, 1977b; Leonard et al., 1986; Skjoldebrand, et al., 1983). Two reviews (Thompson, 1982; Villota and Hawkes, 1986) tabulate data on thiamine degradation, which generally show first order reaction rate kinetics with activation energies in the range of 33 to 124 kJ/mole. Some specific studies (Booth, 1943; Dwivedi and Arnold, 1973; Farrer, 1945, 1955; Farrer and Morrison, 1949; Sabrie et al., 1968; Tanaka, 1966a,b) indicate that the type of food product, temperature range, oxygen level and other factors can influence the degradation kinetics of thiamine. As with ascorbic acid, much of the published information (Guzman-Tello and Cheftel, 1987; Mulley et al., 1975a,c) on thiamine degradation is based on real food systems with several unknown variables and hence are of limited value unless carried out under conditions specific to the reported study. No published systematic information is available on thermal destruction of thiamine in aqueous systems at natural pH (without added buffer).

2.4.3 Maillard Reaction Color

Color is one of the more immediate quality attributes associated with food products and in the case of canned goods, both color formation and degradation can be undesirable. Often, as in the case of chlorophyll or carotenoids, color degradation is of concern, while in the case of fruit syrups, color formation due to the reaction of reducing sugars and amino acids by the Maillard reaction is considered undesirable. Extensive literature is available on Maillard reactions in which temperature, pH, moisture content, water activity, presence of other agents, the nature of the reacting components and their concentrations are just some factors shown influencing the color formation (Eskin et al., 1971; Stamp and Labuza, 1983; Walford, 1980; Waller and Feather, 1983; Villota and Hawkes, 1986). The majority of the studies related to food systems deals with browning reactions during storage as influenced by specific factors (Cornwell and Wrolstad, 1981; Kadas and Lindner, 1980; Kanner et al., 1982; Petriella et al., 1985; Saguy and Karel, 1980; Toribio and Lozano, 1984; Wang et al., 1971). A few studies have also attempted to characterize the kinetic behavior of color formation/degradation at temperatures comparable to thermal processing operations. Among these, most have concentrated on the thermal degradation of natural colors such as chlorophylls, carotenoids and anthocyanins (Clydesdale and Francis; 1968; Gold and Weckel, 1959; Gupte et al., 1964; Hayakawa and Timbers, 1977; Huang and von Elbe, 1985; Lenz and Lund, 1980; Ramakrishnan and Francis, 1973; Rao et al., 1981; Sastry and Tischer, 1952; Schwartz and von Elbe, 1983). As summarized by Villota and Hawkes (1986), the range of activation energies (E_a) for selected color degradation reactions are: chlorophylls, 22-114 kJ/mole; anthocyanins, 55-125 kJ/mole; betanine, 30-88 kJ/mole; carotenoids, 94 kJ/mole. For non-enzymatic browning reactions, the E_a values reported range from 34-155 kJ/mole (Burton, 1963; Hendel et al. 1955; Herrmann, 1970; Saguy et al., 1978a; Song et al., 1966; Stamp and Labuza, 1983).

2.5 Principles of Thermal Processing

Thermal processing of foods is the basis of the canning industry and ranges from mild heat treatments such as pasteurization through to cooking, to the relatively severe heat treatments required to attain commercial sterility. Although an increasing volume of products are commercially sterilized prior to being packaged aseptically, the majority of food is still packaged in metal cans or a process commonly referred to as canning (Cleland and Robertson, 1985).

The basis for successful canning is the concept of attaining commercial sterility, that is providing a sufficient thermal treatment which ensures that neither microorganisms nor their spores grow under conditions normally encountered in the container during storage. This implies that there could be some dormant nonpathogenic microorganisms in the product but that the environmental conditions are such that these organisms are not able to reproduce (Lund, 1975). Canned foods which meet these criteria are usually referred to as "commercially sterile" and are defined as such based on having undergone a 12D process which reduces the microbial population by a factor of 10^{12} (Charm, 1978). The processing conditions for low acid foods (pH>4.5) must guarantee the complete inactivation (12D) of *Clostridium botulinum* and should also eliminate any other organisms that could cause health or spoilage problems (Pelczar et al., 1977). The number of microorganisms most of thermal processing studies are based on is 60 billion spores of *Clostridium botulinum* per mL (Esty and Meyer, 1922) and therefore canners throughout the world calculate their processes to go through 12 log cycles; however, Goldblith (1971) suggested this to be high and recommended that the destruction be based on 8 log cycles reductions.

Another way of defining commercial sterility is in terms of probability, i.e., that a 12D process results in one viable spore in one out of 10^{12} cans (Stumbo, 1973) since fractions of a spore are physically undefined. Lethality and unit of lethality are two other terms established to denote the extent of a thermal process, which are used to compare relative sterilizing capacities. The total lethality or sterilizing value is usually designated by the symbol F^{z}_{T}. The subscript T indicates the reference temperature used

for the process while the superscript refers to z value which characterizes the relative resistance of spores of a specific organism to temperature. F_0 values without any additional notation are based on a reference temperature of 121.1°C (250°F) and a z value of 10°C (18°F). For convenience a unit of lethality required for sterilization processes is defined as 1 minute at a specified reference temperature, i.e., if a process is assigned an F value of 3 min, it means that the sum of all lethal effects of the process is equivalent to the lethal effect of 3 minutes of heating at the designated reference temperature, assuming instantaneous heating and cooling. F may also refer to the sum of lethal effects at a single point in a container of food or to the sum of lethal effects at an infinite number of points throughout a container. In all circumstances, F is a sum of all lethal effects considered expressed in minutes at some reference temperature (Stumbo, 1973). The thermal conditions needed to produce commercial sterility depend on many factors including: (a) the nature of the food (e.g. pH and a_w); (b) storage conditions of the food following the thermal process; (c) heat resistance of the microorganisms or spores; (d) heat transfer characteristics of the food, its container and the heating medium; and (e) the initial load of microorganisms.

The cylindrical can is the main type of container used in the industry and the most common method of processing is the application of steam under pressure followed by cooling in water, consequently, most of the published work in the literature have concentrated on this type of container and process. The establishment of a thermal process should always involve two phases, (a) the determination of heating time for a product using heat penetration data to determine the temperature/time required to achieve a selected F followed by (b) microbiological methods to confirm the calculated process. A crucial factor in designing a process is the way in which the cooling phase is handled. Steam may be shut down before the total target F is reached in the expectation that the cooling phase will increase the overall lethality to the required value, although when this has been done, the lethal effect of the process is virtually fixed, even though the contribution of the cooling phase is still unknown (Cleland and Robertson, 1985). It is more common practice to attain the target F first during the heating

phase and using the subsequent cooling phase effect as a safety factor, although this results in over-processing and significantly affect heat-labile quality factors.

2.5.1 Calculation Methods

Thermal processing involves placing a food product into a container of known dimensions and subjecting it to a defined thermal regimen. The methods for the determination of thermal processes to attain commercial sterility have undergone considerable development over the last 80 years. Many formulas are available for determining temperature response characteristics of food to be sterilized and can be classified into theoretical formulas (Ball and Olson, 1957; Charm, 1971; Gillespy, 1953; Hayakawa, 1970, 1971; Hayakawa and Ball, 1968, 1969, 1971; Hicks, 1951; Stevens, 1972; Stumbo, 1973) and empirical formulas (Ball, 1923; Ball and Olson, 1957; Griffin et al., 1971; Stumbo, 1973). The theoretical formulas are analytical or numerical solutions of theoretical heat equations while empirical formulas are based on heat penetration data.

Hayakawa (1977) further classified the calculation methods into two groups additional groups, one which is based on the evaluation of lethality at the slowest heating point (Ball, 1923; Ball and Olson, 1957; Bigelow et al., 1920; Flambert and Deltour, 1972; Gillespy, 1953; Griffen et al., 1969,1971; Hayakawa, 1968,1970,1973; Herndon, 1971; Hicks, 1958; Jakobsen, 1954; Pflug, 1968; Shapton and Lovelock, 1971; and Stumbo, 1973) and a second based on the mass average lethality of the entire volume of the food (Ball and Olson, 1957; Gillespy 1953; Hayakawa, 1969; and Stumbo, 1953, 1973). Both procedures are further subdivided into the general methods (Original General Method and Improved General Method), formula methods and the mass average or volume average method. The general methods do not provide a means for predicting temperature history curves of food products subjected to heat processing and require a temperature history curve as a basis for process calculations, while the formula methods provide a means for predicting temperature history curves.

Thermal processing parameters determined by either method are identical in terms of expressing results in the form of lethalities, however because the slowest heating point methods require less calculation they are generally used. For circumstances where one wishes to make predictions about the nutritional or organoleptic properties of a food system, the formula methods are more useful as they provide information for the entire volume/mass of the food product.

2.5.1.1 Conduction Centerpoint Method

The cold point method was originally developed by Bigelow et al. (1920) and their basic concepts and methodology are still used in the food industry today. The cold point method uses plots of heat penetration and spore survival data to predict process lethality. In general, can heating and cooling data obtained by thermocouples yield almost straight lines when plotted on semi-logarithmic paper, with the exception of a lag period for each cycle (heating or cooling). These simple logarithmic equations were considered by Ball (1923) to be an adequate approximation for the heating curve since the early lag heating temperatures are generally not high enough to affect sterilizing values significantly. The lag in the initial part of the cooling curve is important and Ball (1928) developed a method to calculate the center temperature/time histories to take into account the cooling lag. The cooling curve was assumed to initially be hyperbolic, then logarithmic to account for the deviation caused by the cooling curve lag factor (j_c). The equations developed were based on a lag factor (j value) of 1.41 for both the heating and the cooling curves, although later this value was modified to 2.04 (Hicks, 1951; Ball and Olson, 1957). Jackson and Olson (1940) further refined the method by developing broken heating curves which assumed that the heating and cooling curves are always asymptotic to a straight line and that the ambient temperature and the thermal diffusivity remain constant with respect to time. Additional refinements occurred when Carslaw and Jaeger (1947) derived solutions to classical heat conduction equations through the use of Duhamel's theorem providing temperature estimates for various shapes, including finite cylinders and bricks. Hicks (1951) modified the equations and used the j value to more accurately

determine can center temperatures. He recommended a j value of 2.04 for the cooling curve which was verified experimentally by Ball and Olson (1957).

Patashnik (1953) estimated sterilization values by considering the temperature history curve as a series of constant temperatures and used trapezoidal integration rather than the graphical method to calculate the lethality. Gillespy (1953) calculated integrated center temperatures of cylindrical can utilizing equations developed by Riedel (1947) based on a restricted version of Duhamel's theorem. Hayakawa (1968) also used the numerical integration for process calculations, his method simplifying the calculations required for process estimation. Several researchers (Hayakawa, 1969, 1973; Leonhardt, 1976; Newman, 1936; Shapton and Lovelock, 1971) have devised nomograms, charts or tables to aid in calculating center temperatures.

2.5.1.1.1 Single Point Methods

2.5.1.1.1.1 General Methods

The general method was considered one of the most accurate procedures for estimating sterilizing values. Experimentally derived temperature values are used for the computation without any assumptions about the temperature/time relationship of food. The Original General Method was first described by Bigelow et al. (1920) and although now rarely used, most improved methods are still based on the fundamental concepts of the original method. The Original General Method is a graphical procedure for integrating lethal effects of various temperature/time relationships existent at some given point in a confined body of food during processing. Usually this point is at the geometric center of the product container (Hicks, 1958) and a thermocouple is used to obtain the heat penetration data during the process. By obtaining the time from the TDT curve of *Cl. botulinum* spores representing a 12D reduction at specified temperatures it is possible to assign a lethal rate value to each point on the temperature/time graph. The lethal rate value assigned to each temperature is numerically equal to the reciprocal of the number of minutes required to obtain 12 decimal reductions at this temperature.

Lethality is therefore defined as a product of lethal rate and the time (in minutes) during which the corresponding temperature is operative. Thus, a process of unit lethality is adequate to accomplish the same percentage of destruction of an identical population as represented by the TDT curve (Stumbo, 1973). By using this graphical method, the area under the lethal rate curve obtained as compared with a unit sterilization area (having a lethal value of one) represents the total lethality of the process (Bigelow et al., 1920). Thus, a lethal value of one indicates that the spores of *Cl. botulinum* have been reduced cumulatively by a factor of 12 D. If the area under the trial process curve does not equal unity, then the holding time is extended and cooling portion of the lethality curve is shifted to the right to give an area of one. This approach requires some trial and error in order to optimize the process.

The Improved General Method was designed after the work by Ball (1928) and by Schultz and Olson (1940). The major contribution by Ball was the construction of a hypothetical TDT curve passing through one minute at 121.1°C. The lethal rate obtained from such a TDT curve when plotted against time, is a lethality curve, the area beneath this curve being directly proportional to the equivalent of the entire process at 121.1°C. This approach permitted a direct comparison of relative sterilizing capacities of differing thermal processes (Stumbo, 1965). Schultz and Olson (1940) modified Ball's method (1928) by using a specially designed lethal rate paper which simplified the process calculations and reduced the chances of miss-plotting. They also included a formula which could be used to standardize heat penetration data obtained for different foods at varying food and retort temperatures. Although still time consuming and requiring special lethal rate paper for each z, these two modifications greatly enhanced the applicability of the General Method. Patashnik (1953) estimated an F_0 value by approximating a temperature history curve with a series of constant temperatures as this approach did not need special lethal rate paper and the lethality could be calculated by numerical trapezoidal integration method rather than graphical integration. Hayakawa (1977) reported that the error of this approximation is probably greater than that associated with estimating F values by Simpson's rule or by the Gaussian integration formula (Hayakawa, 1968). Shapton and Lovelock (1971) prepared L-value tables to estimate and inter-convert sterilizing values based on degrees Fahrenheit to Celsius without any conversion units.

Hayakawa (1973) developed a method for allowing the use of lethal rate paper of a fixed z value to determine the sterilizing values at different z values. The limitation is that his method can only be used when the lethal rate paper temperature scale is defined along with the unit area under the lethal rate curve according to the temperature scale used. Hayakawa's concept was improved by Leonhardt (1976), who proposed a general lethal rate paper that eliminated the above restrictions. Leonhardt's general lethal rate paper can be used to represent heat penetration data directly regardless of the z value, reference temperature and does not require a definition of a unit area for any particular case.

2.5.1.1.1.2 Formula Methods

The first analytical formula used to perform process calculations was developed by Ball in 1923. He used mathematical formula accompanied by charts which related various factors to simplify the process evaluation. The formula method was based on a number of mathematical and empirical assumptions with restricted applicability. According to Hayakawa's analysis (1978), Ball's Formula Method will underestimate the F value significantly when the cooling factor is greater than 1.41 as assumed by Ball (1923). On the other hand Steele and Board (1979) have compared the accuracy of the formula method to the general method for a wide range of process conditions with almost no difference. Olson and Stevens (1939) simplified Ball's formula method by developing a nomogram for canned foods which exhibit linear simple heating curves allowing process computations to be carried out graphically. Ball and Olson (1957) improved Ball's first formula method by using two dimensionless parameters, P_h and P_c which were used to estimate the sterilizing values of the heating and cooling phases. The use of these parameters greatly simplified the calculations required for process estimation, especially, for the products with broken heating curves and/or products in which the slopes of heating and cooling curves are not equal. There are still errors associated with such procedures because the original assumptions relative to the cooling curve lag factor value (j_c) for terminating the curvilinear portion were not

modified. Hicks (1958) recalculated and corrected Ball and Olson's (1957) standard process values after noting errors in their dimensionless parameter tables. Hyperbolic functions were used by Jakobsen (1954) to represent heating and cooling curves assuming a cooling lag factor value of 2.04; however Hayakawa, (1978) found that these were of limited value because the lag factor of many experimental cooling curves were quite different. Deindoerfer and Humphrey (1959) derived a set of analytical formulas for estimating the sterilizing effects when liquid products are processed by various heat exchangers, assuming a uniform temperature distribution throughout the food when processed batch-wise, and a uniform cross sectional temperature distribution when processed continuously.

Stumbo and Longley (1966) published a modified formula method in which variable cooling curve lag factors (j_c) could be used for the process calculations. Parametric values, estimated from heat penetration curves drawn on lethal rate paper and the areas quantified using a planimeter, were tabulated. These tables were applicable only when the difference between the slope of cooling curve was less than twenty percent of the slope of heating curve (f_h). Pflug (1975) compiled tables of parametric values using data from both Ball and Olson's and Hick's tables which simplified process calculations. Hayakawa (1970; 1971) developed sets of empirical formulae which could be used for process calculations when the cooling curve lag factor (j_c) greater or less than 1.41. Based on these formulae he tabulated a new set of parametric values which significantly reduced the calculation time relative to previous formula methods. Griffin et al. (1971) derived equations for calculating food temperatures in the cooling phase but has since been criticized by Hayakawa (1977) who indicated that results from these equations would considerably underestimate the process F value. Herndon et al. (1968) reported numerical values of a new dimensionless parameter for estimating the process F values, however, there is no significant difference between their parametric value and those originally derived by Ball and Olson (1957). Stumbo (1973) recalculated the parametric values by using transient state temperatures theoretically predicted by means of a formula for heat conduction in a finite cylinder, however its use is only applicable when the slopes of the heating and cooling curves are approximately equal.

All formula methods described above are based on empirically derived temperature histories. Other formula methods have been developed using a theoretical approach to determine the temperature/time data. Gillespy (1953) used an analytical solution of Duhamel's theorem (Carslaw and Jaeger, 1947) to create a table of food temperature values. Using these temperatures, his method calculated the sterilizing values of a heat process by applying the general method and allowed one to evaluate heat processes which involved variable retort times and temperatures. Flambert and Deltour (1972) also used heat conduction equations to estimate food temperatures assuming that the heating and cooling media temperatures remain constant with time. They prepared tables of parametric values which are simpler to use than those of Gillespy (1953).

2.5.1.2 Centerpoint Nutrient Degradation

Controlled evaluation of nutrient destruction in thermoprocessed foods is difficult due to the lack of an efficient, heat stable and chemically inert conduction heating medium which can support a uniform suspension of nutrients in its matrix for heat penetration tests. Beyond the requirement for inertness, one must be able to obtain efficient recovery of residual nutrients following the heat processing and it would be useful to be able to isolate and recover nutrients from a specific test location. Bentonite suspensions have traditionally been used to simulate the heating behavior of foods (Adams et al., 1983; Ball and Olson, 1957; Yamano, 1976). While bentonite is adequate to simulate heat transfer responses, nutrient dispersion in these suspensions and their subsequent recovery is a serious problem. Others (Manji and van de Voort, 1985) have used compressed glass wool to form a three-dimensional matrix to restrict the mobility of water to simulate conduction heating conditions, however our preliminary studies have indicated that the compressed glasswool does not efficiently suppress convection currents, especially at higher temperatures.

Thermal processing is based on reducing the heat resistant microbial population at the slowest heating point to a level that is considered statistically satisfactory. In the case of conduction heating

foods, each point in the container receives a different thermal process than every other point. From a microbial safety standpoint the primary interest is achieving commercial sterility at the slowest heating point; in the case of nutrient retention, it is the overall integrated destruction at every point in the container that is important. Such studies have been carried out by a number of researchers either employing finite difference/element computer simulations of the heat transfer process or by experimental techniques based on average destruction (Castillo et al., 1980; Downes and Hayakawa, 1977; Holdsworth, 1985; Jen et al., 1971; Lenz and Lund, 1980; Manson et al., 1970; Ohlsson, 1980; Teixeira et al., 1969a; Thijssen and Kochen, 1980). Biological validation methods (Hersom and Shore, 1981; Hunter, 1972; Pflug et al., 1980a,b) developed for verification of continuous aseptic processes employ somewhat similar approaches, but the sample sizes used in such studies are too large for approximating changes in concentration in specific spatial locations. To date there has been no experimental verification of computer simulated predictions for nutrient destruction at specific container locations during thermal processing and will be one of the objectives of our research.

2.5.1.3 Conduction Mass/Volume Average Methods

The second approach to thermal process calculations involves the mass average or volume average method. Williamson and Adams (1919) originally developed solutions to the classical heat conduction equations describing temperature distributions throughout various objects and are based on assumptions of uniform initial temperature, constant thermal diffusivity and negligible surface convective heat transfer. Although many subsequent solutions have been developed (Ball and Olson, 1957; Jackson, 1940; Luikov, 1968), all include the assumption that surface convective heat transfer is negligible. Carslaw and Jaeger (1959) extended the solutions to different shapes, including bricks, cylinders and spheres to determine the temperature distributions when the surface resistance cannot be assumed to be equal to zero. These equations were simplified by Ramaswamy et al. (1982) and still shown to be sufficiently accurate for use in process calculations. Merson et al. (1978) provided a theoretical basis for formula methods and Smith and Tung (1982) numerically assessed the prediction

accuracy of various formulas methods as applied to pure conduction situations using finite difference heat transfer calculations and numerical integration to obtain process lethalities. These concepts have been extended and applied to nutrient retention work and several theoretical mathematical models predicting nutrient retention in conduction heated products have been developed (Flambert and Deltour, 1972; Jen et al., 1971; Lund, 1975; Manson et al., 1970; Pham, 1987; Steel and Broad, 1979; Teixeira et al., 1969a, 1975; Thijssen and Kochen, 1980).

Another group of thermal process evaluation procedures utilize the mass average lethality value and can be used to calculate average retention values of heat-labile components. Four models are available, including a kinetic model for thermal destruction, a model for temperature effects on the kinetics, a model for heat transfer in the container and a model which can include the previous three so that the mass average or volume average retention can be calculated. Six common methods which may be used to predict average lethality or retention include i) average formula method (Ball and Olson, 1957), ii) improved average formula method (Jen et al., 1971), iii) dimensionless group method (Hayakawa, 1969), iv) finite difference method (Teixeira et al., 1969a), v) average general method (Cohen and Wall, 1971) and vi) lethality Fourier number method (Lenz and Lund, 1977a). The first five use the TDT concept to describe the dependence of reaction rate on temperature while the sixth uses the Arrhenius approach. The methods of Ball and Olson (1957) and Jen et al. (1971) use empirical relations to describe temperature as a function of process time, while the method of Cohen and Wall (1971) requires experimental heat penetration curves at various position in the product as it is heated. Hayakawa's (1969) and Teixeira et al. (1969a) methods are based on theoretical equations developed for heat transfer by conduction.

One of the perceived shortcomings of most of the methods noted above is that they are all based on the TDT method for relating the reaction rate to temperature. This relationship is not considered as scientifically sound as the traditional Arrhenius equation over substantive temperature ranges for components having low activation energies. Due to this limitation, Lenz and Lund (1977a) combined a

Fourier number technique with the Arrhenius equation to predict the mass average retention of thermally vulnerable components in conduction heated foods.

The averaging technique is unique to the individual method used and thus some of the methods are very specific in terms of their application. The average general method requires experimental heat penetration curves for each prediction, while Teixeira's approach (Teixeira et al., 1969a) requires a computer run for each prediction. Hicks (1951), Thijssen et al. (1980), Hayakawa (1969) and Lenz and Lund (1977a) used numerical integration over volume for predicting temperature/time profiles in cans. Provided all non-negligible terms in the Fourier series are used, the temperature/time profiles at any point in the can should reflect the heating process. Hayakawa (1977) developed computer programs to carry out similar calculations, however it is unclear from the literature how widely any of these methods are actually being used. All of these methods are expected to work in situations where conduction is the sole mode of heat transfer. It has been well established that numerical techniques such as finite differences closely model heat conduction and therefore one would expect that the methods developed by Teixeira et al. (1969a) and Flambert et al. (1977) should be similar to other integration methods. Computer simulations are generally much simpler to carry out than actual heat penetration studies in terms of time, effort and resources, however, verification of computer predictions rarely accompany such work. Verification is a necessity in order to have confidence in simulation results and is an integral part of the work proposed.

2.5.2 Convection Heating

Convection heating is assumed to take place in a product which is sufficiently fluid in nature to allow substantial mixing of its contents due to the formation of density gradients created by temperature differences. Convection heating is substantially more complex than conduction heating and the level of understanding and capability to predict temperature/time relationships and nutrient retention are far

from being completely understood. In contrast to the abundant information presented in the literature for foods heated by conduction, relatively little work has been carried out on foods heated by convection (Charm, 1971; Desrosier and Desrosier, 1977; Jackson, 1940) with even fewer studies directly related to the prediction of temperature/time relationships and nutrient retention of foods heated by convection (Bimbenet and Duquenoy, 1974; Hiddink et al., 1975; Sidaway-Wolf, 1984; Stevens, 1972).

2.6 Heat Transfer

Heat can be transferred from one body to another either by conduction, convection or radiation. In conventional thermal processes, only conduction and convection heat transfer mechanisms are involved, although radiation may also be an important heat transfer mechanism in flame sterilization radiation. The heating rate in containers is a function of the geometry of the container, physical properties of the food product, heat transfer characteristics of the heating medium and the heat transfer characteristics of the container. In addition, the makeup of the food product, i.e., solid, particulate or liquid and/or the presence of sugars and starches determine whether a product heats by convection, conduction or a combination of both mechanisms.

Heat transfer concepts are basically divided into two basic modes of analysis, the steady state and unsteady state or transient concepts. In steady state heat transfer the temperature gradient or difference does not change with time and the mathematical analysis is relatively simple compared to transient state problems where the temperature gradient or difference changes with time. Heat transfer to and from containers of food is considered a transient state problem and the graphical methods of analyzing heating or cooling data as developed by Ball (1923) are unique in treating a very complex problem. The external heat transfer characteristics of the medium used to heat the container can be very important, as is composition of the container, both of which will affect the heating rate. The heat transfer rate through metal containers is much more rapid than glass or plastic, however, these rate differences are often overshadowed by the heating rate of the product.

An important factor in carrying out heat penetration work is the location of the thermocouple, as the temperature distribution within a container may not uniform with respect to position. The selection of the slowest heating zone as the point of measurement is a logical choice (Pflug, 1975), can be determined experimentally and is reproducible for consistent food systems. By designing a sterilization process on the basis of the temperature/time history at the slowest heating zone of the container, the processor is generally assured that the process will be adequate for all other points in the container.

When heat is transferred by conduction, energy transfer is essentially a molecular phenomenon, where molecules with a higher energy content transmit some of their energy to adjacent lower-temperature molecules through inter-molecular collisions. This means that conduction heat transfer is the slowest way that heat can pass through a material. The mathematics of heat transfer by conduction is considered to be on a very firm foundation (Pflug, 1975) and heat transfer rates can be predicted accurately if the thermal diffusivity of the product is known for objects of standard geometry. In conduction heating products, the heating phenomenon is well ordered, proceeding from the outer layers through toward the center. If the food product is in contact with all the inner surface of the container, the slowest heating zone will be located at the geometrical center of the container. If the container has a headspace, the slowest heating zone will be located along the center line of the container a short distance toward the headspace from the geometrical center and container orientation has no major affect on the cold point location.

Convection heating is the transfer of heat from one point in a fluid to another point by the movement of the fluid itself. If the movement or fluid flow is due to differences in fluid density then the heat transfer is considered to be natural convection, while fluid flow by pumping or other form of mechanical agitation is considered forced convection. Convection heat transfer in a can of food is a very complex process, being affected by the properties of the fluid and the geometric effects of the container itself, including container orientation which affects product flow distribution.

The heat capacity of a food product is the quantity of thermal energy which must be added or removed from a unit mass of food for a specified temperature change. Specific heat is a related measure and is the ratio of the heat capacity of a material to the heat capacity of water. In transient state heat conduction, thermal diffusivity is an important parameter that relates heat conduction to heat storage and is defined as:

$$\alpha = k / \rho C_p \qquad [10]$$

where:

α = thermal diffusivity

k = thermal conductivity

ρ = density

C_p = specific heat capacity at constant pressure

The rate of heat flow is directly proportional to the temperature difference between the heat source and the lower object temperature to which the heat is flowing and inversely proportional to the resistance to heat flow of the space between two objects. Resistance to heat flow is expressed as a unit of conductance termed "thermal conductivity" and most high-moisture foods have thermal conductivities close to those of water. In order to carry out in-container commercial sterilization processes, thermal energy must first added to the product in the container and later, after sterilization has taken place, removed to obtain ambient temperatures levels. Sterilization processes are therefore, heat transfer unit operations and the most common heat source is usually pressurized steam. Heat transfer from steam to the container is a major concern in heat penetration studies and three important process design variables to be considered include; come-up time, point-to-point temperature variation in the retort and temperature cycling with time at a given point in the retort. The objectives of all retort control systems are to minimize come-up time, point-to-point temperature differences and temperature cycling. In the

final analysis, overall retort performance is determined by the interaction of the many elements that make up the system, however, certain elements are more crucial such as (a) the steam supply system, including the design of the piping system, control valve size and boiler or line pressure which primarily determine the come-up time of the retort, (b) the retort geometry, loading pattern, spreader design, vent size and location and type of heating media are the variables that influence point-to-point temperature variation, and (c) the control system which includes the control valves determines the temperature cycle.

In the thermal processing the goal is uniform and reproducible heating conditions, of which the rate of heating of the package is in itself not critical because the process design takes the package heating rate into account. Variation in the rate of heating in different parts of the retort can be a major problem and when this occurs the process must be designed based on cans located in the slowest heating zone of the retort (Pflug, 1964).

The length of the retort come-up time varies inversely with the rate of steam flow to the retort, which in turn is a function of the difference in pressure between the steam source and the retort, and the flow resistance of the pipe which is a function of pipe size and length, fitting size and equivalent length. Come-up time can be decreased by increasing boiler or line pressure and/or by increasing the size of the steam lines and associated fittings. For most food products it is important to bring the retort up to process temperature as rapidly as possible because the z value of quality factors is generally much larger than the z value of microbial destruction and therefore a long come-up time will have a relatively greater effect on quality than on microbial destruction.

2.7 Computer Models

Computer have been used by researchers for lethality calculations, particularly for those based on the formula methods. A number of programs have been published and available as commercial software packages, on floppy disks for micro-computers or on magnetic tape for mainframes. Any such package

would require user-friendly features in terms of input/output and carry out calculations by most of the recognized lethality estimation procedures. In order to be effective, an international group of experts would be required to define the basis of the package and to provide overall guidance to the software developer (Cleland and Robertson, 1985). The present practice of publishing the listings of programs in the literature can no longer be regarded as an effective way of making programs available to industrial processors. Finite difference calculations should play a greater role in predicting lethality for pure conduction cases in the future and allow calculations to be done without having to resort to charts and/or tables.

As noted in the introduction, market demands are likely to drive cannery technologists to adopt processes that also minimize quality degradation. In order to achieve this, reductions in present safety margins will be required and subsequently the techniques for assessing the safety must be refined. Limited work has been done in this regard and more specifically in relation to simulating and predicting lethality and/or nutrient retention in thermoprocessed foods. A number of models have been developed for the prediction of lethality and/or nutrient retention in conduction heated canned foods in cylindrical cans (Ball and Olson, 1957; Barreiro-Mendez, 1979; Finnegan, 1984; Flambert and Deltour, 1972; Hayakawa, 1969b; Jen et al., 1971; Lenz and Lund, 1977a; 1977b; Stumbo, 1953; Teixeira et al., 1975). Some procedures have also been developed for rectangular cans (Manson et al., 1970; Herrera, 1978) and for retortable pouches (Castillo et al., 1980).

Ball and Olson (1957) presented a method to determine the retention of a nutrient in a cylindrical container during thermal processing of food. According to Jen et al. (1971), good lethality accuracy could not be expected from their approach, because of the finite layer procedure used to integrate the lethal effects, and because of the way the cooling curve lags were treated mathematically. Manson et al. (1970) developed a computer method to determine the effects of thermal processing on the nutrients in foods being heated in rectangular containers. The temperature history was calculated using a finite difference numerical solution to the three-dimensional transient heat conduction equation, with the

effect on the nutrients being calculated at all points in the container and integrated to give the final nutrient retention value. A similar approach was used by Manson et al. (1974) for pear-shaped containers.

Jen et al. (1971) modified Stumbo's original method to obtain a solution that could be applied to either nutrient or microbial destruction during thermal processing. A new formula was derived to integrate the heat effects throughout the container during heating and cooling, and these workers also extended the parameter tables to cover a higher range of z values. Lenz and Lund (1977a) developed the lethality-Fourier number method for calculating the center point sterilizing value of a thermal process applied to conduction heating foods. This method was extended (Lenz and Lund, 1977b) so that mass average retention of heat-labile quality factors such as color and nutrients could be estimated for conduction heating foods packaged in cylindrical containers.

Castillo et al. (1980) developed and experimentally verified a model to predict the retention of nutrients based on the first order kinetics of nutrient degradation in foods processed in retortable pouches. With their model, the prediction of nutrient retention at any point in the pouch could be made and the results could be integrated over time and volume to give the final nutrient fraction retained after processing. These workers found the predictions of nutrient retention to be within ninety percent of the experimental nutrient fractions.

For canned products heated by convection there are few methods available for the prediction of temperature/time relationships. Bimbenet and Duquenoy (1974), Barreiro-Mendez (1979), Stevens (1972) and Hiddink (1975) have reported methods for predicting heat transfer by convection which may be used for lethality and nutrient retention calculations.

The Bimbenet and Duquenoy (1974) model is restricted to cases where perfect mixing exists for convective heated products. Barreiro-Mendez (1979) developed and experimentally verified a model for

the prediction of temperature/time relationships in canned products heated by convection using a non-dimensional equation that related the Nusselt, Grashof and Prandtl numbers. They reported a satisfactory agreement between the predicted and experimental values for the high lethality region. Using a similar concept, they developed a model for predicting nutrient retention during thermal processing of products heated by convection, utilizing the heat transfer equations and the first order kinetics equation for the nutrient studied. A computer program was developed to solve the model and to perform simulations of the actual processes using a digital computer. Hiddink (1975) and Hiddink et al. (1975) presented a model based on simulating the process as a number of tanks in series, however, this approach has a serious drawback in that the number of tanks have to be assigned arbitrarily in order to match the experimental data, therefore restricting, the predictive use. Stevens (1972) approach based on equations for conservation of mass, energy and momentum did not work satisfactorily due to simplifications required to solve the equations.

Simple optimization techniques have been developed for optimal nutrient retention in thermally processed foods (Barreiro-Mendez, 1979; Finnegan, 1984; Harris and Karmas, 1975; Teixeira et al., 1969b; 1975). More accurate optimization techniques have not been applied to foods because the complexity of the system and heat transfer processes make any analytical treatment difficult. The analytical approach for predicting nutrient retention during thermal processing requires a mathematical model of the process into which the temperature effects on the nutrients must be incorporated. Several components are required in structuring such a model: 1) the process must be defined, 2) the theory governing the process must be determined and verified, 3) the theory must be translated into mathematical equations, 4) the algorithm which incorporates these equations must be created and 5) the results must be checked to verify the validity of the model (Saguy and Karel, 1980).

Once a model has been formulated to describe the effects of the process on a quality factor such as a specific or group of nutrients, it can be used to simulate the process. These simulations are the basis of optimization procedures and in some systems it may be clear what an optimal situation is, whereas in

others the development of an objective function may be difficult. There are many parameters that need to be considered in the optimization of food sterilization processes, including process lethality, maximum operating temperature, color and flavor development or destruction, enzyme inactivation, and nutrient retention. The choices are usually related to the economic importance of the quality factors under consideration, however once determined, the objective function may be used to calculate an optimal process.

2.7.1 The Ball Methods (Finnegan Program)

This approach (Finnegan, 1984) was based on the temperature at the slowest heating region of a cylindrical container undergoing a sterilization process and makes use of the original Ball formula method (1923; 1928) and/or the modified Ball method (1923; 1928). Ball treated the heating curve as logarithmic and the cooling curve as first hyperbolic and then logarithmic. In the second model both the heating and the cooling curves were treated as a combination of first hyperbolic and then logarithmic sections. The third model differs from the second in the way the hyperbolic cooling equation is calculated, and in the way the cooling curve lag factor (j_c) is used. The slowest heating region is assumed to be the geometric center of the can for conduction heating foods, and is considered to be first heated, held for a specified period of time if necessary and cooled. The assumptions for the model include: 1) thermal diffusivity is isotroptic and independent of temperature, 2) the heat transfer coefficient at the container surface is infinite, and 3) the food is initially at a uniform temperature. A complete description of the mathematical aspects of the three models used in the Finnegan approach are presented in Appendix [1].

2.7.2 The Teixeira Program

This approach is based on a computer technique developed by Teixeira et al. (1969b) for determining the lethality and nutrient retention in foods heated in cylindrical containers. The procedure makes use of a finite difference simulation of two-dimensional transient heat conduction equation to produce a temperature distribution throughout the container at any time. The resultant temperature distribution is used to estimate the mass average concentration of a vulnerable factor in each volumetric element of a cylindrical can of solid food. By applying the rate equation for nutrient degradation to small volume elements, over short time intervals, the final residual nutrient concentration is obtained by numerically integrating the remaining nutrient amounts over the container volume and over process time. This technique does not require the use of any tables or consideration of lag factors or iso-j regions as in the method of Ball and Olson (1957). Optimization can be performed by calculating the locus of thermal processes having equivalent lethality for a given product which can be represented by combinations of retort temperatures and process times producing the same lethal effect. Teixeira et al. (1975) used a trial and error search technique to determine the best conditions for improving thiamine retention in thermally processed foods. By employing an optimization technique which varied the retort temperature with time using a sinusoidal, ramp and step temperature input function, they found that a ramp function resulted in optimum thiamine retention. However, since only a slight increase in retention was noted, they concluded that the results did not justify the use of time-varying retort temperatures. A complete printout of Teixeira's program is given in Appendix [2] as it is used for predicting nutrient retention and color development in our studies.

2.8 Summary

Basic kinetic questions still remain to be answered regarding the fundamental relation between the TDT and Arrhenius methods. The integration of kinetic fundamentals through to their subsequent application to thermal processes is a very complex task. Beyond further improvements to process predictions, changing circumstances in consumer preceptions and competition from other preservation techniques are making the consideration of quality factors a part of the canning process. Although this evolutionary process has been slow and daunting, the integration of food safety and quality retention will be a problem which future research will have to resolve.

III. MATERIALS AND METHODS

3.1 Introduction

In order to obtain kinetic data for the thermal destruction of quality factors such as vitamins and color, the vitamins ascorbic acid (AA) and thiamine (B1) were selected because they are heat-labile, water soluble, and their thermal destruction is considered to follow first order reaction kinetics. Color development by the Maillard reaction via the reducing sugar glucose, in conjunction with the amino acid glycine was chosen for its simplicity in color development. Kinetic characterization of these component reactions was required in order to evaluate thermal processing simulations.

3.2 Sample Preparation

All solutions were prepared in double distilled water (DDW) at concentrations considered to be representative of common food systems (Health and Welfare Canada, 1985) and their composition is listed below:

a) Ascorbic acid: 1.000 g of L-ascorbic acid dissolved in one L DDW.

b) Thiamine: 0.100 g thiamine hydrochloride dissolved in one L DDW.

c) Glucose and glycine: 10.00 g D-glucose and 8.00 g glycine dissolved in one L DDW.

d) Mixture: 1.000 g L-ascorbic acid, 0.100 g thiamine hydrochloride, 10.00 g D-glucose and 8.00 g glycine dissolved in one L DDW.

The samples were evaluated kinetically in ampoules and capillaries heated in temperature controlled oil baths and in cans subjected to thermal processing runs in retort in relation to the

component of interest. To differentiate as to which component is being considered in a particular analytical processing situation, the mixtures were designated as AA/MIX, B1/MIX and Color/MIX, while the individual components alone were designated as AA/DDW, B1/DDW and Color/DDW, representing ascorbic acid, thiamine and the color forming compounds, glucose and glycine respectively.

The majority of kinetic work was carried out at temperatures of 110, 120, 130, 140 and 150°C, in order to cover a temperature range including both conventional and ultra high temperature (UHT) thermal processes. For ascorbic acid, a subsequent set of experiments based on a factorial design were carried out using the ampoule technique at 115.6 and 121.1°C to further evaluate the influence of headspace volume and pH on the kinetics of ascorbic acid destruction. The associated variables were; a) fill volume: 4 and 8 mL, b) temperature: 115.6 and 121.1°C, and c) pH: unbuffered at pH 4.1, pH buffered at 4.1 and adjusted to pH 5.6 and buffered. Phosphate buffer was used in the buffered solutions and prepared from stock solutions of sodium phosphate monobasic, sodium phosphate dibasic and metaphosphoric acid.

3.3 Experimental Kinetics

The kinetics of thermal destruction of the ascorbic acid, thiamine and the mixture were studied at selected temperatures. Two techniques were employed to subject test samples to different temperature-time treatments; the ampoule technique and the capillary tube technique. In the ampoule technique, kinetic determinations were carried out with 4 mL aliquots of sample (at natural pH) placed in 10 mL glass ampoules (Canlab Canada, Montreal, PQ). The ampoules were sealed using an oxygen-natural gas flame and for each temperature run, 24 sample-sealed ampoules held in a wire basket were placed into a circulating oil bath maintained at the desired temperature. The samples were heated for various pre-determined time intervals, with the hot oil circulating vigorously and the bath controlled to within ± 0.2°C. Pairs of ampoules were removed from the bath at the end of each time interval and

immediately plunged into an ice water bath to stop any additional thermal degradation. All the heat treated samples plus two unheated controls were analyzed for their ascorbic acid and thiamine contents by HPLC.

For the capillary tube technique, 100 μL of solution was introduced into thin walled, glass capillary tubes, size 1.5-1.8 x 90 mm (Kimble Kimx-51; Canlab Canada, Montreal, PQ), using a micro-syringe. The tubes were then sealed in a gas flame and for each test run, 48 capillary tubes were held in a basket and placed into the circulating oil bath and heated to various pre-determined time intervals. Four tubes were removed from the bath at the end of each time interval, cooled with ice and analyzed. For color kinetics, only the ampoule technique was used.

3.4 HPLC Analyses

Ascorbic acid and thiamine were determined by high pressure liquid chromatography HPLC (Waters, 1986) using a Waters Liquid chromatograph (Chromatography Division, Millipore Corp., Milford, MA) consisting of a WISP Model 710B Intelligent Sample Processor, Model 510 HPLC Pump, Model 441 Absorbance Detector and a QA-1 Data Analysis System. The column was a μ-Bondapak C18 3.9 mm x 30 cm stainless steel column with a Guard-Pak Precolumn (end capped) with a mobile phase composed of methanol:water (25:75) containing 20% low UV PIC B6 (hexane sulfonic acid) running at a flow rate of 1 mL/min. The detector was set to 254 nm with 0.1 absorbance unit full scale and a standard sample injection of 15 μL was used. Uniform peaks were obtained for ascorbic acid and thiamine at retention times of 3.10 and 9.00 min respectively and the integrator was programmed to convert the area under the peak directly into mg/L based on pre-determined calibrations from serial dilutions.

3.5 Color Measurement

The color which developed in the samples was measured using a Minolta Chroma Meter Model CT-210 (Minolta Corp., Ramsey, NJ), a tristimulus colorimeter for measuring the color of non-turbid fluids. The CT-210 features a pulsed xenon arc lamp to provide illumination while two diffuser plates and a mixing box ensure that the light passes through the sample liquid in a uniform and completely diffused manner. The Chroma Meter makes use of six high-sensitivity silicon photocells, filtered to match the CIE Standard Observer Response, with a double-beam feedback system to measure both incident and transmitted light. The output from the CT-210 could be programmed to give color coordinates in any one of the following systems: Y, x, y; L, a^*, b^*; L^*, C^*, H^o. Color difference can also be measured in all three systems, including absolute colorimetric densities and density differences. The results can easily be converted from one system to another by using built in conversion procedures.

CIE parameters, Y%, x and y were measured using a 2 mm cell at room temperature after calibrating the colorimeter to Illuminant C with Y = 100, x = 0.3101 and y = 0.3162. The CIE system is based on three parameters, X, Y, and Z, known as tristimulus values (Francis and Clydesdale, 1975) and when expressed as fractions of their total, they are known as chromaticity coordinates, x, y and z. Thus, x = X/(X+Y+Z); y = Y/(X+Y+Z) and z = Z/(X+Y+Z). Since the sum of these three is unity, only two need be specified. Generally, x and y are measured and these values will represent color in terms of hue and chroma on the chromaticity diagram (Francis and Clydesdale, 1975). In addition to these two co-ordinates, a lightness or luminosity factor, Y or Y% expresses the degree of lightness or darkness of a color. The changes in Y%, x and y were employed to monitor color formation in the test samples.

3.6 Data Collection and Analyses

Retention data were expressed as percentage by dividing the concentration (or measured color) obtained after heat treatments by the concentration of the control solutions. The retention (%) data at a given temperature were analyzed using a first order kinetic model by linear regression of the natural logarithm of retention vs time. The slope or reaction rate constant, k or the decimal reduction time, D are related in the following manner:

$$k = - \text{slope coefficient} \quad [11]$$

$$D = - 2.303 / (\text{slope coefficient}) \quad [12]$$

The temperature sensitivity of the reaction rate constants were analyzed by both the Arrhenius and the TDT techniques. In the Arrhenius technique, ln (k) values were regressed against the reciprocal of absolute temperature ($^{o}K^{-1}$) and the activation energy, E_a, was obtained from the regression slope:

$$E_a = - (\text{slope coefficient}) \times R \quad [13]$$

where R is the gas constant. In the TDT concept, log (D) values were regressed against temperature (^{o}C) and the z value was obtained from the regression slope:

$$z = -1 / (\text{slope coefficient}) \quad [14]$$

The R^2 values from the regression equations were used to compare the two kinetic approaches in describing the degradation behavior of ascorbic acid, thiamine and Maillard color formation.

3.7 Kinetic Conversions (Arrhenius and TDT)

As previously outlined in the literature review, the TDT method and Arrhenius concept contradict each other since the kinetic parameters are proportional to temperature in the TDT method (equation [8]), and proportional to its reciprocal in the Arrhenius (equation [6]) technique. Both methods have their merits, however, the application of the TDT method has mainly been limited to process calculations.

In this study, initial analyses relating E_a to z were carried out using Lund's equation [9]) and a regression analysis was subsequently used. E_a values were first obtained at a constant z, and in order to do this, D values at ten different temperatures within a specified temperature range were initially computed using equation [4] with an arbitrarily chosen reference D value of 1 min at $120^{o}C$. The corresponding k values were then calculated using equation [3], and the logarithms of the resulting k values were regressed linearly against 1/T to obtain the respective E_a value from the regression slope. Conversely, z values were obtained from known E_a values and a reference k value. Several k values were obtained using equation [8] to correspond to different temperatures, followed by their conversion into D values using equation [3], and then log-transformed and regressed linearly against T. The negative reciprocal slopes of the regression lines gave the corresponding z values. A z value of 10 centigrade degrees (C^{o}) and a theoretical E_a of 318 kJ/mole (at z = 10 C^{o} and reference temperature = $135^{o}C$) were chosen as base values for comparing the influence of temperature and temperature ranges. When testing the effect of a reference temperature, a small temperature range of 5 C^{o} was employed, while for studying

wider ranges a reference temperature of 135°C was used. The variation in E_a was then evaluated at a constant z of 10 C° and z was studied at an E_a of 318 kJ/mole.

To determine the accuracy of conversion from E_a to z, equation [9] was rearranged as follows, in order to obtain the factor, $U_{EQ[9]}$:

$$U_{EQ[9]} = E_a \; z / (2.303 \; R \; T_1 \; T_2) \qquad [15]$$

Using the factor $U_{EQ[9]}$ a perfect conversion of E_a to z, should result in a value of 1.0 and the extent of its deviation from unity was used as a criterion for assessing the accuracy of equation [9].

3.8 Thermal Processing

The thermal destruction of both selected vitamins (ascorbic acid and thiamine) and of color forming compounds (glucose and glycine) were evaluated in both conduction heating and convection heating systems to determine the effect of various temperature-time combinations on nutrient retention and color formation. All experiments were carried out using 211 x 400 can in a Dixie RDTI-3 pilot scale vertical still steam retort (Dixie Canner Equipment Co., Athens, Georgia) located in the Department of Food Science pilot plant at Macdonald College, Montreal, Quebec. Its dimensions were 1.22m x 0.61m i.d capable of operating at up to 379 kPa (absolute), 40 Psig, pressure. Process conditions were selected to provide data suitable for the verification of the computer models over a wide range of processes.

3.8.1 Conduction Heating

These experiments were conducted using simulated conduction heating model composed of acid-washed celite (diatomaceous earth, approximately 95% SiO_2; Sigma Chemical Co., St. Louis, MO) in which the quality factor solutions were incorporated. The concentration of each component or quality factor was doubled to account for the additional 180 mL which had to be used to wash the components out of the celite after the process. Each 211 x 400 can was carefully packed in duplicate with 85g celite and soaked with the 180 mL of test solution, leaving a headspace of 25 mm. For post-process analyses, triplicate samples were recovered from each can by vacuum filtration of the contents at 85 kPa for 10 min and after processing. Triplicate control cans were also prepared for each run and treated identically, with the exceptions of being processed. All the recovered samples were placed in 20 mL glass containers and kept in a refrigerator at $4^{o}C$ and analyzed for nutrients within 24 hours.

3.8.1.1 Processing Conditions

Processing conditions (Table 1) were selected to study the influence of process time on the retention of ascorbic acid, thiamine and color formation at different temperatures. Equivalent lethality processes were initially calculated using a computer program based on Ball's formula method. The heat penetration parameters, f_h and j_h, were evaluated experimentally for the conduction heating model packed in cans and processed at various temperatures. A process lethality of 3 min was chosen for experiments 1-4 and 8 min for numbers 5-8 for the equivalent lethality work. Additional runs, some of which were not typical of commercial practice were also carried out to assess the effect of more severe process conditions on the components and to compare to the computer model predictions.

Table 1. Experimental conditions used for thermal processing of cans filled with celite.

Experiment number	Retort Temp. (^{o}C)	Process Time (min)
1	110.0	84.0
2	115.6	58.5
3	121.1	47.5
4	126.7	45.0
5	110.0	132.0
6	115.6	75.0
7	121.1	57.0
8	126.7	49.0
9	121.1	81.5
10	126.7	69.5
11	121.1	31.0
12	126.7	29.5
13	121.1	129.0
14	126.7	89.5
15	126.7	109.5
16	126.7	129.5

3.8.1.2 Heat Penetration Parameters

For the conduction work, precalibrated copper-constantan thermocouples (O. F. Ecklund, Cape Coral, Florida.) were placed at the geometric center of the test cans, assuming that heat would flow uniformly from all sides toward this center point. All thermocouples were precalibrated against a certified mercury-in-glass thermometer at the ice point and the maximum retort operating temperature, with appropriate corrections subsequently made to the temperature data gathered. For every process run, 14 precalibrated thermocouples were positioned inside the retort with one thermocouple in each of the 8 test cans. The 6 remaining thermocouples were placed at various locations within retort, two along the edge at the top and bottom, in the center of the basket and at four points around the periphery of the basket. These thermocouples were connected to a CR7 data logger (Campbell Scientific Inc., Logan, Utah) to collect heat penetration data. The temperature-time data from the data logger were

recorded on magnetic tape at 30 second intervals for conduction heating and every 15 seconds for convection heating. In order to predict heat transfer rates for the conduction system, the thermal diffusivity was calculated using the following relationship (Ball and Olson, 1957):

$$\alpha = 0.398/[f_h(1/a^2+0.427/L^2)] \qquad [16]$$

Where 2a and 2L are the diameter and height of the can respectively. Based on the thermal diffusivity determined, the heat transfer rates could be accurately predicted. Temperature differences between the heating medium (steam) and the centerpoint temperature of the cans were plotted on a logarithmic ordinate against time on a linear abscissa. The slopes of heating curves (f_h) were evaluated by computing a least squares fit to linear portions of semi-logarithmic heating curves. In a similar manner, the slopes of the cooling curves (f_c) were determined from the semi-logarithmic cooling curves (Ball, 1923). The heating curve lag factors (j_h) and the cooling lag factors (j_c) were computed at 42% effectiveness (Ball, 1923) for the come-up time.

3.8.2 Centerpoint Nutrient Degradation

A method was devised to make measurements at the center of the conduction can via the placement of a small differential scanning calorimetry (DSC) capsule at the center of the can within the celite medium. This technique was used to facilitate the recovery of test solution from a specific locale (centerpoint in this case), which, because of its small volume could be assumed to have only undergone a thermal process associated with the centerpoint. A small volume (75 μL) of the test solution was introduced into a circular 7.7 mm diameter x 2.9 mm height stainless steel sample pan (Perkin Elmer Corp., Norwalk, CT), crimp-sealed with a stainless steel cap and on o - ring, and carefully positioned at

the geometric center of a conduction heating can. Three temperature-time combinations were employed for these special centerpoint thermal processing runs: 115.6°C for 80 min; 121.1°C for 50 min and 126.7°C for 30 min. Eight cans were processed simultaneously in the retort, four of which contained the capsule and the remaining cans were controls containing thermocouples, but no capsules, to determine the heat penetration data for determining f_h, j_h, f_c and j_c of the conduction system. The come-up time of the retort was 10 min.

3.8.2.1 Computer Predictions

The kinetic parameters for ascorbic acid and thiamine degradation (D and z values), the experimentally evaluated heat penetration parameters (f_h, j_h, f_c and j_c), and the corresponding process conditions (retort temperature, initial temperature, cooling water temperature, process time) were used in computer models. These models were based on (a) the Ball original formula method (Ball, 1923); (b) the modified Ball formula method which adopts an initial hyperbolic temperature response followed by a logarithmic response at the beginning of both heating and cooling periods (Finnegan, 1984); and (c) a finite difference computer program (Teixeira et al., 1969b) using a 10 x 10 spatial matrix and a 0.125 min time interval to predict the retention of the above nutrients at the can center. The retention values predicted for each process were subsequently compared to experimental retention values.

3.8.3 Convection Heating

Experiments were carried to compute quality factor degradation kinetic parameters using heat penetration data for convection versions of the quality factor solutions (i.e., no celite present). These experiments followed a procedure similar to the ampoule method, i.e., a temperature-time series, except that separate retort runs were required for additional times at any one temperature. Heat penetration

data were recorded and used as a basis for calculating predicted retentions based on the kinetic parameters determined for the ampoule system and compared with the actual recoveries. Each can contained 250 mL, leaving a residual headspace of 25 mm and was processed according to the schedule presented in Table 2.

Table 2. Experimental conditions used for thermal processing of cans filled with convection heating samples.

Experiment number	Retort Temp. (^{o}C)	Process Time (min)
1	110.0	40.0
2	115.6	13.0
3	121.1	9.0
4	126.7	7.0
5	110.0	320.0
6	115.6	280.0
7	121.1	29.0
8	126.7	13.0
9	121.1	60.0
10	126.7	50.0
11	121.1	120.0
12	126.7	80.0
13	121.1	210.0
14	126.7	150.0
15	121.1	300.0
16	126.7	240.0

At the end of the heating cycle, cans were cooled with water until the centerpoint temperature of the cans was approximately 20^{o}C. For both vitamin and color analyses, triplicate samples were taken and analyzed for nutrient content within 24 hours.

3.8.3.1 Temperature Measurement

There are two practical ways of measuring the temperature inside cans in convection heated foods, calorimeteric techniques capable of measuring the bulk temperature inside the can (Jowitt and Mynott, 1974) and thermocouples, the more common method (Pflug, 1975). The single point thermocouple method was chosen for this work because bulk temperature measurements are known to lead to underprocessing when sterilization times are calculated from heat penetration data based on this measurement (Jowitt and Mynott, 1974). For natural convection heating, the bulk flow destroys any symmetry associated with product heating found in conduction heating foods so that the slowest heating zone represents the first 10 to 15% of the container height above the bottom (Pflug, 1975). Hence, the thermocouple was placed 25.4 mm from the bottom of the can (slowest heating point) assuming that heat would flow by natural convection caused by differences in fluid density.

3.9 Verification of Quality Factors

3.9.1 The Original Ball Method (Finnegan Program)

This model was based directly on equations derived by Ball (1923; 1928) and Ball and Olson (1957), treating the heating curve as being logarithmic (Appendix [1]). For the cooling curve, Ball initially used a hyperbolic and then a logarithmic model, assuming a fixed value of 1.41 for both the heating and cooling curve lag factors. According to Finnegan (1984), the rationale of Ball's original approach was that if the slowest heating region of the can reached a specified temperature, the rest of the can must have attained at least the same temperature (Ball, 1923) and any extra lethality caused by the higher outer temperatures could be considered a safety factor. To facilitate process calculations, the total processing time was considered to be subdivided into increments and the calculations carried out for each increment with the lethal rate for each time increment calculated by:

$$\text{lethal rate} = (1/TDT) = (1/F^{z}_{Tref})\ 10^{(T_{avg}-T_{ref})/z} \quad [17]$$

where:

TDT = is the thermal death time

F^{z}_{Tref} = is the F value of a specific microorganism/nutrient at a reference temperature

T_{avg} = is the mathematical average of the can temperatures at the start and end of the time increment

T_{ref} = is the reference temperature (usually 121.1°C)

z = is the z value of the microorganism

If the lethal rate is integrated over the processing period to determine the lethality imparted by the heating regimen, the accuracy of the lethality obtained increases with the number of time increments and the resulting lethality imparted by the process can be approximated by:

$$\text{Lethality} = \sum_{n=1}^{n\ \text{time}\ -\ 1} \text{lethal rate} \times \text{time increment} \quad [18]$$

The fraction of nutrient retained in the food after processing was determined using a probabilistic approach. The amount of nutrient left at the end of a time increment was compared to that present at the start of processing and the nutrient destruction rate (NDR) over each time increment calculated by:

$$NDR = (1/F_{nutr})\ 10^{(T_{avg}-T_{ref})/z_{nutr}} \quad [19]$$

where F_{nutr} and z_{nutr} are the destruction characteristics of the nutrient. This destruction rate was used to calculate the lethality imparted to the nutrient at the end of each time increment:

$$\text{Lethality}_{nutr} = \sum_{n=1}^{n\ time\ -\ 1} \text{lethal rate} \times \text{time increment} \qquad [20]$$

This Lethality_{nutr} value was used to determine how much of the nutrient remained in absolute terms at the end of each time increment. When the lethality equals 1.0, a nutrient reduction factor of 10^{12} has been attained and the nutrient retained at the end of each time increment can be predicted by:

$$X_{nutot} = X_{nutst}\ 10^{(12.0 \times \text{Lethality}_{nutr})} \qquad [21]$$

where X_{nutot} is the amount of nutrient remaining at the end of each time increment and X_{nutst} is the amount of nutrient that was present at the start of the time increment. To determine the fraction of nutrient retained at the end of the time increment compared to the original amount (1.0 g) present in the food, the nutrient fraction is given by:

$$FR_{nutr} = X_{nutot} / 1.0 \qquad [22]$$

where FR_{nutr} is the fraction of nutrient retained at the end of the time increment. At the end of the last time increment, this FR_{nutr} represents the overall fraction of nutrient retained after processing (Finnegan, 1984).

The input information required for this microcomputer model included the following: initial product temperature, operating temperature of the retort, temperature of the cooling water, slope of the heating curve (f_h), slope of the cooling curve (f_c), total processing time, the time when cooling started, the number of time increments, and the F and z values of the components of concern. These input data were used to calculate the temperature-time profile at the center point of the can, and then used to calculate the lethality and nutrient retention values with the output presented in either graphical or tabular forms.

3.9.2 The Modified Ball Method (Finnegan Program)

Finnegan considered both the heating and the cooling curves as a combination of a hyperbolic portion followed by a logarithmic section and modified the way the cooling curve lag factor (j_c) value was treated, Appendix [1]. Rather than being assumed to be 1.41, the j_c value could be chosen by the user, however, other than this change, the equations and input data required are similar to the original method.

3.9.3 The Teixeira Program

Teixeira et al. (1969b) developed a finite difference computer technique for the determination of lethality and nutrient retention in conduction-heated foods in cylindrical containers, for which thermal diffusivity was known, as shown in Appendix [2]. By means of this technique, an optimum combination of retort temperature and process time can be found to maximize component retention. This computer program consists of: (1) a basic program to integrate the general rate equation using finite volume elements, (2) a temperature distribution program to obtain the temperature distribution throughout a

container at any instant in time using a finite difference technique, and (3) the programs for steps (1) and (2) which were combined to obtain an integrated program that would determine the number of survivors or the percent vitamin retention associated with any thermal process having a constant retort temperature. Teixeira determined the thermal diffusivity (α) from an experimentally derived, f_h, which can be calculated using equation [16].

Teixeira's method (Teixeira et al., 1969b) makes use of equation [1], describing any first order reaction at a constant temperature. After rearranging the terms in equation [1] and integrating over a small time interval, Δt, equation [1] becomes:

$$c^{(t+\Delta t)} = c^{(t)} \exp(-\Delta t/D) \qquad [23]$$

where $c^{(t+\Delta t)}$ and $c^{(t)}$ represent the concentration at time $(t+\Delta t)$ and at time (t), respectively. Since both k and D values are temperature-dependent, they were assumed to be given by:

$$-dD/dT = (1/z)\, D \qquad [24]$$

where T is temperature and z is the temperature difference affecting a ten-fold change in the D value. The following expression for D resulted from re-arrangement and integration of terms over temperature:

$$D = Dr \exp((To-T)/z) \qquad [25]$$

where Dr is the death rate at To, which is usually taken to be 250°F (121.1°C). Since D varies with time, a different value should be used at the beginning of each time interval in equation [23], however, it was assumed to remain constant over the interval. In any actual conduction heating process, the temperature within the container is neither uniform nor steady, but is a function of both time and position. Equations [23] and [25] indicate that the concentration of component retention is both temperature and time dependent, and therefore can be only calculated for a specific point in the container at a particular time. This point was taken as the center of a very small element relative to the entire container. The temperature and subsequent concentration at that point were considered representative of these values throughout the volume element surrounding it and is the basis of the finite difference method applied by Teixeira. Using this concept, the cylindrical container was divided into volume elements consisting of concentric rings having rectangular cross sections. Teixeira used a high-speed digital computer (CDC 3600) to perform iterative calculations and the lethality calculation proceeds in the following basic sequence. For the first time interval, an average temperature over the time interval at the center of each element was supplied and this was used to calculate the death rate over the given time interval for each element using equation [25]. The concentration at the end of that time interval was calculated by equation [23]. This new concentration became the initial concentration for the next time interval, and the procedure was repeated. At the completion of this iterative process the resulting concentrations were multiplied by the volume of their respective elements to give the number of survivors in each element. The total number of survivors in the entire container was obtained by summing the values for each element.

The temperature distribution throughout the container was based on the general differential equation for two-dimensional, unsteady heat conduction in a finite cylinder, and was given as:

$$\delta^2 T/\delta r^2 + (1/r)\ \delta T/\delta r + \delta^2 T/\delta y^2 = (1/\alpha)(\delta T/\delta t) \qquad [26]$$

where:

T = is the temperature at any point at any time

r = is radial distance from center line

y = is the vertical distance from mid-plane

α = thermal diffusivity of the material

t = time

Each term in equation [26] was written in finite difference form and rearranged to obtain an expression for the temperature at a given point after a given time interval, in terms of the temperatures at surrounding points at the beginning of the given time interval:

$$T_{(i,j)}^{(t+\Delta t)} = T_{(i,j)}^{(t)} + \left(\alpha \Delta t / \Delta r^2\right)\{T_{(i-1,j)} - 2T_{(i,j)} + T_{(i+1,j)}\}^{(t)} + \left(\alpha \Delta t / 2r \Delta r\right)\{T_{(i-1,j)} - T_{(i+1,j)}\}^{(t)} + \left(\alpha \Delta t / \Delta y^2\right)\{T_{(i,j-1)} - 2T_{(i,j)} + T_{(i,j+1)}\}^{(t)} \quad [27]$$

In equation [27], i and j are subscripts denoting the sequence of radial and vertical volume elements, respectively. By using equation [27], the temperature distribution history can be obtained in the following manner: At the beginning of the process time, all interior points were set to the initial product temperature, while the points on the surface were set at retort temperature. In this way, a complete set of initial temperatures was known for the first time interval, and equation [27] was used to obtain the temperatures at every point after the time interval, Δt. This new temperature distribution was taken to replace the initial one and the procedure was repeated to find the temperature distribution after another time interval. The temperature distribution during the cooling portion of the thermal process was determined by changing the temperatures of the surface nodes at the end of process time and continuing with the iterative process.

The input data required for this model consisted of: the initial spore load or vitamin content, the radius and height of the container, the total process time (time from steam on to steam off including correction for retort come-up time), the initial product temperature, the retort temperature, the mean cooling water temperature, the terminal temperature (usually slightly lower than initial food temperature), the reference temperature (usually 121.1^{o}C (250^{o}F)), the reciprocal slope of the center point heating curve, the number of radial and vertical increments, decimal reduction time of the target microorganism/nutrient at reference temperature, and the z value of the target microorganism/nutrient. All the input data were given in British units because of the conversion factors used in the program. The output of this program are the number of survivors or component retention at the end of the process, the total time for the process including cooling, and the final temperature at the center of the container. The temperature distribution throughout the container and the nutrient retention at any instant in time could also be obtained from the program.

3.10 Optimization of Quality Factors

To determine the optimal processing conditions (i.e. temperature-time combinations), an optimization technique should be employed. There are many factors to be considered in the optimization of sterilization processes, including lethality, maximum practical operating temperature, minimum destruction of nutrients and minimum changes in organoleptic properties. An optimum process can be found for a number of quality factors by using an objective function which relates the importance of each factor. With the availability of computerized techniques, it is possible to define a particular thermal process with a constant retort temperature which maximizes nutrient retention while maintaining the required lethality constant.

For any set of lethality data, there are a number of processes that will produce a set lethality, each defined by a process time-temperature combination. The approach used in this study to select the optimal processing conditions for the conduction model relied upon the data for which the heat penetration had been determined experimentally. The process time required for a constant lethality corresponding to process temperatures of 110 to 144^{o}C, determined using temperature intervals of 2^{o}C were obtained using Stumbo's centerpoint model and an "equal lethality" curve was obtained by plotting these temperature-time combinations. Any point on such a curve represents a thermal process that would produce the prescribed lethality and a specified amount of each nutrient was associated with each of these points. The nutrient retention for a variety of quality factors, differing in their F and z and associated with each process used to establish the equal lethality curve were calculated using Teixeira's program were calculated. An optimization graph was prepared by plotting individual nutrient retention data versus process temperature.

3.10.1 The Objective Function

An objective function is a relationship that associates the importance of each factor based on specific criteria, such as a distinctive color and/or flavor that should be developed, or the amount of a particular component that should be maintained or destroyed. This objective function might consist of the sum of the retention of various components, each multiplied by a weight factor to indicate the relative significance given to it by the quality factor requirements. The resulting optimal temperature-time combination determined by the optimization technique depends not only on the kinetic parameters (F and z values) of each of the components considered, but also on arbitrarily chosen weight factors, with the weight factor depending on economic and/or nutritional considerations.

In this study, the objective function chosen can be used to assess any number of quality factors. For example, nutrient retention combined with their respective weight factors in a normalized dot product-arrangement will yield the following objective function (OF):

$$OF = \sum_{n=1}^{n=n} (Wn \,.\, Rn) / n \qquad [28]$$

where Rn is the nutrient retention (%), Wn is the corresponding weight factor and n is an integer representing the number of quality factors (not be equal to zero and/or infinity). Rn can range from 0 (*no nutrient retained*) to 100. Wn can vary from -1 to 1, where higher weight factors indicate that a correspondingly greater importance is attached to that particular nutrient. A negative weight factor indicates an undesirable component that need to be minimized. Accordingly, the value of the objective function can range from 0 (complete nutrient destruction) to 100. The process which yields the highest value for the objective function is the one which will result in maximal nutrient retention and is therefore considered to be the optimal process

3.11 Summary

The analytical methods used were chosen for their reproducibility, accuracy and speed. The capillary, ampoule and conventional scale process were studied to compare their efficacy for determining the kinetic process parameters. In terms of the computer models, established centerpoint and mass average methods were tested to determine which of the two could better predict the process and if workable, whether optimization could also be a viable addition to the computational procedures.

IV. RESULTS AND DISCUSSION

4.1 Introduction

Quality factors as they might be affected by thermal processing were represented by ascorbic acid, thiamine and a mixture of glucose and glycine, and were studied in isolation and as mixtures, the latter representing a model food system. Through the analysis of the data and a re-consideration of the fundamental relationship between the TDT and the Arrhenius approaches, a new concept was developed as to how the constants E_a and z are related to each other and how they might be interpreted. These concepts are developed in relation to the results obtained for ascorbic acid and are used subsequently to compare the kinetic results.

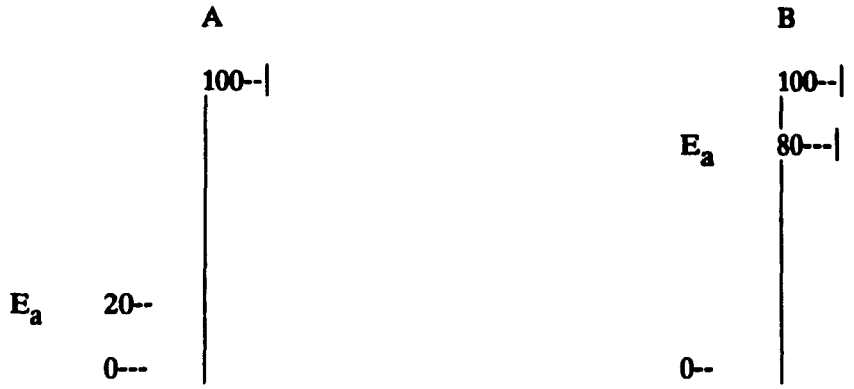
4.2 TDT vs Arrhenius Approaches

An initial analysis of the kinetic data and the fundamentally contradictory concepts associated with the TDT and Arrhenius approaches led to a preliminary conceptual approach relating the TDT and Arrhenius parameters (z and E_a). Although these two measures are both supposed to be "temperature independent", they are difficult to relate to each other because E_a is estimated from a plot of ln (k) vs the reciprocal of temperature, while z is estimated from log (D) vs temperature. E_a is a thermodynamic constant considered to be the energy barrier to be overcome for a reaction to proceed, however it bears no direct relationship to the rate at which the reaction takes place. Hence two reactions can have the same E_a, but can take substantially different lengths of time to go to completion. On the other hand, z is considered a measure of the resistance of a microorganism to a temperature change, with organisms having a higher z being considered more resistant to destruction for an equivalent increase in temperature. The z value is a function of a rate difference derived from two temperatures rather than defined temperature values as shown in equation [5] reproduced below:

$$\log (k_2/k_1) = (T_2-T_1)/z \qquad [5]$$

In this equation, if z increases, it implies that the differences in the rates of reaction have decreased without knowing their actual magnitude. Mathematically then, E_a and z are inversely related to each other (Lund, 1975) on the basis of a reference temperature, but are difficult to reconcile in terms of physical meaning.

It is important to assign some meaning to z beyond the concept of "thermal resistance", since a high value of z conventional has implied that it is more difficult to reduce the concentration of an organism or nutrient, while a low "activation energy" implies that it is relatively easy to initiate the destruction of an nutrient/organism, and these are contradictory concepts. One way of rationalizing z is to consider it to resemble acceleration, independent of temperature per se, but affected by temperature differences or the energy available to drive the reaction forward at a greater speed, but still tied to the activation energy required to initiate a reaction. Although not interpreted in this way, this sort of relation has been alluded to indirectly by Lund (1975) who conceived a purely mathematical relation (Equation [9]) between E_a and z based on the tenous assumption that over a small temperature range T and 1/T are proportional. Beyond this purely mathematical relation, published data also shows this inverse relation, although not necessarily in harmony with Lund's conversion. If one views activation energy as a barrier to the initiation of the reaction and z as a value related to the acceleration of a reaction, a low z indicates that a small increase in temperature will speed up the reaction tenfold, while a high z indicates a larger temperature difference is required to obtain a similar degree of change. Based on both published data and the approximations derived for converting z into E_a, high E_a values tend to produce low z values and vice versa. This implies that the acceleration of a reaction is more difficult in circumstances where E_a is low than when it is high. If one considers a constant input of energy (100 units) into two different reaction systems, A and B,



each of which have different E_a values, but the same rate of reaction (k or D), the concept can be rationalized. In system A, 20 units of energy are used to activate the reaction, and 80 units of kinetic energy are left to drive the reaction forward. If these units are temperature differences (z) and all other factors constant, it would take 160 units of energy to double the rate of the reaction in system A. In system B, 80 units of energy are required to activate the reaction and only 20 units of energy are available to drive the reaction forward. The rate of this reaction can be doubled by increasing the energy input by only 20 units. In these circumstances, reactions with a low activation energy presented with a constant energy input (100 units), require larger relative increases in temperature differences to double their reaction rate, while those with a higher activation energy require a smaller temperature differential to double their reaction rate. This implies that z, which is a temperature differential, could be considered to behave like an acceleration factor for the reaction over a fixed temperature range (kinetic energy range), which has to be lower for high E_a reactions and higher for low E_a reactions. Beyond the standard interpretations of E_a and z, this conceptual view of their relationship was used and developed further in the course of interpreting the data obtained for the quality factors studied.

4.3 Kinetics of Ascorbic Acid Degradation

4.3.1 Ascorbic Acid in Distilled Water (AA/DDW)

The destruction of ascorbic acid in aqueous solutions was studied in ampoule and capillary systems over a temperature range of 110 to 150°C. The capillary technique was included to expand the

usefulness of the data base so that the information gathered could be used for UHT systems if needed, as they reduce the heating lag period in relation to the shorter heating times associated with the higher temperatures. Based on the plots presented in Figures 2 and 3, the loss of ascorbic acid occurs in a first-order fashion for both the ampoule and the capillary techniques. Detailed regression analysis data for the ampoule and capillary systems is presented in Table 3, with the mean R^2 of all the data being 0.982 and the lowest value being 0.946, with the ampoule technique giving slightly better correlation coefficients overall. The reaction rate constant (k) and its inverse, the decimal reduction time (D) were determined from the regression slope coefficients and are also presented in Table 3. The basic Arrhenius and TDT parameters (E_a and z) for ascorbic acid are presenting in Table 4, including k_o and D_o reference (121.1°C) values. Some difference in the values of D_o and k_o for the ampoule and capillary systems appear to indicate that the two behave somewhat differently, with the D_o for the ampoule being 455 vs 402 minutes for the capillary, indicating that ascorbic acid is being lost more rapidly in the capillary system at any one temperature as indicated in Table 3. In practical terms, the capillary system allows the destruction of ascorbic acid at a rate of 1.13 times faster than the ampoules based on reference D_o values. The plots used to determine the activation energy (E_a) and thermal resistance (z) of ascorbic acid for the ampoule method and capillary methods are presented in Figures 4 and 5. The respective values for E_a and z were 78.6 and 63.4 kJ/mole, and 39.4 and 48.8 C^o for the ampoule and capillary methods. In terms of the conventional interpretation of E_a and z, it would be difficult to reach a general conclusion about the overall reaction based on these two parameters. If one were to attempt to make a judgment about rates, it would have to be based on k_o, a reference reaction rate constant, which indicates that ascorbic acid destruction is more rapid at 121.1°C in the capillary system.

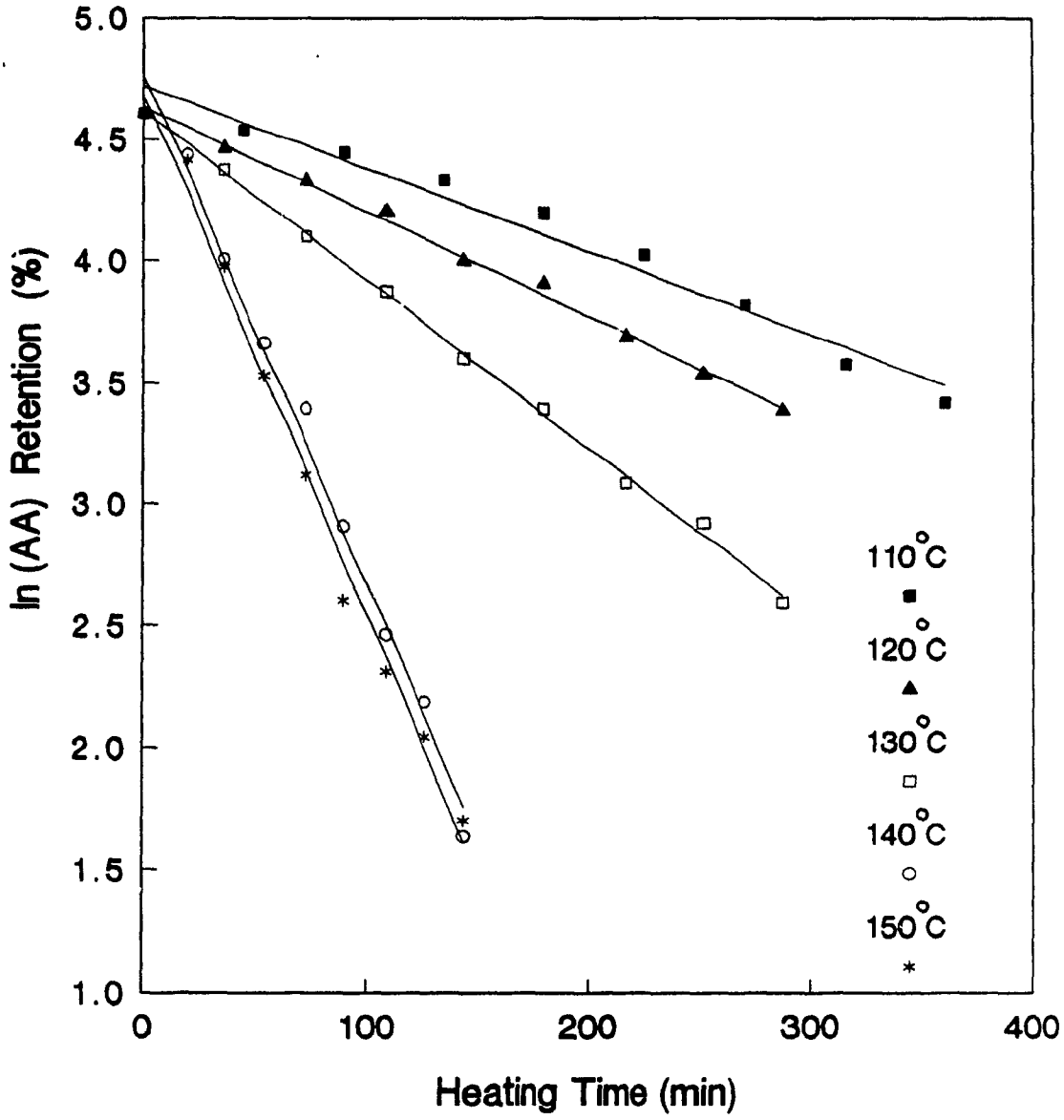


Figure 2. Retention of ascorbic acid (AA/DDW) following various temperature-time treatments using the ampoule heating technique.

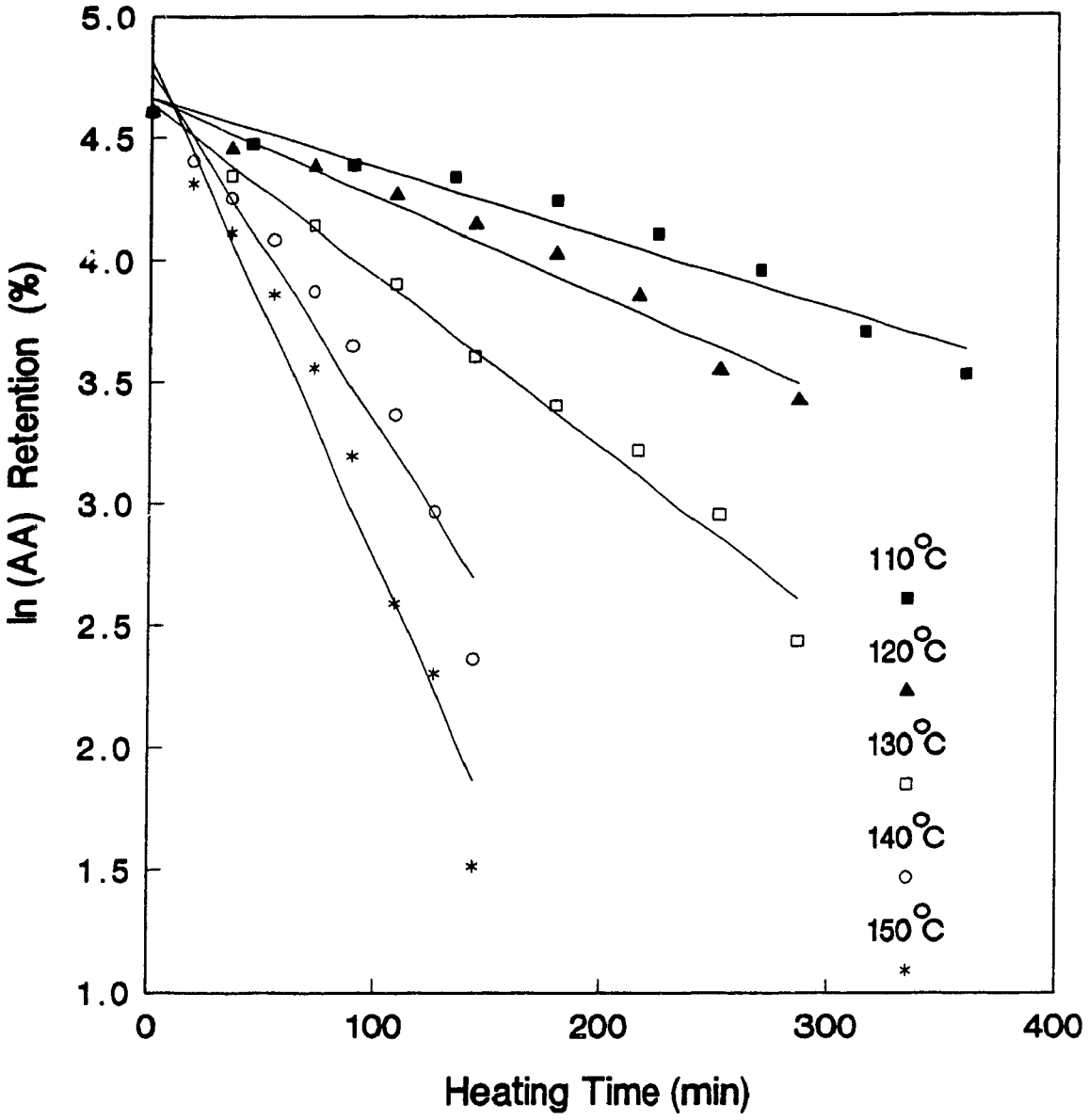


Figure 3. Retention of ascorbic acid (AA/DDW) following various temperature-time treatments using the capillary heating technique.

Table 3. Kinetic parameters for ascorbic acid (AA) degradation.

Sample Description	Method	Temperature (^{0}C)	R^2	k value (min^{-1})	D value (min)
AA/DDW (4.05 NB*)	Ampoule (4 mL)	110	0.9699	0.0029	797.6
		120	0.9966	0.0044	519.4
		130	0.9984	0.0069	333.4
		140	0.9923	0.0201	114.7
		150	0.9978	0.0251	91.7
	Capillary	110	0.9784	0.0037	623.1
		120	0.9806	0.0052	441.9
		130	0.9845	0.0077	298.0
		140	0.9458	0.0144	160.2
		150	0.9719	0.0236	97.7
AA/MIX (5.60 NB*)	Ampoule (4 mL)	110	0.9968	0.0098	235.1
		120	0.9974	0.0110	209.5
		130	0.9872	0.0118	195.5
		140	0.9941	0.0140	164.6
		150	0.9963	0.0149	154.4
	Capillary	110	0.9942	0.0088	261.7
		120	0.9956	0.0106	217.3
		130	0.9704	0.0126	183.0
		140	0.9960	0.0150	153.4
		150	0.9946	0.0158	146.0
AA/DDW (4.05 NB*)	Ampoule (4 mL)	115.6	0.9785	0.0028	825.4
		121.1	0.9931	0.0040	571.6
AA/DDW (4.05 WB**)	Ampoule (4 mL)	115.6	0.9824	0.0026	889.3
		121.1	0.9944	0.0038	599.6
AA/DDW (5.60 WB**)	Ampoule (4 mL)	115.6	0.9845	0.0027	846.1
		121.1	0.9849	0.0039	591.2
AA/DDW (4.05 NB*)	Ampoule (8 mL)	115.6	0.9766	0.0026	879.7
		121.1	0.9874	0.0034	685.7
AA/DDW (4.05 WB**)	Ampoule (8 mL)	115.6	0.9696	0.0023	993.9
		121.1	0.9895	0.0032	723.4
AA/DDW (5.60 WB**)	Ampoule (8 mL)	115.6	0.9640	0.0027	863.8
		121.1	0.9942	0.0034	680.1

NB* = sample without buffer. WB** = sample with buffer.

Table 4. Arrhenius and thermal death time (TDT) parameters for ascorbic acid.

Sample Description	Method	Temperature Range (^{0}C)	E_a (kJ/mole)	R^2	z (C^0)	R^2	D_0 (min)	k_0 (min^{-1})
AA/DDW (4.05 NB*)	Ampoule (4 mL)	110-150	78.6	0.96	39.4	0.96	455.0	0.0052
	Capillary	110-150	63.4	0.98	48.8	0.99	402.0	0.0058
AA/MIX (5.60 NB*)	Ampoule (4 mL)	110-150	14.6	0.98	212.8	0.98	208.7	0.0111
	Capillary	110-150	20.5	0.98	151.8	0.97	215.0	0.0108
AA/DDW (4.05 NB*)	Ampoule (4 mL)	115.6-121.1	85.1	na	34.5	na	571.6	0.0040
(4.05 WB**)	Ampoule (4 mL)	115.6-121.1	91.3	na	32.1	na	599.6	0.0038
(5.60 WB**)	Ampoule (4 mL)	115.6-121.1	83.0	na	35.3	na	591.2	0.0039
AA/DDW (4.05 NB*)	Ampoule (8 mL)	115.6-121.1	57.7	na	50.8	na	685.7	0.0034
(4.05 WB**)	Ampoule (8 mL)	115.6-121.1	73.6	na	39.9	na	723.4	0.0032
(5.60 WB**)	Ampoule (8 mL)	115.6-121.1	55.4	na	53.0	na	680.1	0.0034

NB* = sample without buffer. WB** = sample with buffer.
na = not applicable because only two points were used in calculations.

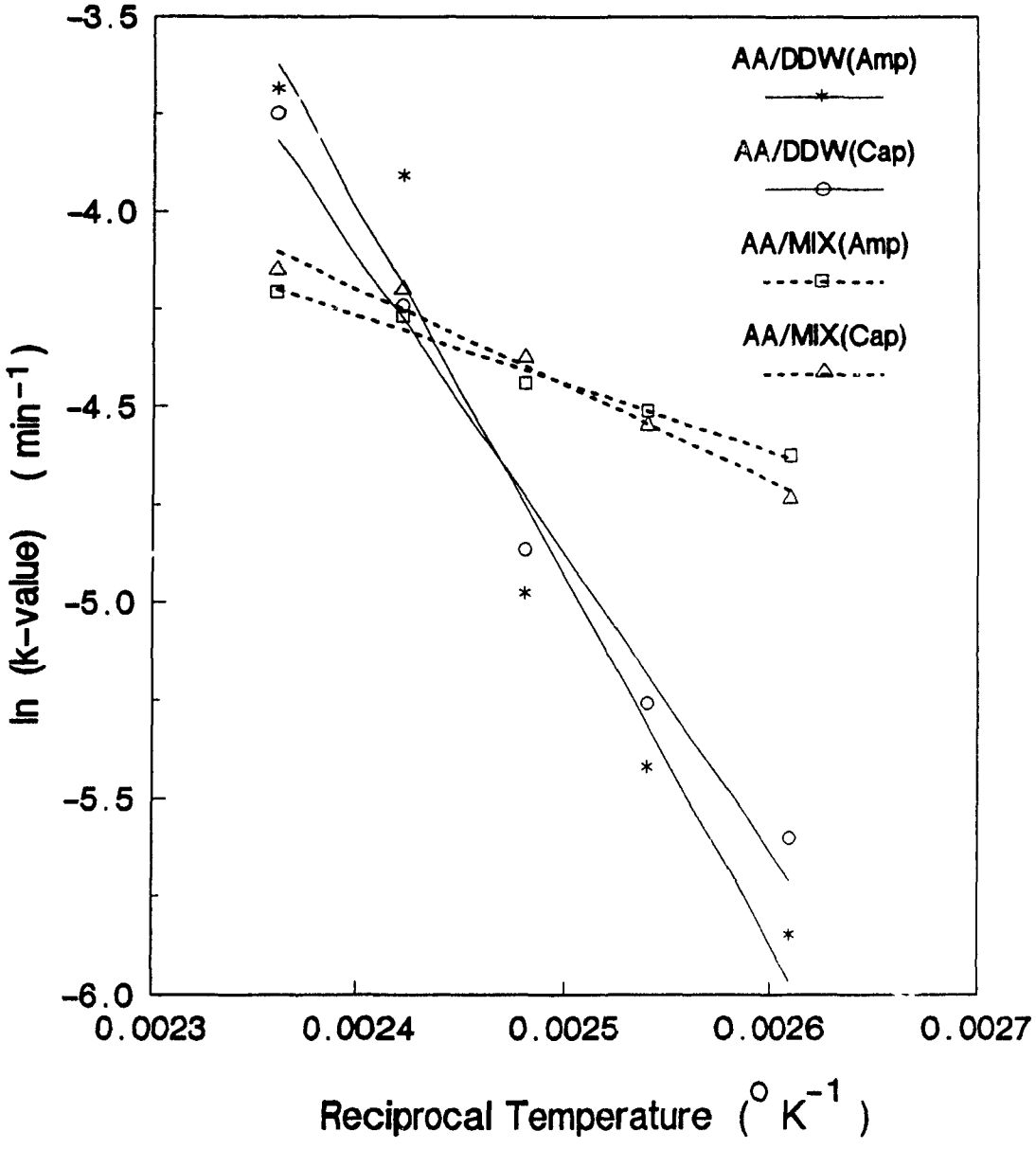


Figure 4. Arrhenius-plot of ascorbic acid destruction (AA/DDW and AA/MIX) employing both ampoule and capillary heating techniques.

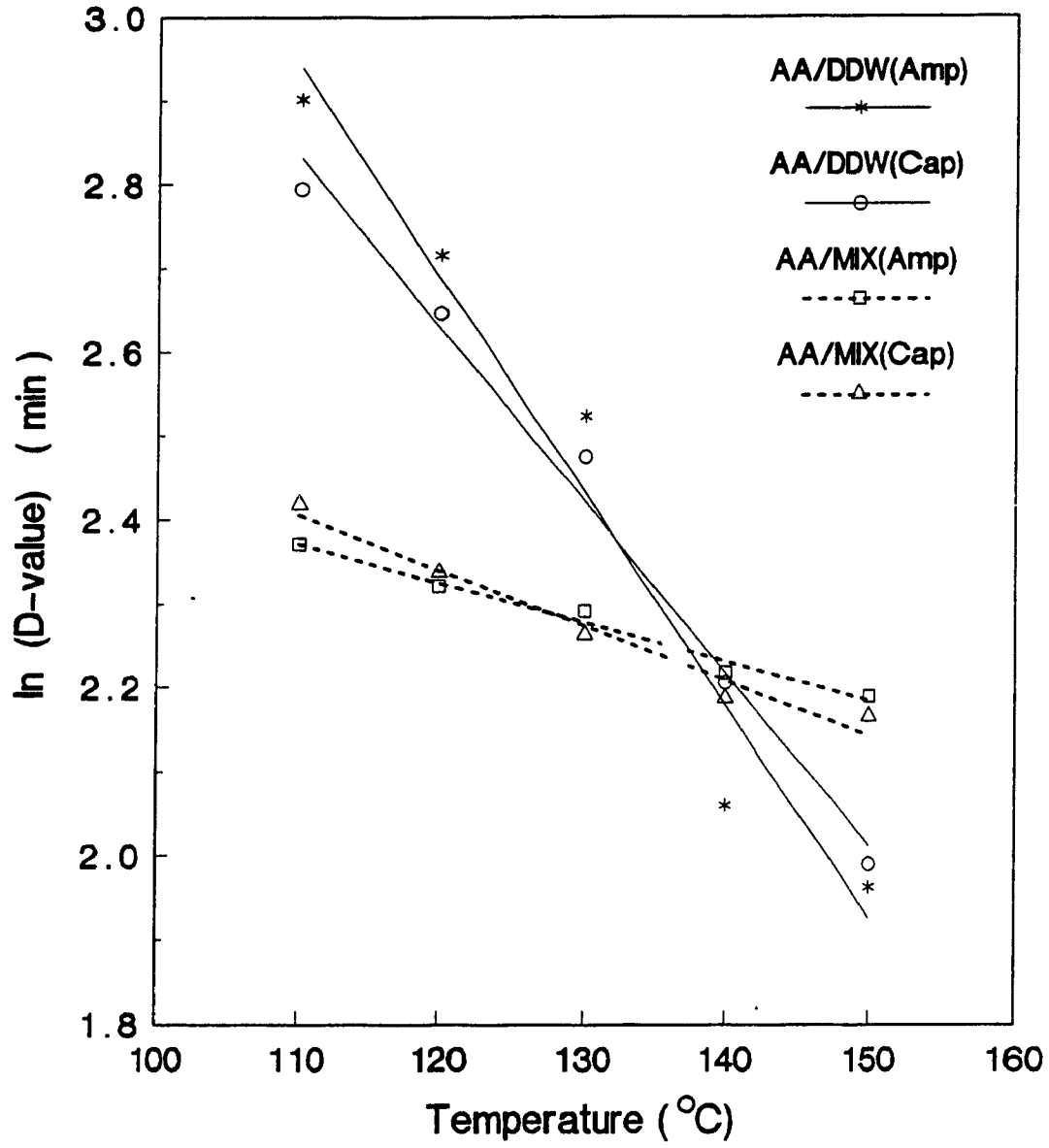


Figure 5. TDT-plot of ascorbic acid destruction (AA/DDW and AA/MIX) employing both ampoule and capillary heating techniques.

Although the rate data implies that the capillaries and ampoules behave differently, the possibility exists that experimental errors related to sampling and/or analytical bias may be the cause of the difference, specifically because the capillary system involves substantially more sample handling to prepare for its analysis. Table 5 presents a comparison of the maxima and minima of the coefficients of variation (100 x SD/mean) for replicate samples of ascorbic acid. The maxima of the coefficient of variation (error) tends to attain larger values at higher temperatures due to the low concentrations of ascorbic acid relative to the mean, upon which the calculation is based. These coefficients of variability for the ampoule and capillary systems, when compared statistically using the T-test, were not significantly different ($p<0.05$) and indicate that the differences obtained were not a result of analytical variability. A subsequent comparison of the retention data itself indicated that the ampoule and capillary tubes were not significantly different ($p<0.05$).

4.3.2 Ascorbic Acid in the Mixture (AA/MIX)

In order to further explore the influence of other compounds on the degradation behavior of ascorbic acid, a simple model system was formulated using an additional nutrient, thiamine, plus Maillard-color forming compounds glucose and glycine. Ascorbic acid destruction in this system (AA/MIX) was carried out at the same time as in the distilled water system. The destruction pattern of ascorbic acid in the mixture also followed a first-order reaction in ampoules and the capillary tubes (Figures 6 and 7) and the regression analysis data presented in Table 3 gave an average R^2 value of 0.992 with the lowest value being 0.995. Clearly the destruction of ascorbic acid is affected in a dramatic fashion in the presence of the other constituents basically doubling in its reference reaction rate (k_o) from 5.2×10^{-3} to 11.1×10^{-3} min^{-1} in the 4 mL ampoule. As noted for ascorbic acid in distilled water (Table 4), similar trends were apparent between the k_o and D_o values obtained by the ampoule and capillary measuring systems. Hence the presence of thiamine, glucose and glycine affected the E_a of ascorbic acid, resulting in E_a values of 14.6 kJ/mole (ampoule) and 20.5 kJ/mole (capillary) as compared

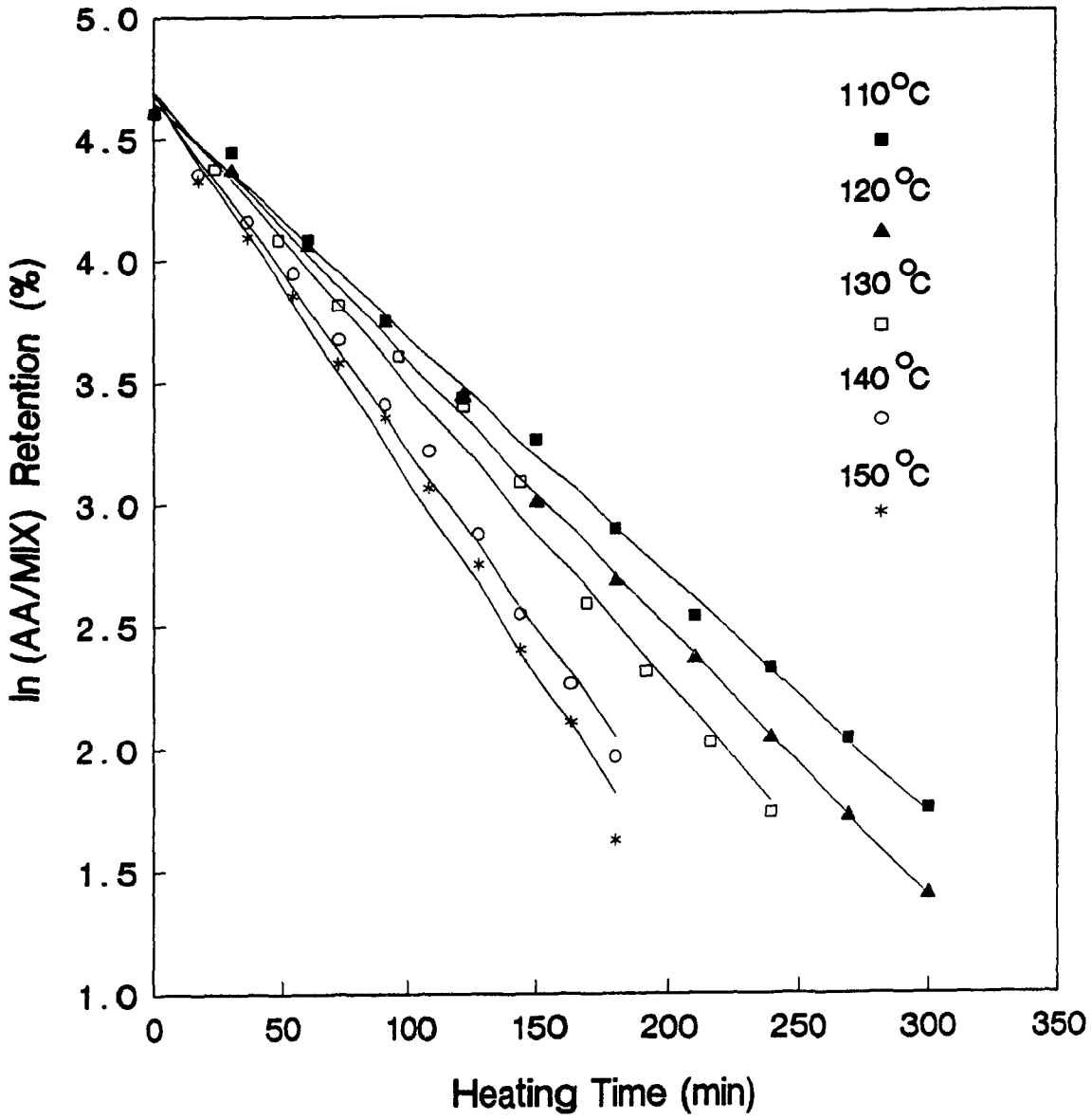


Figure 6. Retention of ascorbic acid (AA/MIX) following various temperature-time treatments using the ampoule heating technique.

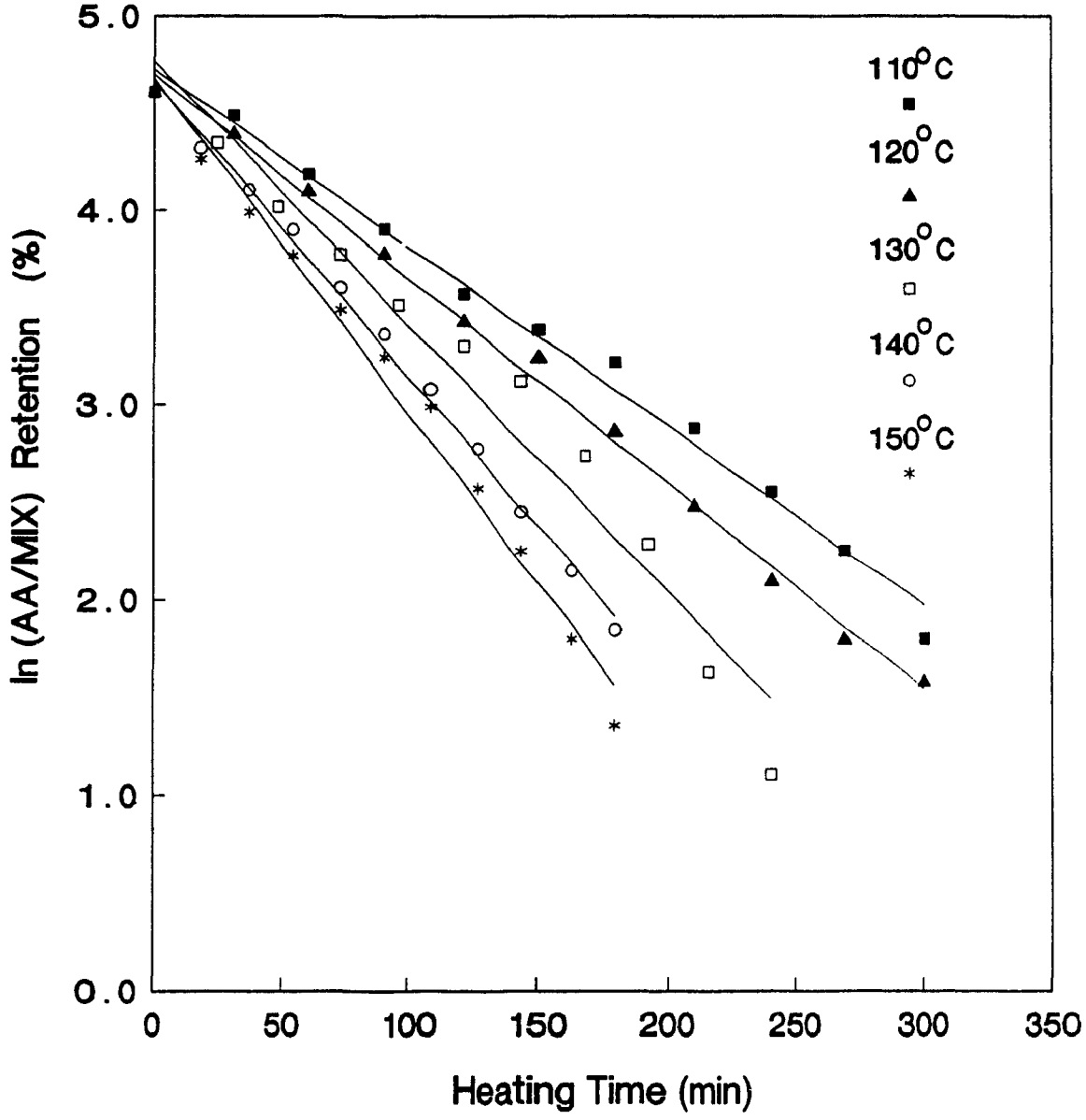


Figure 7. Retention of ascorbic acid (AA/MIX) following various temperature-time treatments using the capillary heating technique.

to the values of 78.6 kJ/mole (ampoule) and 63.4 kJ/mole (capillary) for distilled water, reducing the energy required to initiate ascorbic acid destruction between 3-5 fold.

Table 5. Variability associated with ascorbic acid estimation by the two techniques.

Temperature ^{o}C	Coefficient of variation (%) Ampoule	Capillary
110	0.99-3.24	0.82-2.68
120	1.23-4.57	0.93-2.59
130	1.13-8.76	1.02-9.39
140	1.21-22.6	1.09-10.1
150	1.19-28.3	1.23-27.8

A second set of experiments at two temperatures (115.6 and 121.1^{o}C), two volumes (4 and 8 mL) and three initial pH levels were run to determine the effect of headspace oxygen and/or pH, commonly considered to affect ascorbic acid destruction. The ascorbic acid solutions were prepared, (a) at its natural pH (4.05), (b) buffered at pH 4.05 and (c) buffered at pH 5.60, the pH which ascorbic acid reaches after typical process over temperatures of 110-150^{o}C. Only two temperature (115.6 and 121.1 ^{o}C) were used since good first order kinetics had been attained and Figure 8 presents the plots of the logarithmic Retention (%) as a function of heating time, Appendix [3]. Two basic sets of curves are apparent, related by volume and a covariance test was used to determine whether there was a significant effect relative to pH or volume (Table 6). The results indicated that pH did not have a significant effect on the rate of loss of ascorbic acid, however, the volume of air within the ampoule did. Once again, the kinetic parameters, E_a and z, although they "characterize" the reaction, and are related to the reaction rate, are not very meaningful in describing the system in the absence of a temperature range.

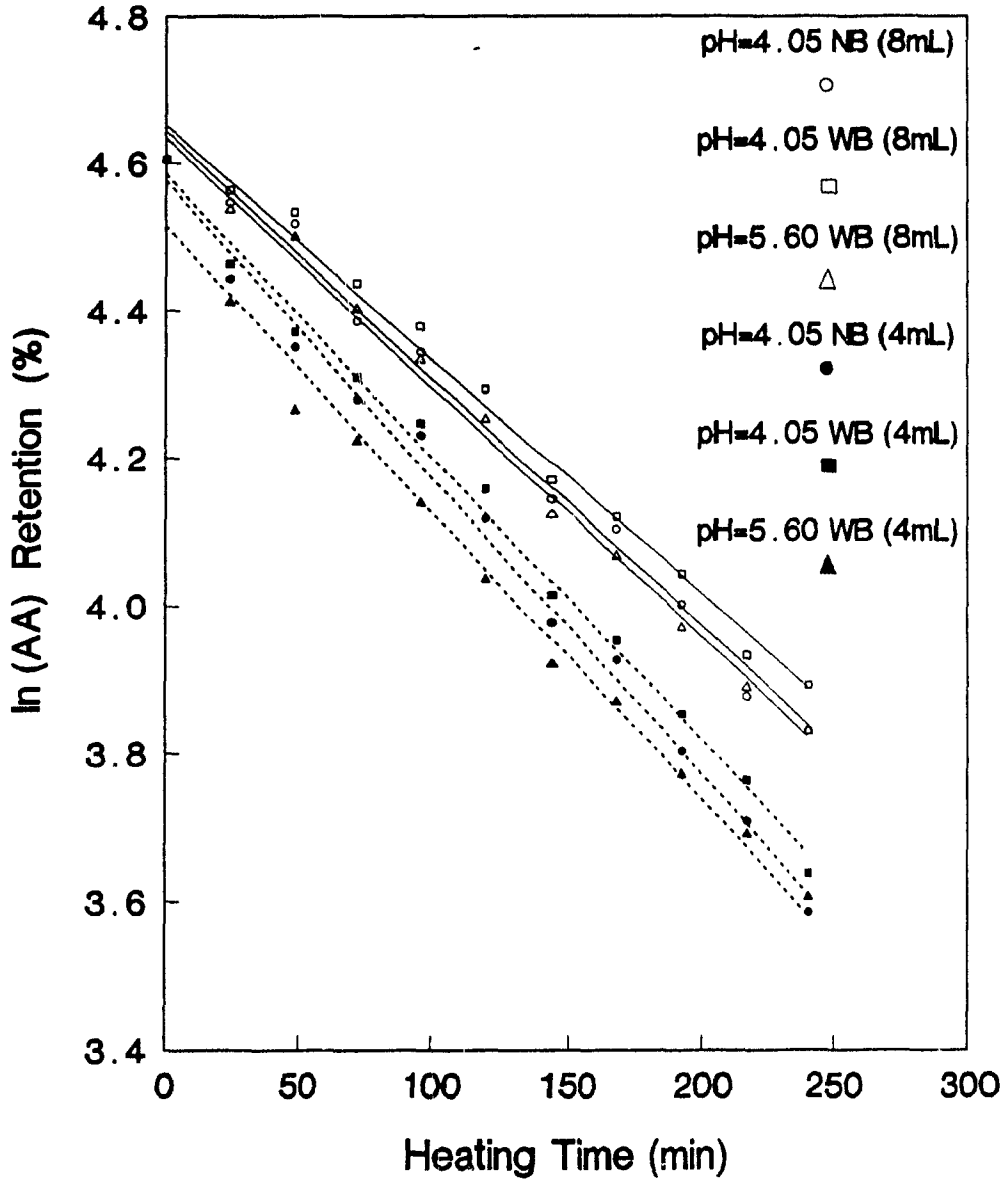


Figure 8. Influence of sample volume and pH on the retention of ascorbic acid (AA/DDW) following various temperature-time treatments using the ampoule heating technique.

Table 6. Effect of pH and volume on ascorbic acid retention following various thermal processing.

Temperature (°C)	pH	Volume (ml)	Regression results			
			Slope	Intercept	R^2	F-value
115.6	4.05WB*	$4^{1,2}$	0.0026	4.6540	0.9820	$1684^{1,2}$
115.6	4.05WB*	$8^{1,3}$	0.0023	4.7011	0.9709	$988^{1,3}$
115.6	5.60WB*	$4^{1,2}$	0.0027	4.6113	0.9844	$1864^{1,2}$
115.6	5.60WB*	$8^{1,3}$	0.0027	4.7021	0.9649	$829^{1,3}$
121.1	4.05WB*	$4^{1,2}$	0.0038	4.5860	0.9956	$5820^{1,2}$
121.1	4.05WB*	$8^{1,3}$	0.0032	4.6523	0.9909	$2922^{1,3}$
121.1	5.60WB*	$4^{1,2}$	0.0039	4.5158	0.9852	$2018^{1,2}$
121.1	5.60WB*	$8^{1,3}$	0.0034	4.6324	0.9945	$4999^{1,3}$

WB* = sample with buffer
** = significant at $p < 0.01$
[1] refers to pH effect
[2,3] refers to volume effect.
Note : values with the same superscripts are not significantly different.

4.3.3 Comparison of AA/DDW and AA/MIX

A striking difference between the destruction behavior of ascorbic acid in AA/DDW and AA/MIX is seen once again in the relation between E_a and z. The reduction in E_a from 78.6 to 14.6 kJ/mole by a factor of 5.38 resulted in a similar 5.40 fold rise in z, from 39.4 to 212.8C°. This inverse and directly proportional relation appears to indicate that any change in E_a causes a proportionate change in z and that the two values are related within a defined set of temperature conditions. A similar inverse relation exists not only between the 4 mL ampoules, but in the capillary system also, with a drop in E_a from 63.4 to 20.5 kJ/mole resulting in a 3.11 fold change reflected in a similar rise in z from 48.8 to 151.8C°. If similar calculations are carried out for the pH/headspace effect studied earlier, this relationship is constant within data obtained over the same temperature range, however it does not exist between differing temperature ranges (i.e., data collected over 110-150°C vs 115.6-121.1°C). This cross relation indicates that E_a and z are inter-changeable as long as the temperature range is the same.

One can calculate a ratio, E_a/z, the units of which are kJ/mole/C^o which appears to relate the kinetic parameters from two very different systems into a potentially meaningful form in terms of units. Table 4 provides kinetic data for ascorbic acid as a reaction rate (k_o), as a decimal reduction time (D_o), as an activation energy (E_a) and as temperature difference or "thermal resistance" (z) required to change the decimal reduction time (proportional to the reaction rate) by a factor of 10 . Although each of these terms has a specific meaning, none of them characterize the reaction system in a holistic manner. The ratio calculated in terms of the kJ/mole/C^o could indicate the work or energy (kJ) required per unit mass (mole) associated with a difference of one degree between two temperatures within a temperature range. These units are not unlike heat capacity (kJ/kg/^{o}K), the energy required to increase the temperature of known weight of material one degree. The basic difference is that in this case, we would be considering a chemical reaction and the work or energy required to drive it forward by increasing the temperature by one degree beyond the activation energy.

Returning to the initial concept of relating E_a and z, the definition of the temperature range limits the energy input into the system, a part of which can be considered to provide the activation energy and while the balance is used to drive the reaction. If the rate data over a temperature range can be correlated to the energy or work required on a molar basis, then E_a/z would be a useful constant or unambiguous value which would characterize a reaction.

In the light of the E_a/z concept, we can re-examine the pH/headspace data obtained for ascorbic acid by calculating the values for 115.6-121.1^{o}C data tabulated in Table 7.

Table 7. A comparison of E_a/z values for two volumes of ascorbic acid at three pH levels between 115.6-121.1°C.

System	Volume (mL)	E_a/z (kJ/mole/C°)$^{115.6\text{-}121.1}$
(a) AA/DDW (4.05 WB*)	4	2.46
(b) AA/DDW (4.05 NB*)	4	2.84
(c) AA/DDW (5.60 WB*)	4	2.35
(d) AA/DDW (4.05 WB*)	8	1.14
(e) AA/DDW (4.05 NB*)	8	1.84
(f) AA/DDW (5.60 WB*)	8	1.05

WB* = sample with buffer NB* = sample without buffer.

The 4 mL ampoule at all pH values requires an average of 2.55 kJ/mole/C° to start and sustain the reaction between 115.6 and 121.1°C, while the 8 mL ampoule requires an average of 1.34 kJ/mole/C° to do the same. Based on this analysis, it would require approximately twice as much work to destroy one mole of ascorbic acid in the 4 mL system than in the 8 mL system over this temperature range. If one looks at the relative reaction rates, $k_0 = 4.0 \times 10^{-3}$ min^{-1}; D_0 = 571.6 min, and $k_0 = 3.4 \times 10^{-3}$ min^{-1}; D_0 = 685.7 min for the 4 mL and 8 mL ampoules, the E_a/z ratio indicates that more energy is required to drive the 4 mL reaction, the opposite of what one would expect. Further inspection of this concept indicated that for some reactions E_a/z did parallel the rate, while others did not. One example which clearly indicated that the tying of E_a/z to an integrated rate or reaction capacity would not work was in the circumstance where two reactions were parallel, with the same E_a and z, but differing in their rates. After pursuing what appeared to be an interesting concept in some detail, it became clear that the E_a/z ratio could not be turned into a meaningful concept and that the characterization of a reaction could only be done on a relative basis, through the use of two parameters, E_a and k_0 or z and D_0.

4.4 Kinetics of Thiamine Degradation

4.4.1 Thiamine in Distilled Water and in the Mixture (B1/DDW and B1/MIX)

The destruction pattern of thiamine in aqueous solutions over the temperature range of 110 to 150°C also indicated a first-order reaction rate by both the ampoule and the capillary techniques (Figures 9 and 10). Regression analysis (Table 8) generally indicated that the R^2 values associated with the kinetic data at various temperatures were very similar for both, and R^2 values of greater than or equal to 0.97 were obtained for all temperatures. D and k, and D_0 and k_0 values for thiamine are presented in Tables 8 and 9 respectively and similar values were obtained for both ampoules and capillaries.

The temperature sensitivity of the reaction rate constant, k, for thiamine in distilled water was evaluated by the Arrhenius concept for data from both ampoule and capillary techniques (Figure 11). The regression analysis (Table 9) indicated a slightly better fit of data with the ampoule technique (R^2 = 0.96 vs 0.94) and the associated activation energies were 118 kJ/mole (ampoule) and 103 kJ/mole (capillary). Reference k_0 values at 121.1°C were 6.0×10^{-3} min^{-1} and 6.7×10^{-3} min^{-1} for ampoules and capillary systems respectively.

A similar analysis of the temperature sensitivity of D, (Figure 12) also yielded a better regression fits with the ampoule technique (Table 9) giving z values of 26.4 C^0 for the ampoule and 30.6 C^0 for the capillary techniques and D_0 values of 394 min and 350 min, respectively. Regression analyses to determine E_a and z values for either ampoule or capillary techniques produced similar R^2 values. The ampoule and capillary data were not significantly different and the coefficient of variability associated with the analysis (Table 10) was similar to that obtained for ascorbic acid.

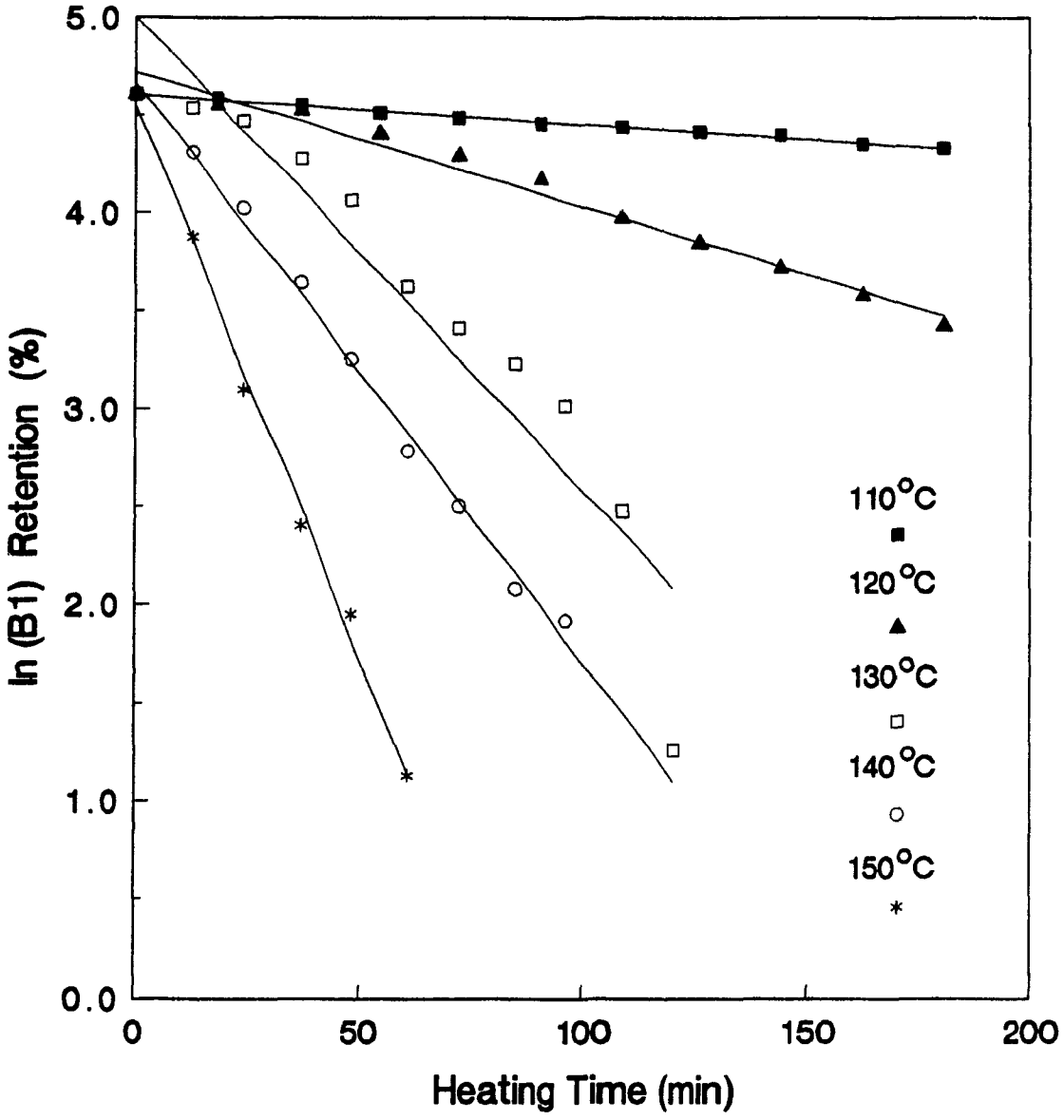


Figure 9. Retention of thiamine (B1/DDW) following various temperature-time treatments using the ampoule heating technique.

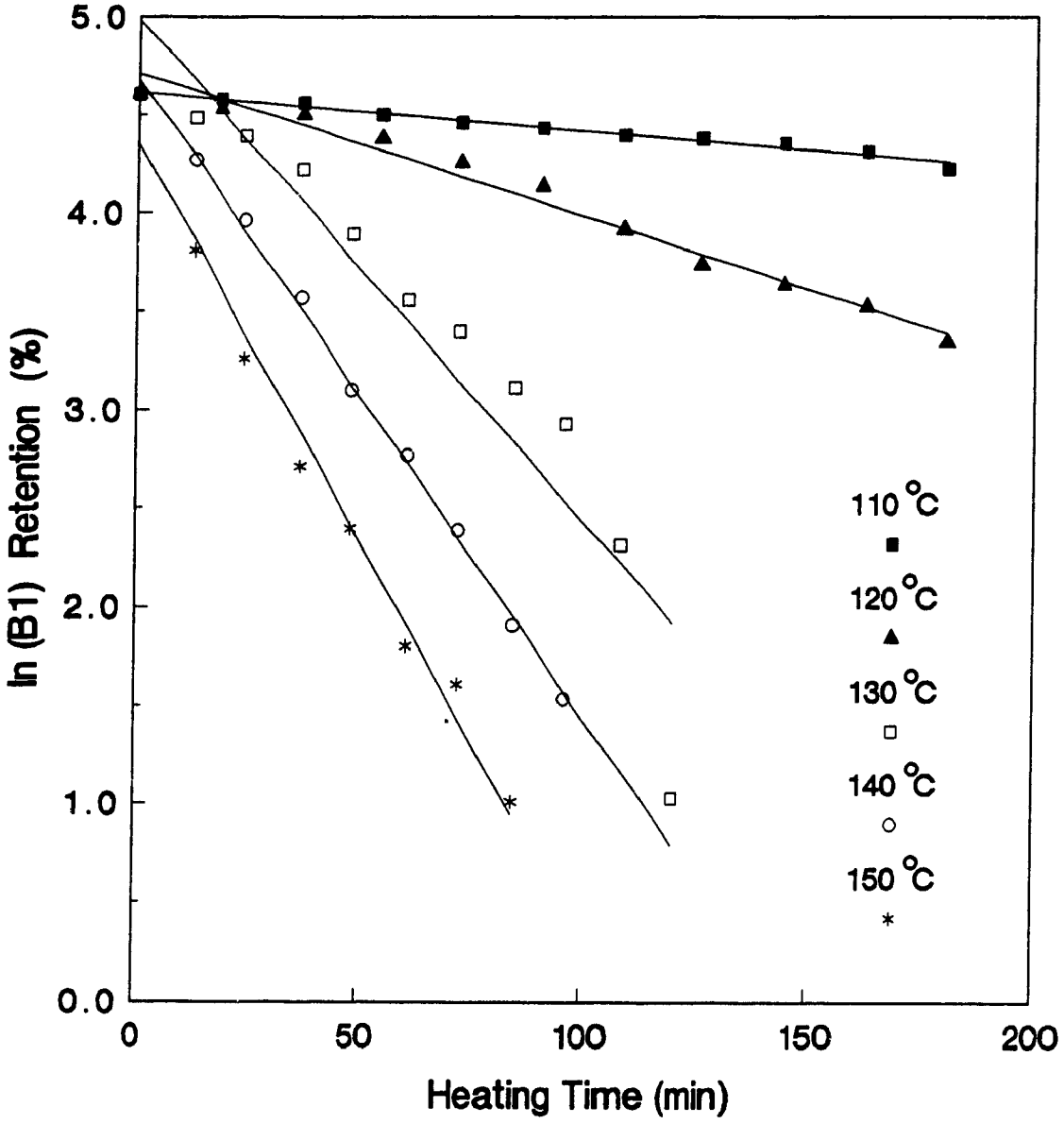


Figure 10. Retention of thiamine (B1/DDW) following various temperature-time treatments using the capillary heating technique.

Table 8. Kinetic parameters for thiamine (B1) degradation.

Sample Description	Method	Temperature (^oC)	R^2	k value (min^{-1})	D value (min)
B1/DDW (pH 4.11)	Ampoule (4 mL)	110	0.9927	0.0015	1509
		120	0.9803	0.0069	333.1
		130	0.9654	0.0181	127.0
		140	0.9944	0.0302	76.3
		150	0.9955	0.0568	40.5
	Capillary	110	0.9804	0.0020	1167
		120	0.9807	0.0073	313.5
		130	0.9799	0.0187	123.2
		140	0.9978	0.0324	71.0
		150	0.9840	0.0406	56.8
B1/MIX (pH 5.60)	Ampoule (4 mL)	110	0.9958	0.0032	717.1
		120	0.9951	0.0065	354.0
		130	0.9942	0.0116	197.8
		140	0.9960	0.0190	121.16
		150	0.9910	0.0260	88.5
	Capillary	110	0.9922	.0034	582.7
		120	0.9930	0.0069	334.4
		130	0.9936	0.0121	190.0
		140	0.9990	0.0194	119.0
		150	0.9954	0.0302	75.8

Table 9. Arrhenius and thermal death time (TDT) parameters for thiamine destruction.

Sample Description	Method	Temperature Range (^oC)	E_a (kJ/mole)	R^2	z (C^o)	R^2	D_o (min)	k_o (min^{-1})
B1/DDW (pH 4.11)	Ampoule (4 mL)	110-150	118.0	0.96	26.4	0.95	394.3	0.0060
	Capillary	110-150	102.6	0.94	30.6	0.92	349.5	0.0067
B1/MIX (pH 5.60)	Ampoule (4 mL)	110-150	71.1	0.99	43.8	0.98	354.3	0.0066
	Capillary	110-150	73.4	0.99	42.4	0.99	337.8	0.0069

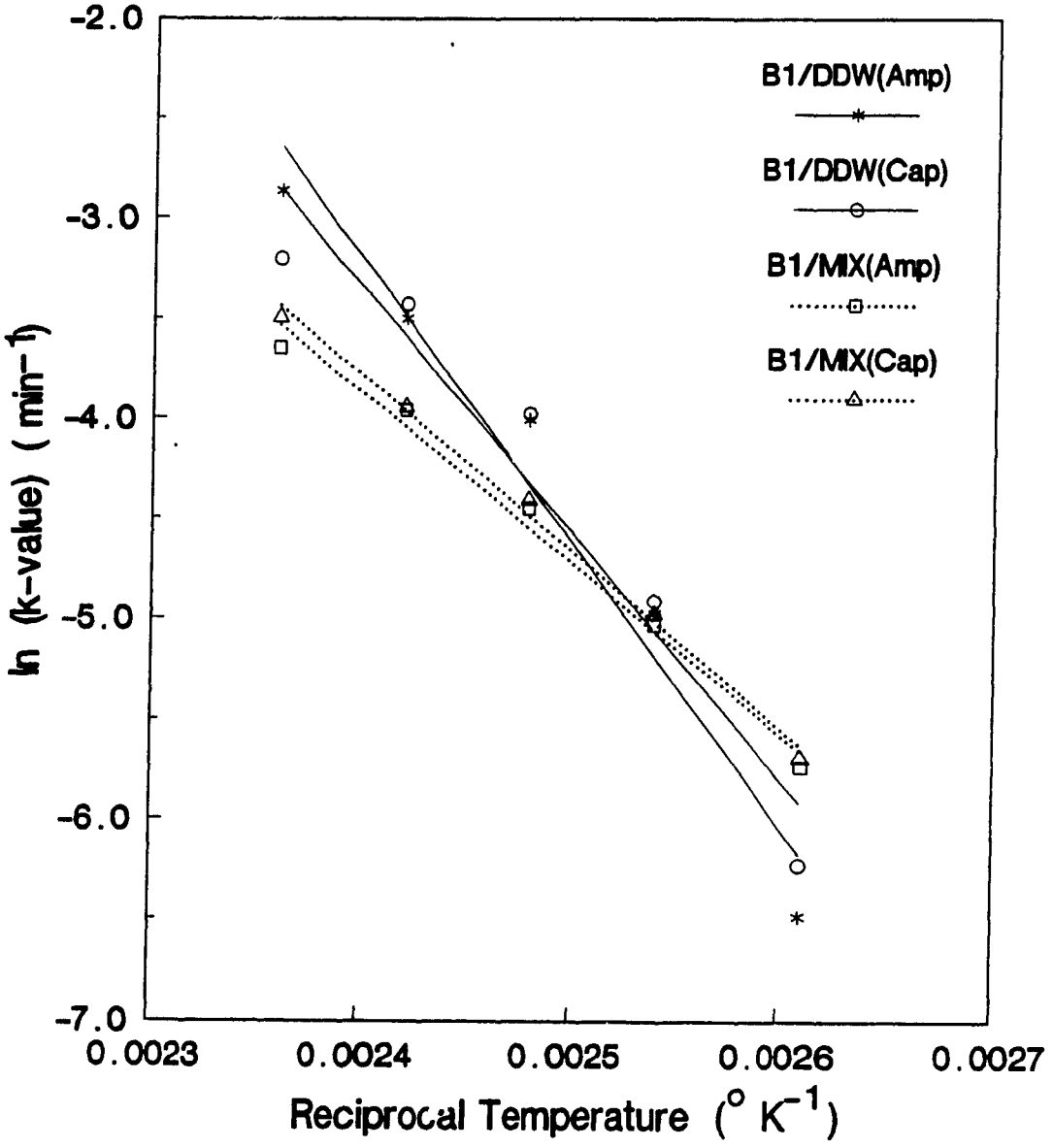


Figure 11. Arrhenius-plot of thiamine destruction (B1/DDW and B1/MIX) employing both ampoule and capillary heating techniques.

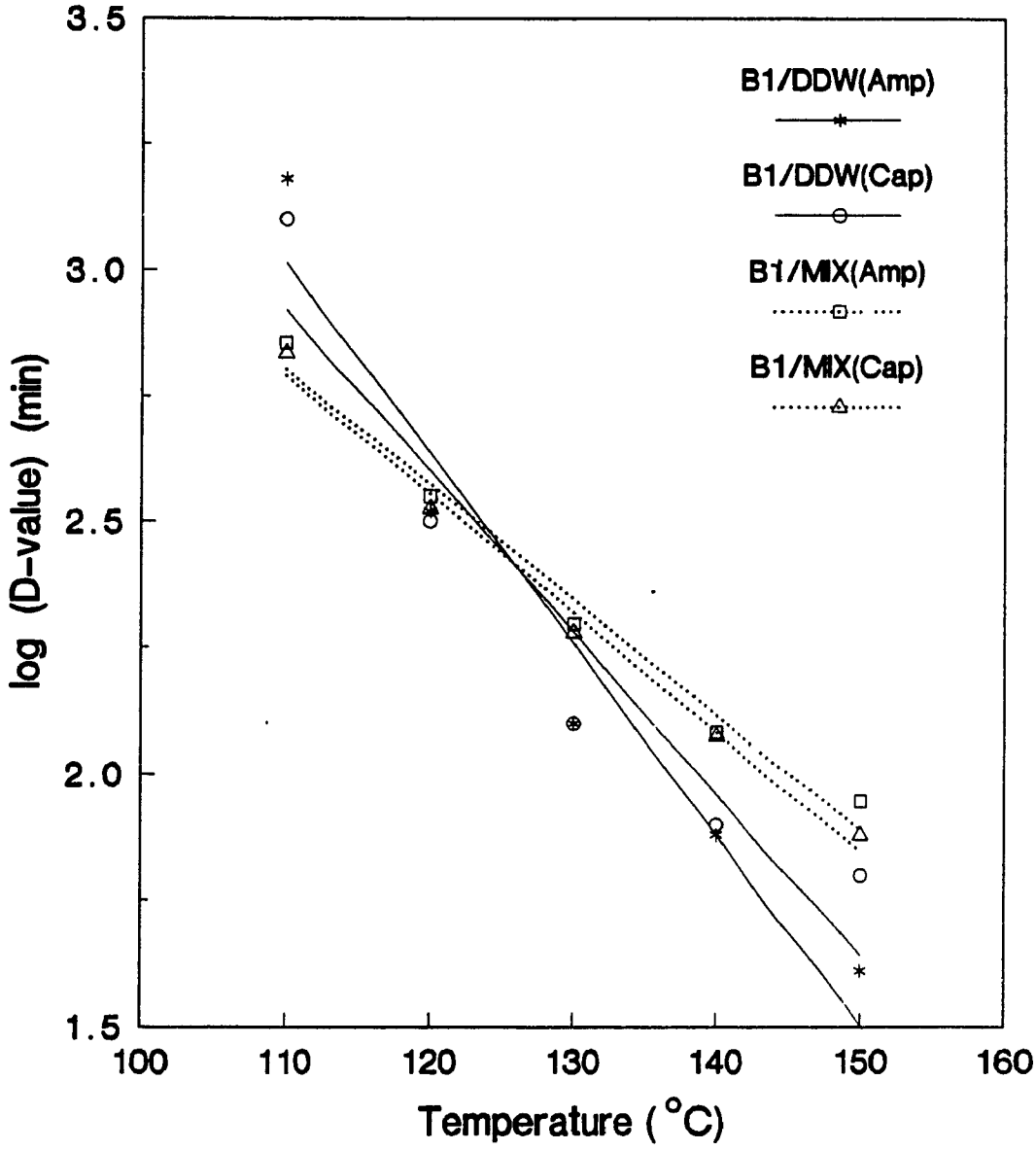


Figure 12. TDT-plot of thiamine destruction (B1/DDW and B1/MIX) employing both ampoule and capillary heating techniques.

Table 10. Variability associated with thiamine estimation by the two techniques.

Temperature	Coefficient of variation (%)	
^{o}C	Ampoule	Capillary
110	1.03-1.35	0.92-1.30
120	1.01-2.94	0.94-2.87
130	1.26-6.68	1.07-5.93
140	1.36-10.1	1.11-10.4
150	1.53-15.1	1.13-21.3

The destruction pattern of thiamine in a mixture (B1/MIX) also followed a first-order reaction rates in both the ampoule and the capillary systems (Figures 13 and 14). Regression analysis (Table 8) again produced similar R^2 values with both techniques and were greater than or equal to 0.99 for all temperatures. As in the case of distilled water, only small differences were observed between k_o and D_o representative of reaction rate behavior. The E_a and k_o for thiamine in the mixture was evaluated for both the ampoule and capillary techniques (Figure 11). The regression analysis (Table 9) indicated that the two techniques had similar R^2 values (>0.98), had associated activation energies of 71.1 kJ/mole (ampoule) and 73.4 kJ/mole (capillary) and k_o values of 7.01×10^{-3} min^{-1} and 7.02×10^{-3} min^{-1} respectively. A similar determination of z (Figure 12) produced similar R^2 values for both containers, with associated z values of 43.8 C^0 (ampoule) and 42.4 C^0 (capillary) and D_o's of 354 min and 338 min respectively. The differences in results between the capillary and ampoule procedures were not statistically significant.

4.5 Kinetics of Maillard Reaction Color (Y%/DDW and Y%/MIX)

The formation of color due to the Maillard reaction involving glycine and glucose in distilled water temperature was measured over a temperature range of 110 to 150^{o}C using the Minolta Chroma Meter. Evaluating color by the three CIE parameters, the luminance factor, Y% and the chromaticity coordinates, x and y, illustrated a first-order reaction (Figures 15 to 17). As expected the reaction rates

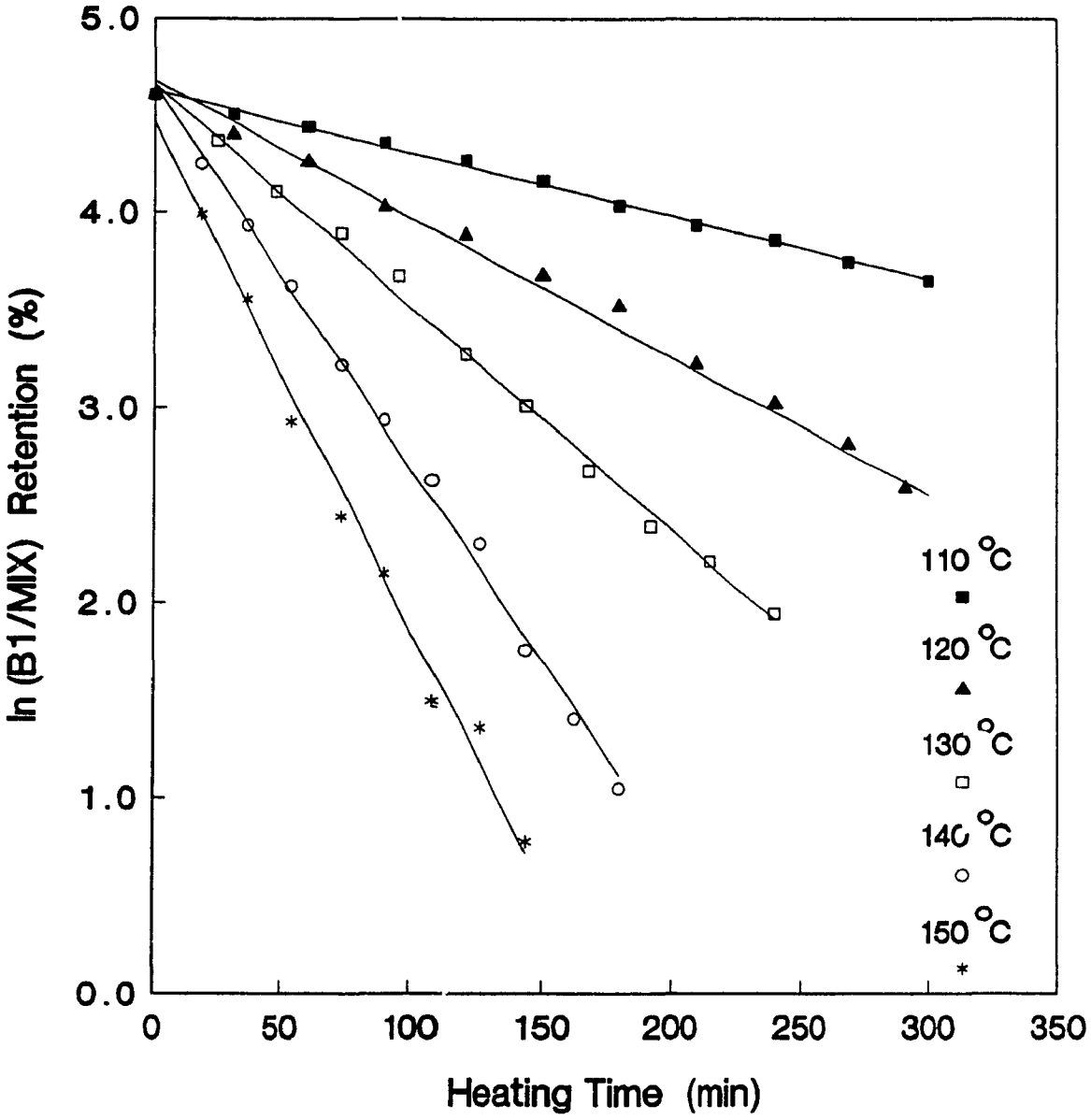


Figure 13. Retention of thiamine (B1/MIX) following various temperature-time treatments using the ampoule heating technique.

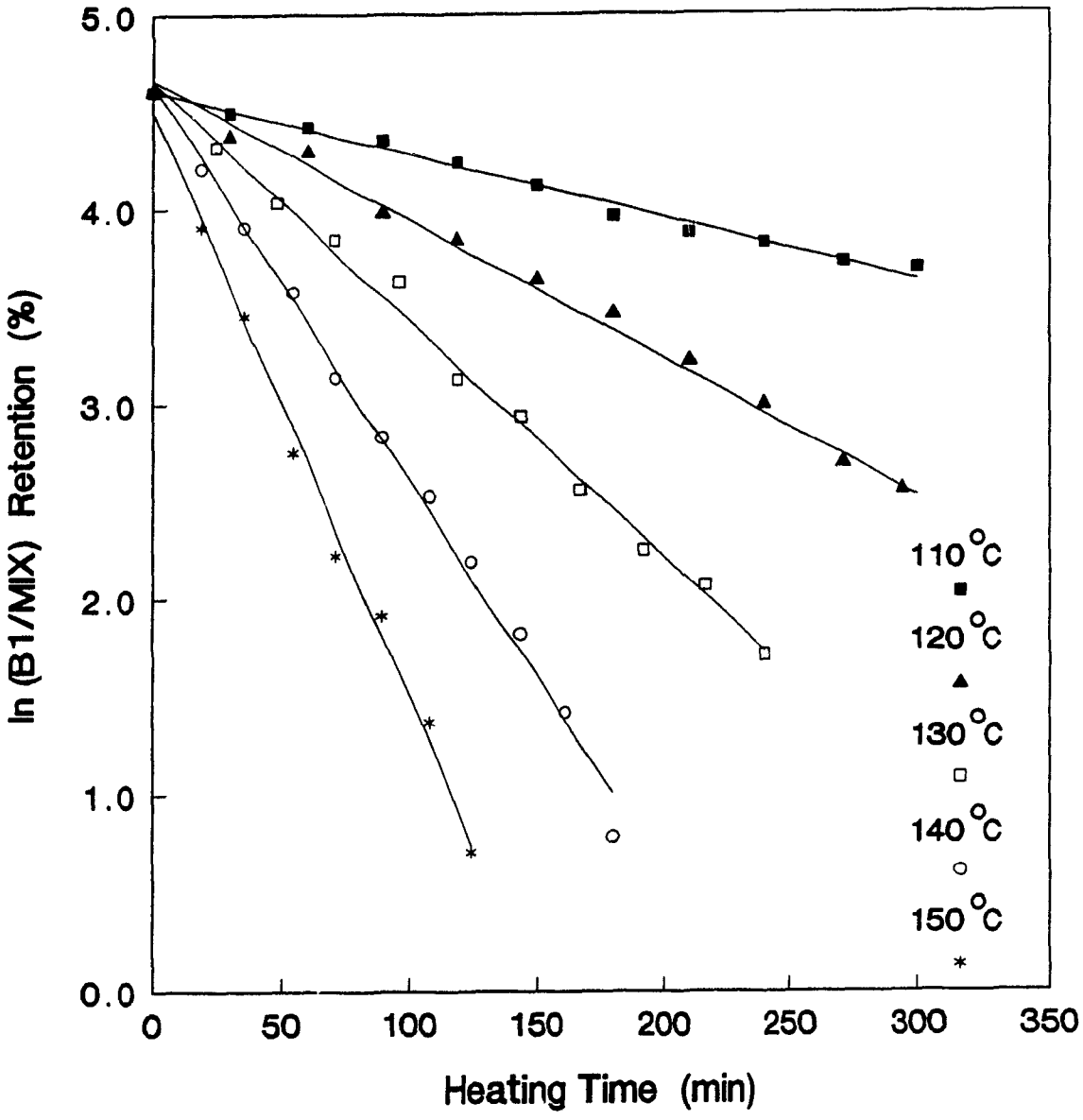


Figure 14. Retention of thiamine (B1/MIX) following various temperature-time treatments using the capillary heating technique.

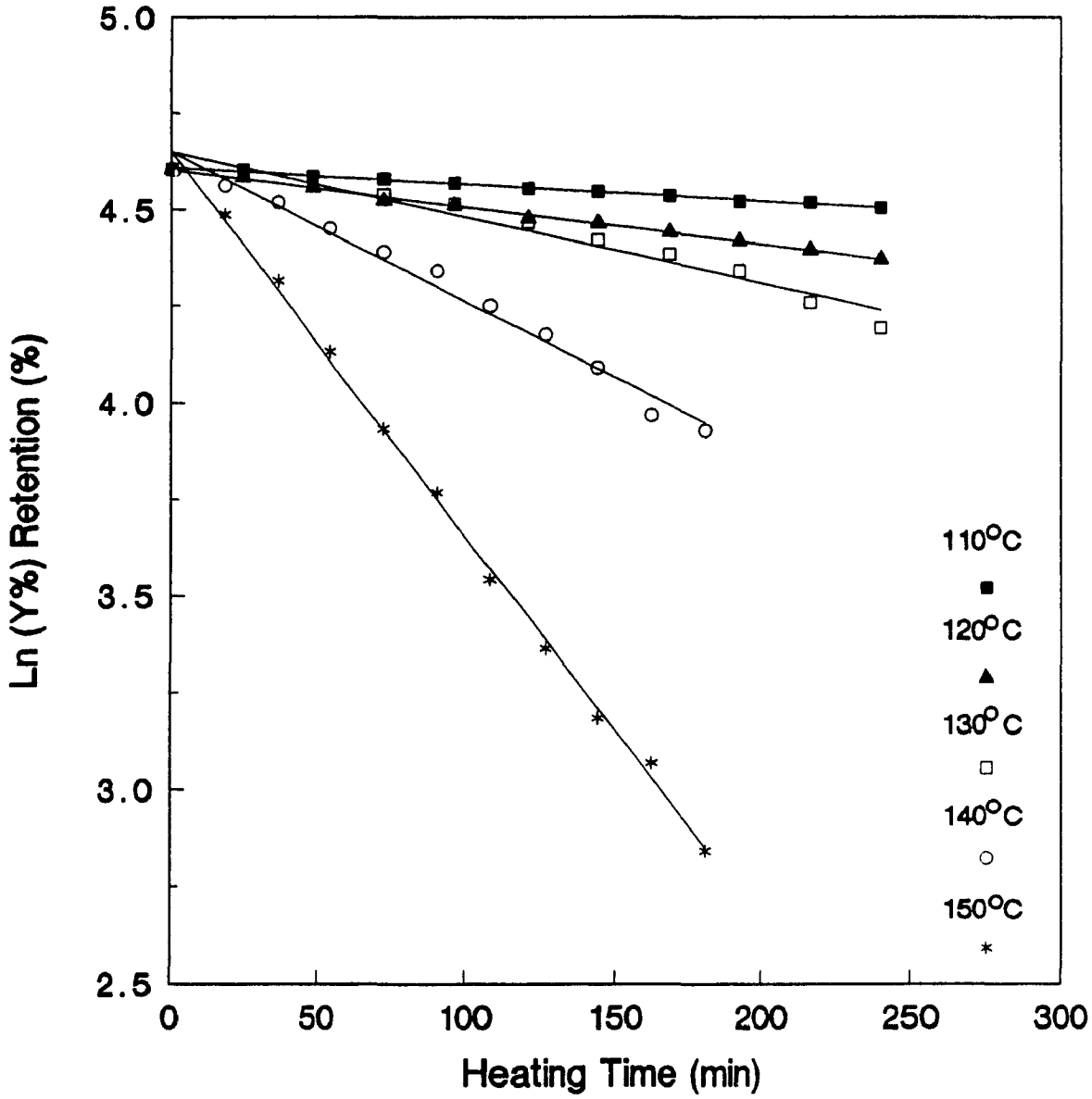


Figure 15. Retention of luminance factor, Y% (Color/DDW) following various temperature-time treatments.

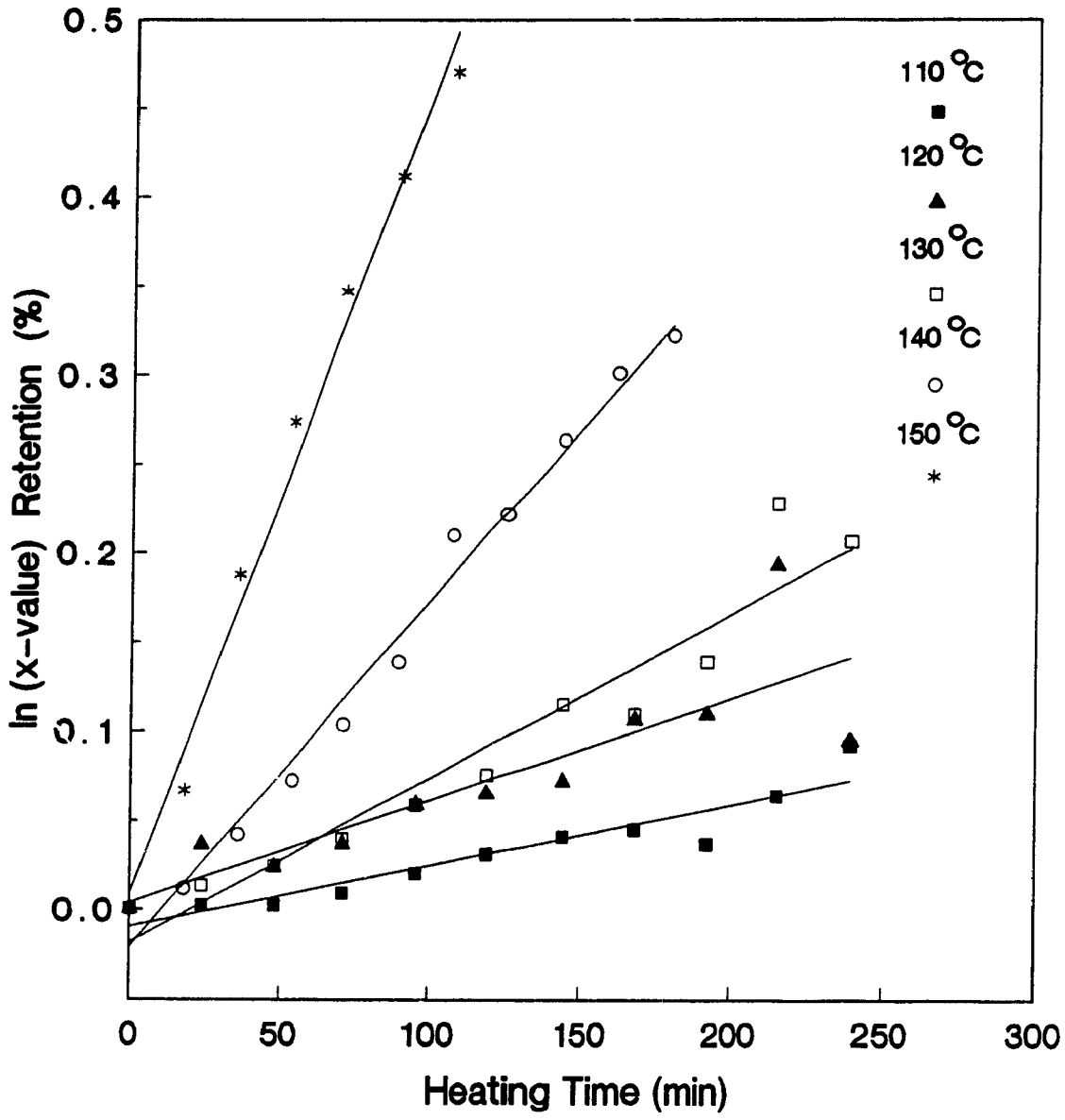


Figure 16. Retention of chromaticity factor, x-value (Color/ DDW) following various temperature-time treatments.

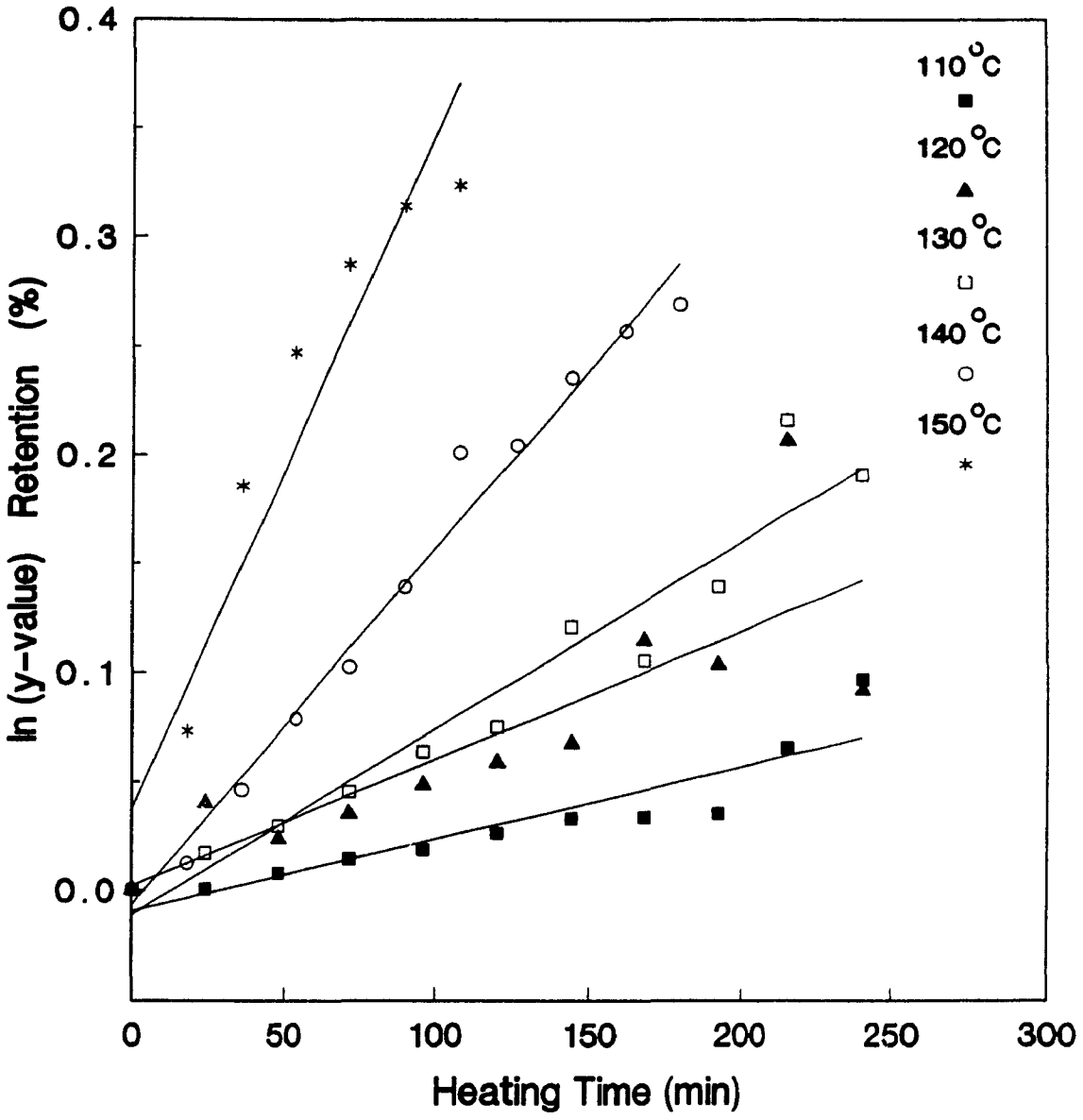


Figure 17. Retention of chromaticity factor, y value (Color/ DDW) following various temperature-time treatments.

for all the color development parameters (x and y) increased as the temperature increased while the luminance factor dropped. Good correlation coefficients (>0.92) were obtained for all the temperature data and the reaction rate constants, k and D, obtained from the slopes are included in Table 11.

The temperature sensitivity of color formation to temperature is illustrated in Figures 18 and 19 and the regression analysis (Table 12) indicated a slightly better fit for the Y% and y values relative to x chromaticity coordinate. The associated activation energies were 102 kJ/mole, 81.4 kJ/mole and 83.1 kJ/mole for Y%, y and x and the k_o values were 9.63×10^{-4} min $^{-1}$, 6.68×10^{-4} min $^{-1}$ and 4.94×10^{-4} min $^{-1}$ respectively. The E_a values for the chromaticity coordinates were similar and lower than the E_a for luminace factor. Figures 20 and 21 illustrate the parallel TDT plots which resulted in D_o values of 2455 min, 3525 min and 4755 min for Y%, x and y, and 30.2 C^o, 37.8 C^o and 37.2 C^o respectively.

The color development was also investigated in relation to the mixture and the plots, regression data, E_a, z, k_o and D_o data are presented in Figures 22-24 and Tables 11 and 12. These also followed first order reaction rates and gave good R^2 values (>0.95). The regression analysis (Table 12) produced activation energies of 81.0, 83.4 and 82.1 kJ/mole for the three color parameters, Y%, x and y values and the k_o values were 11.6×10^{-4} min $^{-1}$, 5.40×10^{-4} min $^{-1}$ and 5.52×10^{-4} min $^{-1}$ respectively. Unlike their color development in distilled water, the E_a values for the mixture were very similar and not significantly different. Using the TDT approach, z values of 38.1 C^o, 37.0 C^o and 37.7 C^o were obtained for Y%, x and y, and D_o values of 2029 min, 4360 min and 4252 min respectively. As expected. the z value for the three parameters were also similar considering the direct inverse relation between E_a and z over the same temperature range.

Table 11. Kinetic parameters for color development (Y%, x-value, y-value) in aqueous systems.

Sample Description	Method	Temperature (°C)	R^2	k value (min^{-1})	D value (min)
Y%/DDW (pH 5.73)	Ampoule (4 mL)	110	0.9891	0.0004	5237
		120	0.9396	0.0010	2350
		130	0.9753	0.0014	1601
		140	0.9877	0.0034	644.1
		150	0.9973	0.0101	227.0
x-value/DDW (pH 5.73)	Ampoule (4 mL)	110	0.9946	0.0004	5630
		120	0.9595	0.0006	3775
		130	0.9981	0.0007	3217
		140	0.9611	0.0022	1029
		150	0.9882	0.0045	514.2
y-value/DDW (pH 5.73)	Ampoule (4 mL)	110	0.9942	0.0003	8918
		120	0.9979	0.0005	4694
		130	0.9918	0.0006	3583
		140	0.9941	0.0017	1376
		150	0.9153	0.0031	747.3
Y%/MIX (pH 5.60)	Ampoule (4 mL)	110	0.9810	0.0007	3370
		120	0.9838	0.0010	2302
		130	0.9833	0.0017	1334
		140	0.9742	0.0029	797.7
		150	0.9825	0.0082	279.4
x-value/MIX (pH 5.60)	Ampoule (4 mL)	110	0.9690	0.0003	7893
		120	0.9666	0.0005	4371
		130	0.9453	0.0007	3104
		140	0.9759	0.0015	1552
		150	0.9665	0.0039	592.7
y-value/MIX (pH 5.60)	Ampoule (4 mL)	110	0.9508	0.0003	8293
		120	0.9493	0.0005	4247
		130	0.9533	0.0009	2667
		140	0.9765	0.0012	1987
		150	0.9815	0.0034	672.8

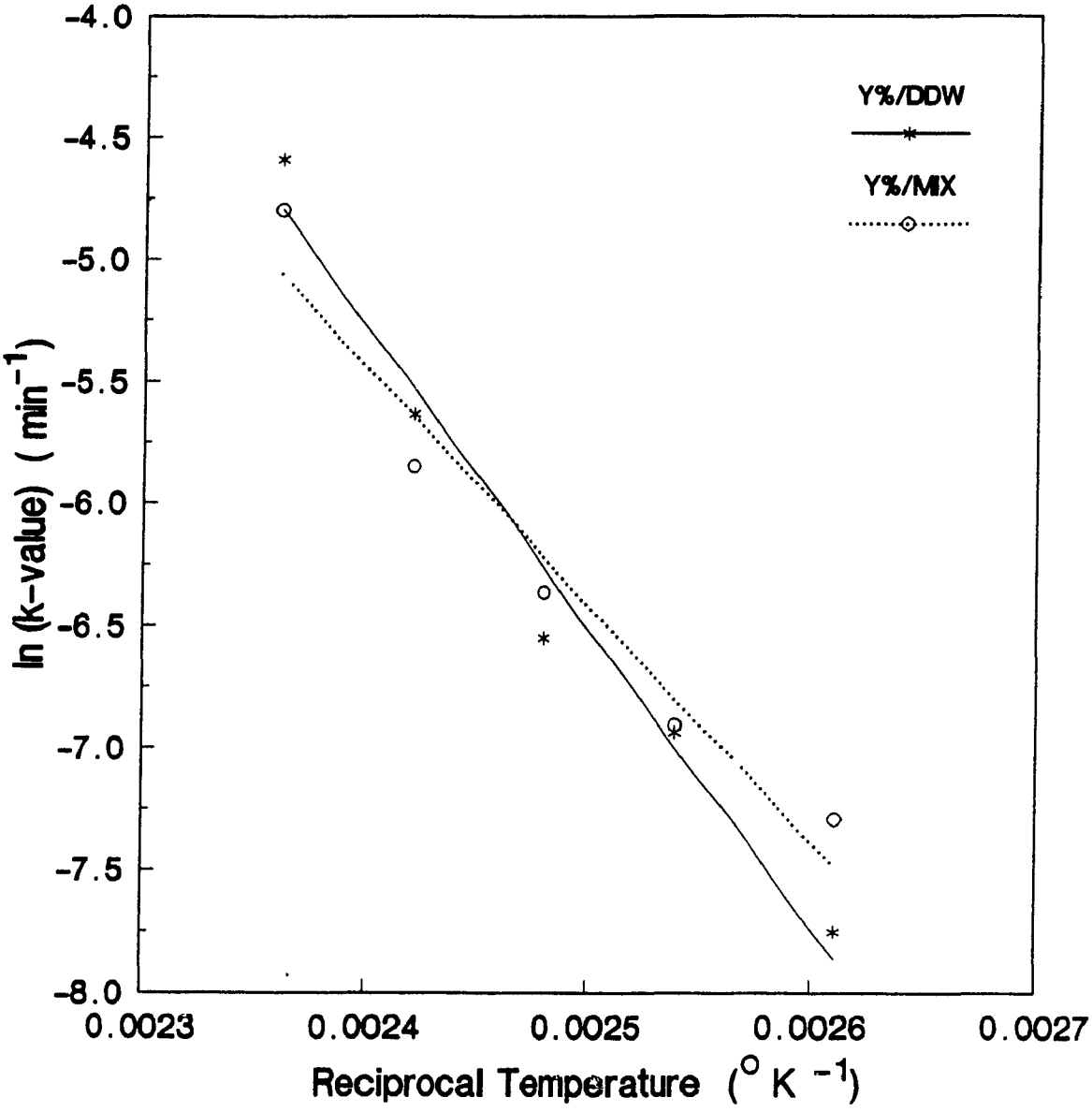


Figure 18. Arrhenius-plot of luminance factor, Y% (Color/DDW and Color/MIX).

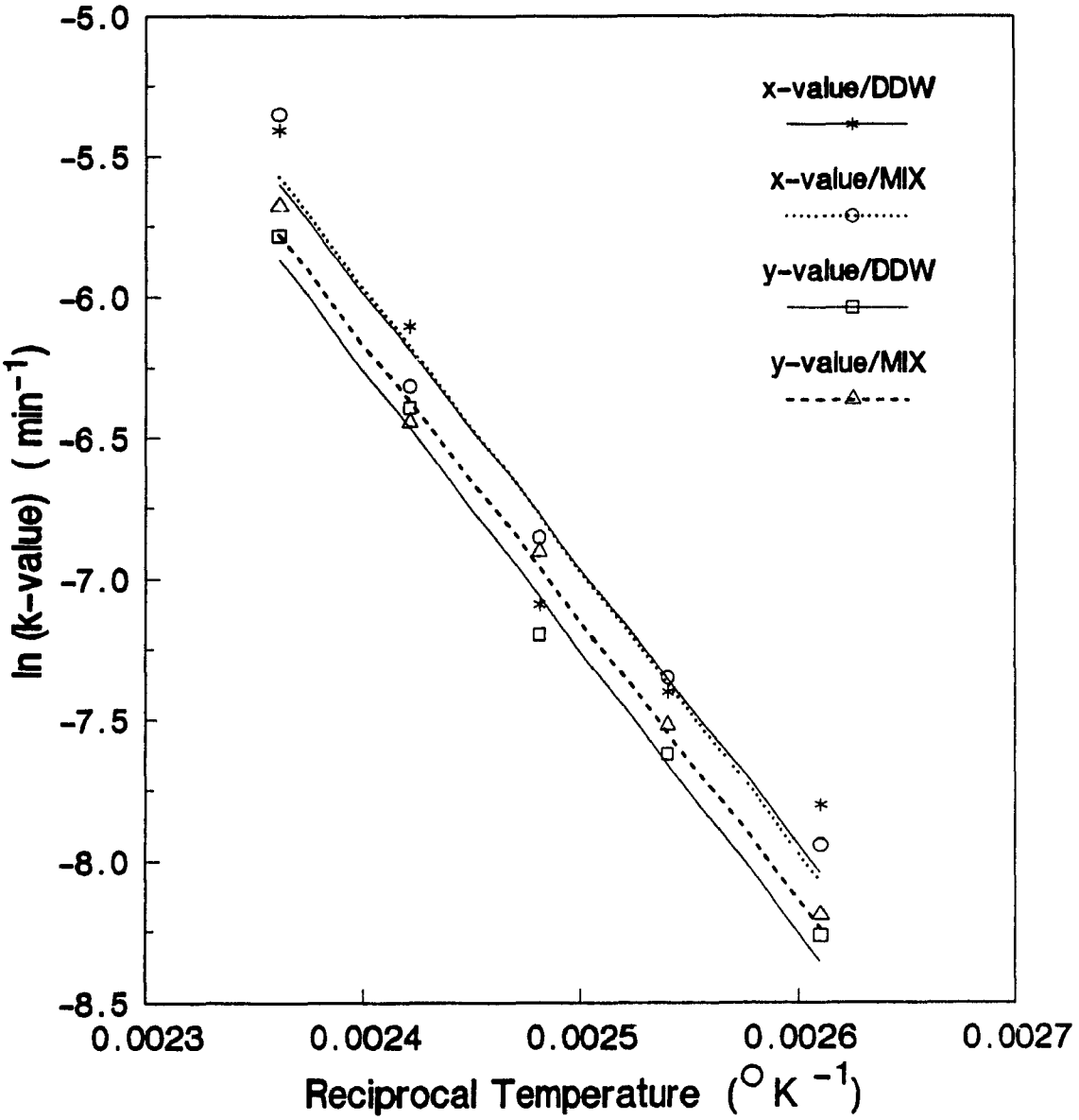


Figure 19. Arrhenius-plot of chromaticity factors, x and y values (Color/DDW and Color/MIX).

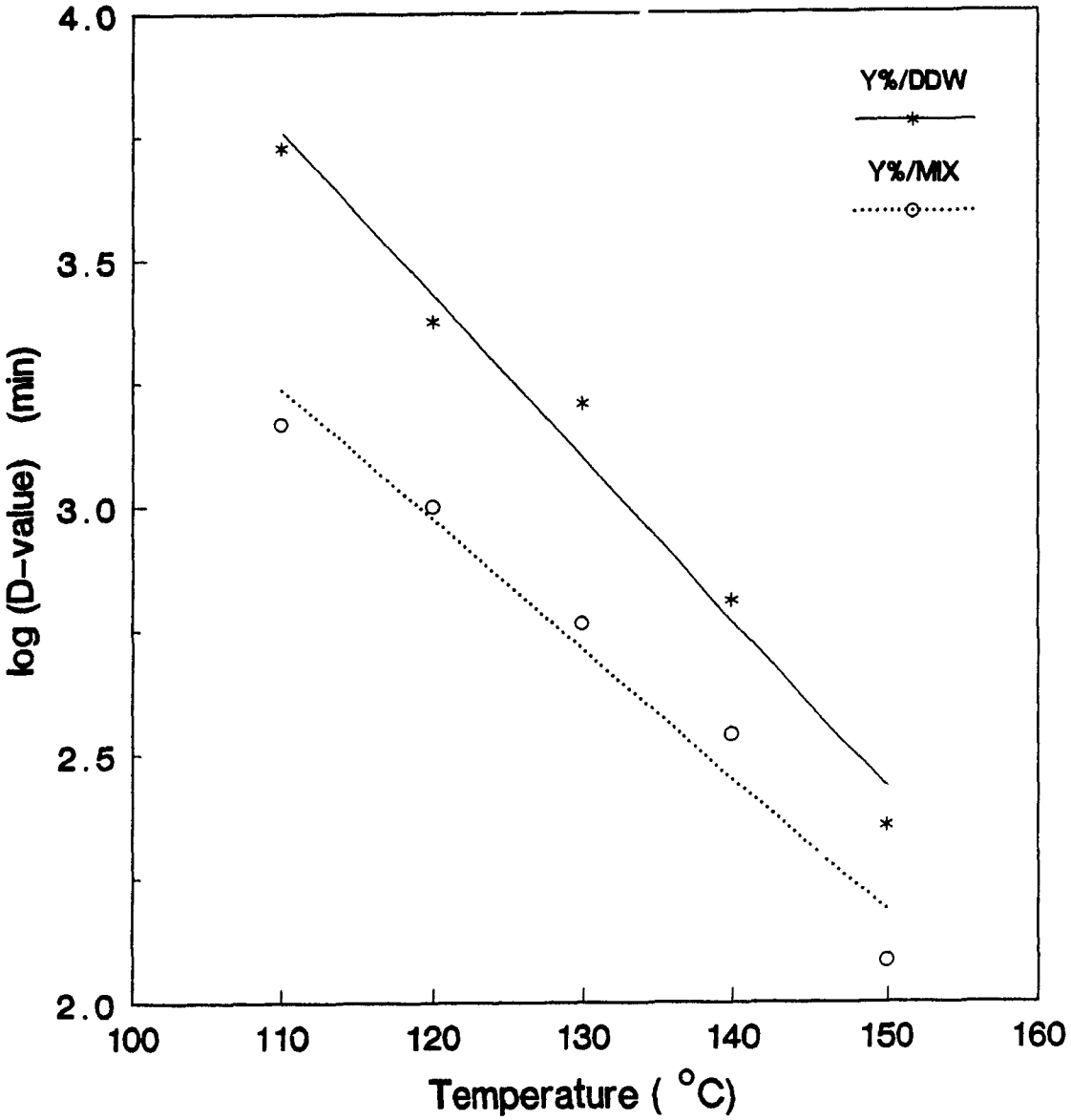


Figure 20. TDT-plot of luminance factor, Y% (Color/DDW and Color/MIX).

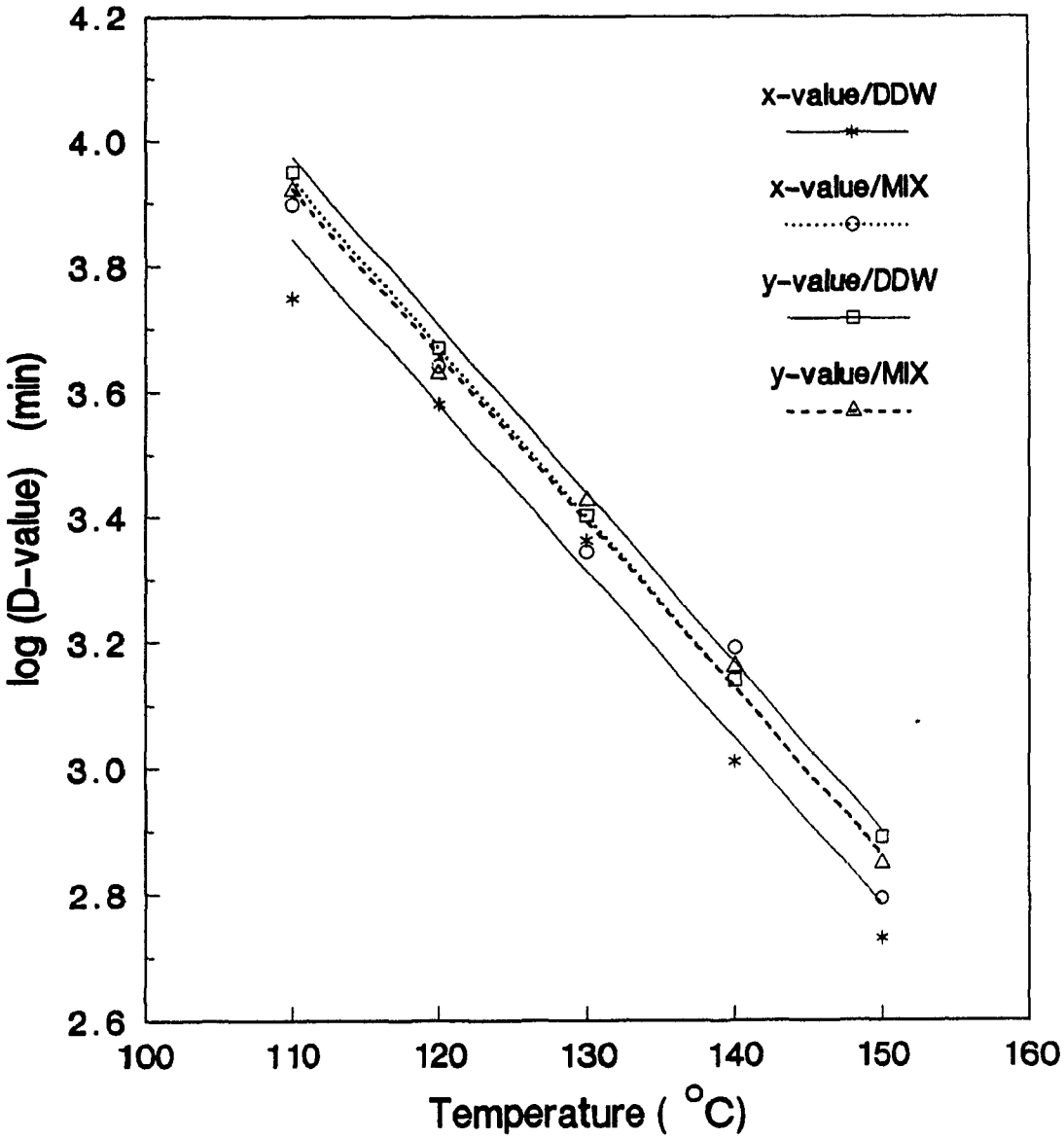


Figure 21. TDT-plot of chromaticity factors, x and y values (Color/DDW and Color/MIX).

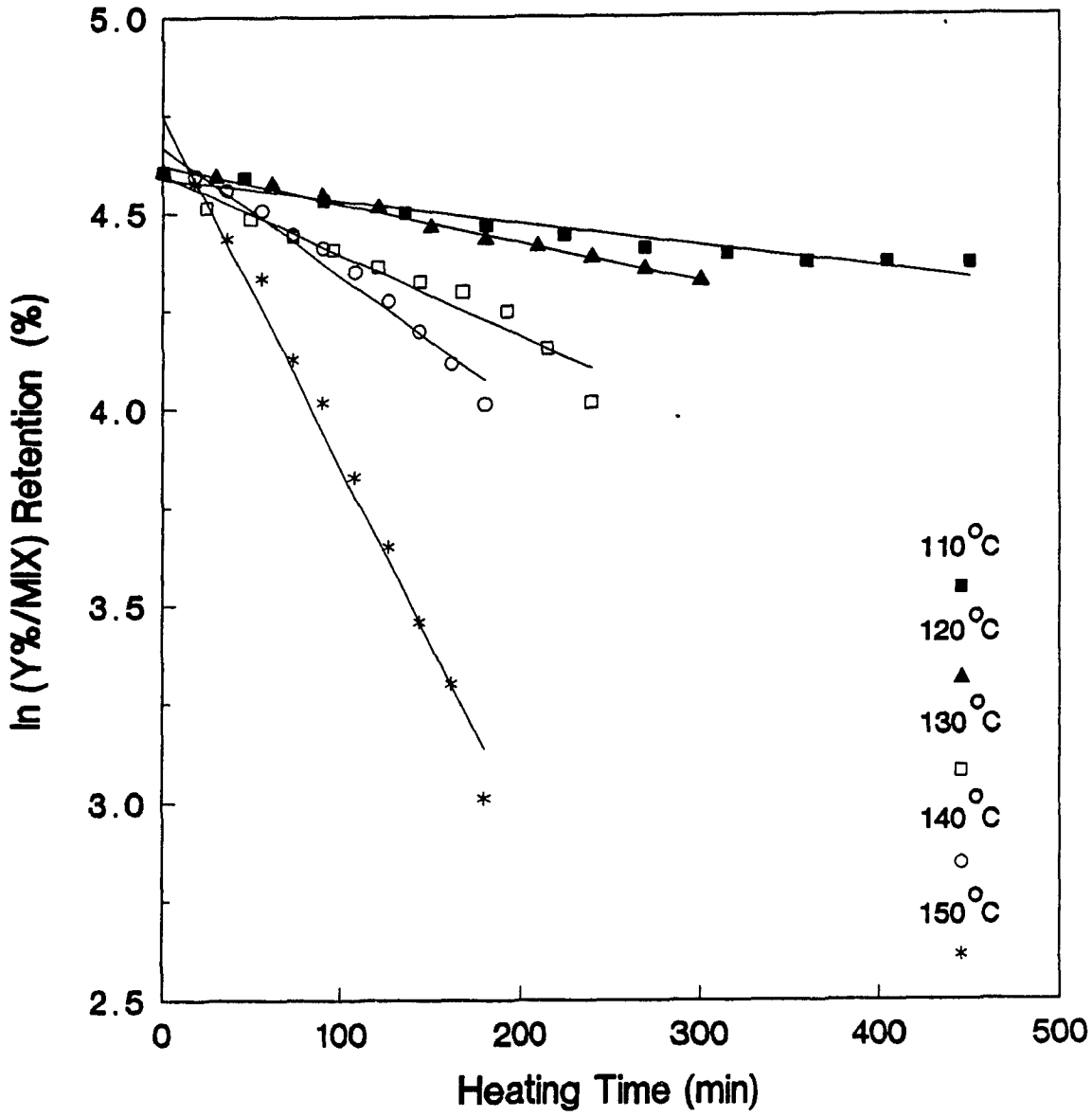


Figure 22. Retention of luminance factor, Y% (Color/MIX) following various temperature-time treatments.

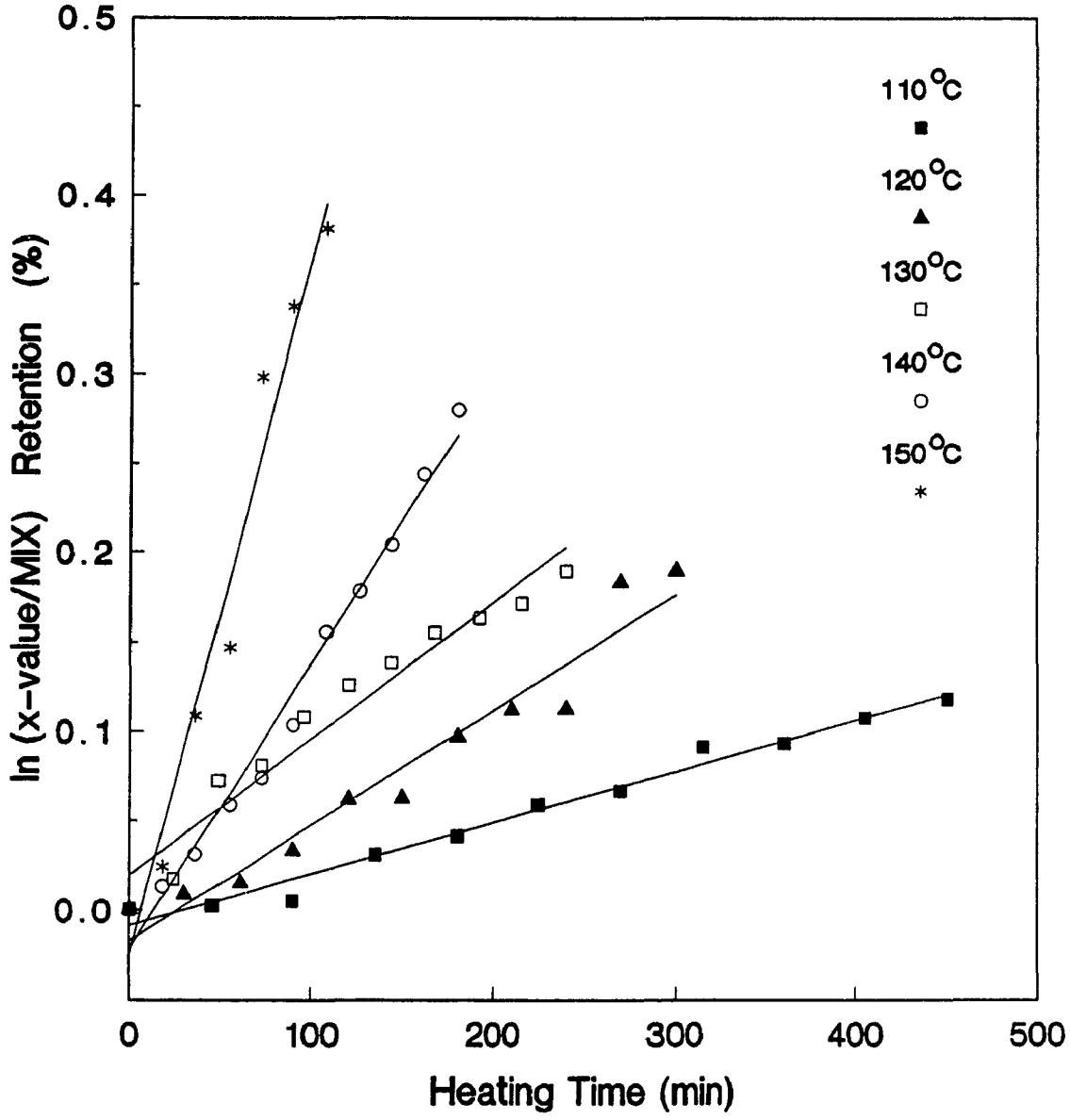


Figure 23. Retention of chromaticity factor, x value (Color/MIX) following various temperature-time treatments.

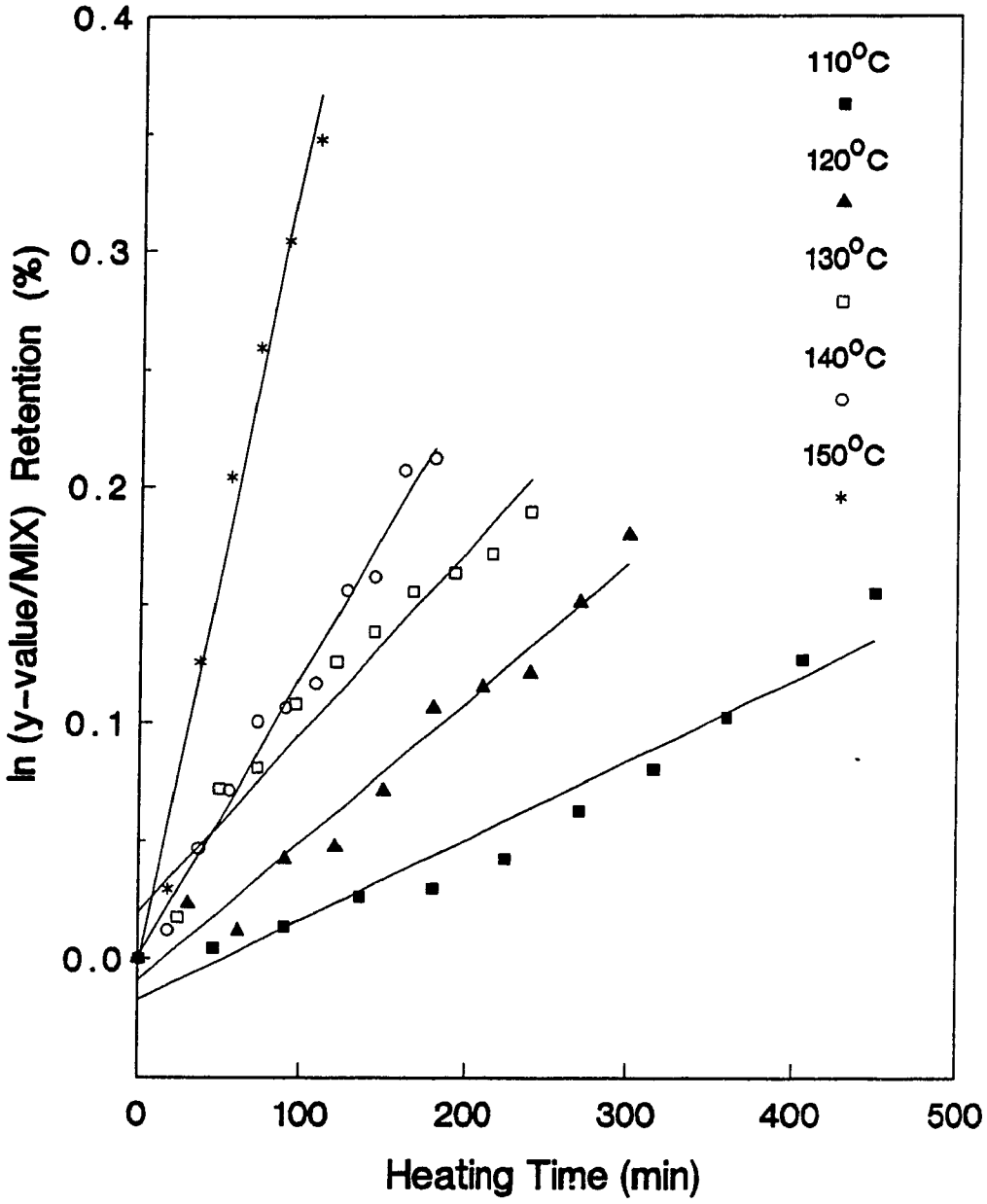


Figure 24. Retention of chromaticity factor, y value (Color/MIX) following various temperature-time treatments.

Table 12. Arrhenius and thermal death time (TDT) parameters for color development using the ampoule technique.

Sample Description	Temperature Range (^{o}C)	E_a (kJ/mole)	R^2	z (C^{o})	R^2	D_o (min)	k_o (min^{-1})
Y%/DDW (pH 5.73)	110-150	102.3	0.97	30.2	0.98	2455	0.000963
x-value/DDW (pH 5.73)	110-150	81.4	0.92	37.8	0.93	3525	0.000668
y-value/DDW (pH 5.73)	110-150	83.1	0.97	37.2	0.98	4755	0.000494
Y%/MIX (pH 5.60)	110-150	81.0	0.95	38.1	0.96	2029	0.001160
x-value/MIX (pH 5.60)	110-150	83.4	0.96	37.0	0.97	4360	0.000540
y-value/MIX (pH 5.60)	110-150	82.1	0.99	37.7	0.99	4252	0.000552

Color formation is related to the chemical reaction of of glycine and glucose resulting in the formation of colored compounds and hence E_a or z can be related to the kinetic parameter defining the loss of these compounds from the system. In the case of the mixture, the relative amount of energy and reaction rates are similar for the three measures of color development, while in the system containing glucose and glycine alone, only the x and y chromaticity coordinates behave in a similar fashion. Color development is in fact slower (requiring more energy) in the distilled water system, since Y% is known to be a more sensitive measure of darkening, while x and y are related to the location of the color in the color space. This indicates that the color is not only being formed but is also shifting in a consistent fashion in the color space in both systems, but that the darkening is slower in the glucose/glycine system. The fact that the Maillard reaction is relatively more difficult to carry out in water than in the presence of ascorbic acid can be explained by the fact that ascorbic acid is known to play a role in non enzymatic browning (Birch and Parker, 1974). Considering the very rapid rate of ascorbic acid degradation in the

mixture, it is likely that ascorbic acid, rather than glucose is the main reactant for the formation of the brown pigment measured.

The analysis of color formation using the Minolta CIE transmission system in relation to reaction kinetics has not been done before, although some studies have been carried out using the Lab Hunterlab reflectance system (Burton, 1963). It is clear that all three parameters, Y%, x and y follow first order reaction kinetics, can be interpreted kinetically and are related to the disappearance of ascorbic acid, glucose and glycine. The direct connection between reaction kinetics and the quality factor, color, is a useful concept and quantifies both the quality attribute and Maillard reaction kinetics simultaneously, although it does not allow one to pinpoint which components are actually reacting. Other than the work of Stamp and Labuza (1983) on the browning reaction of dry (a_w = 0.8) aspartame/glucose and glycine/glucose powders, for which they obtained E_a values of 67.8-94.6 kJ/mole, there is little to draw upon in terms of literature comparisons to our model system. Related research involving other food systems has been carried out, including the work by Herrmann (1970) on non-enzymatic browning in apple juice at 37.8-130 ^{0}C (E_a value ranges of 87-113 kJ/mole and z value 25-30.6 C^{0}), for goats milk by Burton (1963) (E_a = 113 kJ/mole and z = 25 C^{0}) and for the discoloration diced potatoes (E_a= 108.8-154.8 kJ/mole) by Hendel et al. (1955). The basic conclusion from this portion of our study is that the color formation reaction can be characterized kinetically using the CIE system in the transmission mode and serve as a basis for obtaining kinetic data useful for predictive thermal process calculations.

4.6 Summary of Kinetic Data

The kinetic data describing the model food system composed of ascorbic acid, thiamine, glucose and glycine has been determined experimentally by both the Arrhenius and TDT methods using ampoules and capillaries. The capillary system, which was assessed to determine whether smaller volumes and greater heat transfer rates would give better results were not significantly different. The purpose of

obtaining the kinetic data was for its subsequent use in assessing predictive thermal processing models capable of describing the behavior of our "model food system" and verifying the resulting predictions. In the process of analyzing the kinetic data, the relationship between the TDT and Arrhenius methods was re-examined and a physical interpretation conceptualized and developed as relationships became apparent. A new ratio, E_a/z was defined and tested as a tool to holistically characterize and compare the kinetics of a reaction, however it was not found to have the desired "characterizing" properties. In the ensuing section, the Arrhenius and TDT relationship will be examined in detail and its validity determined mathematically independent of our own experimental data.

4.7 Conversion of Kinetic Parameters

4.7.1 Perspective

There is no guidance in the literature on how to select T_1 or T_2 in equation [9] for the purpose of converting E_a to z or vice versa. Equation [9] indicates that there are infinite number of combinations of E_a and z values which can satisfy the relationship. Although E_a and z values are assumed to be temperature independent (equations [4] and [8]), the two parameters are related by temperatures T_1 and T_2 in equation [9]. Lund (1975) noted that the two concepts were reconcilable over small temperature ranges where T could be considered to be proportional to 1/T. Choosing reference temperatures of 121.1°C (250°F) and 98.9°C (210°F) for T_1 and a temperature of z degrees lower for T_2, Lund (1975) used equation [8] to generate a curve relating E_a to z. A series of similar curves relating E_a to z for several reference temperatures (80-130°C) are presented in Figure 25 with Lund's plot (110°C, symbol Δ) matching the data for a reference temperature of 110°C (230°F) which is the average of the two temperatures used in his illustration. Equation [9] also implies that if z is constant over a temperature range, then E_a cannot be a constant in that temperature range and vice versa. Assuming that the kinetic behavior is perfectly described by one system (i.e., TDT), the other cannot be valid theoretically because its constant becomes a variable dependent on the reference temperature and the temperature range. However, as has been demonstrated by numerous investigators over the past 80 years, no single

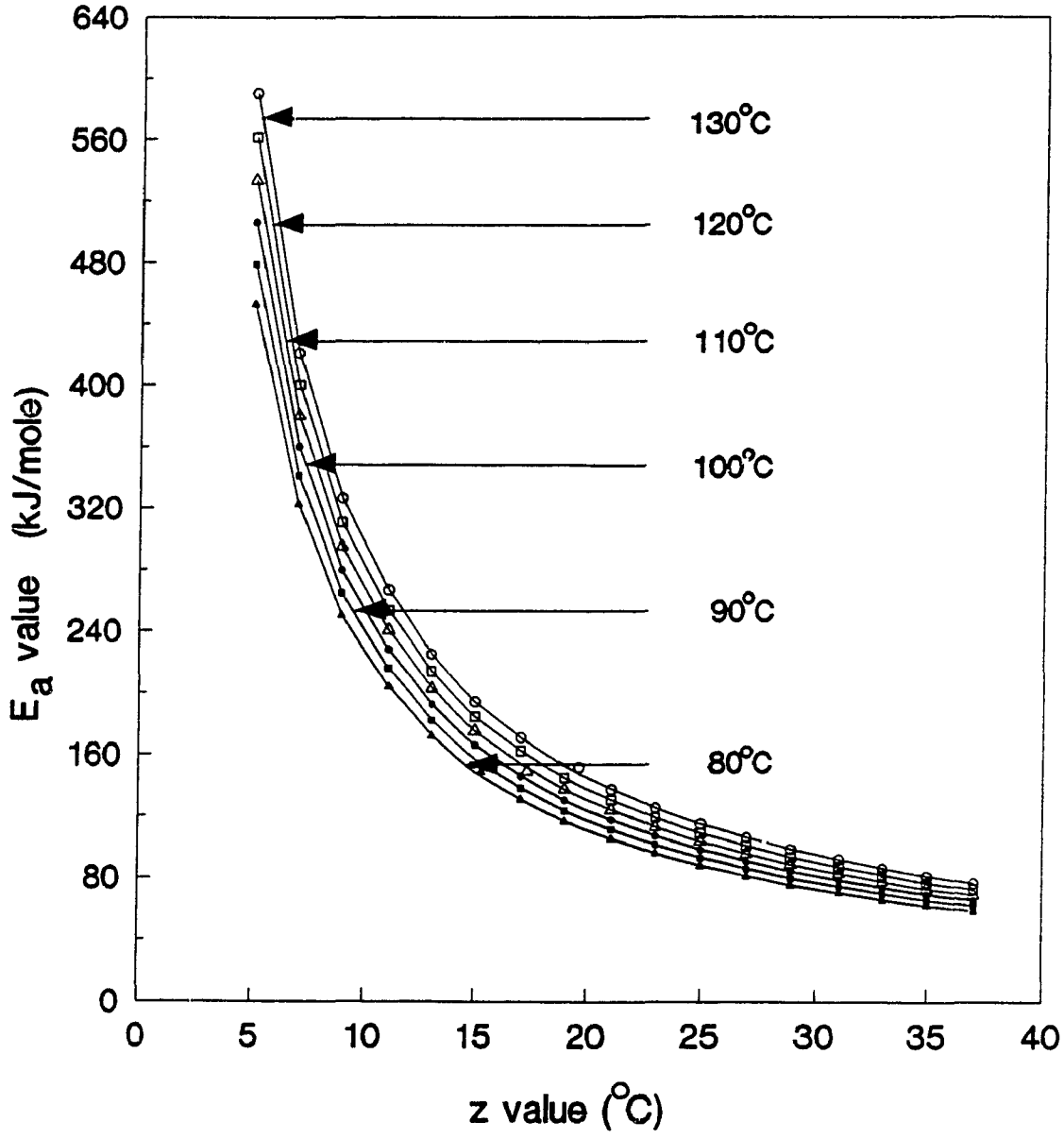


Figure 25. Relationship between E_a and z at selected reference temperatures.

theoretical model for thermal degradation can explain all the experimental observations (Cleland and Robertson, 1985), with both TDT and Arrhenius methods having been shown to be good and/or poor models for experimental data. The results of the present study also confirms the same general conclusion.

Using the regression approach for obtaining values of E_a and z, the influence of reference temperature and temperature range on E_a and z are summarized in Table 13, which demonstrates that conversion of E_a to z or vice versa is strongly influenced by the associated reference temperature and the temperature range. As the reference temperature changes from 80°C to 130°C, the base E_a and z values shift from the base values of 239 kJ/mole and 7.5 C^o to 311 kJ/mole and 9.8 C^o respectively. Similarly, a change in the temperature range from 10 to 50 C^o results in a change in E_a and z values from 311 kJ/mole and 9.8 C^o to 280 kJ/mole and 8.8 C^o, respectively, signifying the importance of both reference temperature and the temperature range in any conversion of E_a to z or vice versa.

Table 13. Influence of reference temperature and temperature range on E_a and z, and their conversions[1].

Temperature °C	E_a[2] kJ/mole	$U_{EQ[9]}$	$U_{EQ[29]}$	z[3] C^o	$U_{EQ[9]}$	$U_{EQ[29]}$
Reference[4]						
80	239	0.823	1.000	7.5	0.823	1.000
90	253	0.871	1.000	7.9	0.867	0.996
100	267	0.920	1.001	8.4	0.922	1.003
110	281	0.969	1.000	8.8	0.966	0.996
120	296	1.021	1.000	9.3	1.020	1.000
130	311	1.073	1.000	9.8	1.075	1.002
Range[5]						
10	311	1.073	1.000	9.8	1.075	1.002
20	303	1.045	0.999	9.5	1.042	0.997
30	295	1.019	1.000	9.3	1.020	1.002
40	288	0.992	1.000	9.0	0.987	0.996
50	280	0.964	1.000	8.8	0.966	1.001

[1] $U_{EQ[9]}$ and $U_{EQ[29]}$ are calculated from equations [9] and [29], respectively
[2] Based on a constant z of 10 C^o
[3] Based on a constant E_a of 318 kJ/mole.
[4] Based on a constant temperature range of 5 C^o (± 2.5 C^o)
[5] Based on a constant reference temperature of 135°C

The results in Table 13 also show that the estimated $U_{EQ[9]}$ values (0.82 to 1.08) differ considerably from unity implying poor conversions of E_a to z values using equation [9]. The deviations were dependent on both the selected reference temperature and the temperature range. Conversions were accurate only within the temperature limits assumed (reference temperature, 121.1°C and a temperature range equal to z value of 10 C°).

4.7.2 The Temperature Range Approach

Based on the concepts developed above relating E_a and z, we concluded that the temperature range is a key factor in relating the two constants and therefore the upper and lower limits of the experimental temperature range were be employed as substitutes for T_1 and T_2. Rewriting equation [9] we obtain:

$$E_a = 2.303\ R\ T_{min}\ T_{max}\ /\ z \qquad [29]$$

where:

T_{min} = lower limit of the temperature range
T_{max} = upper limit of the temperature range

The accuracy of E_a to z conversions using the equation [29] can be evaluated as discussed previously using deviations from unity of the factor $U_{EQ[29]}$ as defined below:

$$U_{EQ[29]} = E_a\ z\ /\ (2.303\ R\ T_{min}\ T_{max}) \qquad [30]$$

Conversion of E_a to z data presented in Table 13 using equation [29] consistently yielded a $U_{EQ[29]}$ value very close or equal to 1.0 under all conditions, justifying the $T_{min/max}$ approach.

The next step in testing the efficacy of the conversion capability of our relation was through the use of published kinetic parameters from the literature and converting their data, including the details of regression analyses and calculated $U_{EQ[9]}$ and $U_{EQ[29]}$ values (Table 14). The results indicated that the kinetic behavior described by both TDT and Arrhenius models are comparable (R^2 values ranging from 0.959 to a high 1.000) and that the equation [29] gives excellent conversion of E_a to z values, with $U_{EQ[29]}$ values essentially equal to unity. However, as before, the $U_{EQ[9]}$ values showed considerable scatter from unity indicating the limitation of equation [9], especially at temperatures other than the selected reference. These results indicate that if the temperature region for kinetic data is known, E_a and z values can be interconverted with confidence to obtain average values in the range. When the E_a to z conversions were made initially using the literature values of kinetic parameters reported by Lund (1975), the calculated $U_{EQ[29]}$ values varied markedly from 0.65 to 1.29. It was later discovered that these specific discrepancies were due to values presented in Lund's table which were at variance with the values from the original literature (Table 14). Furthermore, it was apparent from the computed $U_{EQ[9]}$ values from Lund's data that some E_a or z values might have been obtained from equation [9] rather than the original experimental data.

Based on our own experimental data similar comparisons were made producing similar results (Table 15).

These results indicate that the use of the temperature range is the key factor in interconverting E_a to z and vice versa, for our own and literature data. This indicates that Lund was on the right track in his analysis of the relationship between the two systems, however he did not recognize that it was the range that was the key factor and this relation only becomes apparent when working with the two systems simultaneously. Lund based his discussion on the basis of the proportionality of T and 1/T over a small temperature range, but left the choice of temperatures ambiguous, the results then being variable based on the reference temperature chosen. Hence if one chooses to run a process at a different temperature,

depending on whether the Arrhenius or TDT method were the basis of calculation, the unknown (z) would vary accordingly.

As discussed earlier, Lund's relation leads to the incongruity of two "constants" becoming variables depending on which system is chosen as the measuring vehicle. Based on logic, if both are constants, they cannot be variables. We have selected E_a as the true constant because the preponderance of the evidence indicates that in the temperature range 0-500^{o}K, E_a has consistently been shown experimentally in most reacting systems to be immune to temperature dependence. This is not the case for z, which has been applied almost exclusively to microbial (mainly spore) destruction which is notoriously difficult to measure (most probable number method) with a similar degree of accuracy that well defined chemical reactions have been. Lund did not favor either one of the kinetic measuring systems, but only tried to rationalize the two on a mathematical basis.

Our decision to select E_a as the true constant, makes z a variable of temperature, but can be approximated to a constant within small temperature ranges. This decision along with the subsequent refinement of Lund's relation by determining that the temperature range is the sole combination of T and T_1 which provides a correct conversion, provides a means of obtaining z values for other temperature ranges. The only equation which is valid according to our analysis is:

$$z = 2.303R\,(T_{max} \cdot T_{min})/E_a \qquad [31]$$

and its inverse is not applicable, since E_a is considered the constant. Using this equation, z can be calculated unambiguously for any temperature (< 500^{o}K) in the case of chemical reactions but is limited in the microbiological context to temperatures which arrest growth and reproduction.

Table 14. Kinetic parameters for various food components and their inter-conversion accuracies. [1]

Component	Temperature range (°C)	z (C°)	R^2	E_a kJ/mole	R^2	$U_{EQ[9]}$	$U_{EQ[29]}$
S. uvarum[2]	35-52	5.2	0.998	366	0.998	0.648	0.992
Thiamine (aqueous)[3]	109-149	25.0	0.998	123	0.998	1.104	0.996
Thiamine (carrot)[3]	109-149	26.0	1.000	119	0.999	1.108	0.997
Thiamine (bean)[3]	109-149	25.9	1.000	119	1.000	1.112	1.001
Thiamine (pea)[3]	109-149	26.2	0.999	118	0.998	1.114	1.002
Thiamine (spinach)[3]	109-149	26.1	0.997	118	0.993	1.109	0.998
Thiamine (beef heart)[3]	109-149	26.1	0.998	119	0.998	1.113	1.001
Thiamine (beef liver)[3]	109-149	25.9	0.999	119	0.996	1.108	0.997
Thiamine (lamb)[3]	109-149	26.6	0.999	116	0.998	1.112	0.999
Thiamine (pork)[3]	109-149	26.9	1.000	115	0.998	1.113	0.999
Thiamine peas-brine[4]	104-132	34.0	0.978	88	0.961	1.094	1.017
Thiamine peas-vacuum[4]	104-132	31.9	0.995	92	0.996	1.070	1.000
Peroxidase[5]	82-91	13.8	0.999	179	1.000	0.861	0.999
Staph. toxin B[6]	99-127	26.0	0.998	110	0.997	1.026	1.000
Betanin (pH 7)[7]	25-75	66.5	1.000	30	0.998	0.779	0.995
Betanin (pH 5)[7]	25-75	45.2	1.000	44	0.998	0.754	1.000
Chlorophyll a[8]	127-149	50.0	1.000	64	1.000	1.225	0.984
Chlorophyll b[8]	127-149	101.6	1.000	32	1.000	1.464	1.000
IMP[9]	53-121	19.6	1.000	126	0.999	0.871	1.000
GMP[9]	53-121	20.1	0.994	123	1.000	0.873	1.002
AMP[9]	53-121	19.5	1.000	126	0.994	0.872	1.002

[1] $U_{EQ[9]}$ and $U_{EQ[29]}$ are calculated from equations [15] and [30], respectively
[2] Manji and van de Voort (1985)
[3] Feliciotti and Esselen (1957)
[4] Bendix et al. 1951
[5] Ramaswamy and Ranganna (1981)
[6] Read and Bradshaw (1967)
[7] von Elbe et al. (1974)
[8] Gupte et al. (1964)
[9] Shaous and Sporns (1987)

Table 15. Kinetic parameters from present studies and their inter-conversion accuracies[1].

Sample Description	Method	Temperature Range (^{o}C)	E_a (kJ/mole)	R^2	z (C^{o})	R^2	$U_{EQ[9]}$	$U_{EQ[29]}$
AA/DDW (pH 4.05)	Ampoule (4 mL)	110-150	78.6	0.96	39.4	0.96	1.158	0.999
AA/MIX (pH 5.60)	Ampoule (4 mL)	110-150	14.6	0.98	212.8	0.98	1.160	1.001
B1/DDW (pH 4.11)	Ampoule (4 mL)	110-150	118.0	0.96	26.4	0.95	1.163	1.004
B1/MIX (pH 5.60)	Ampoule (4 mL)	110-150	71.1	0.99	43.8	0.98	1.163	1.003
Y%/DDW (pH 5.73)	Ampoule (4 mL)	110-150	102.3	0.97	30.2	0.98	1.154	0.995
Y%/MIX (pH 5.60)	Ampoule (4 mL)	110-150	81.0	0.95	38.1	0.96	1.152	0.994

[1] $U_{EQ[9]}$ and $U_{EQ[29]}$ are calculated from equations [15] and [30], respectively

4.7.3 Implications on Process Time Predictions

There are specific implications related to process predictions associated with the concept of making E_a to z and vice versa conversions based on the use of Lund's equation without proper reference to the temperature range. Process times are based on achieving a desired level of sterility usually represented by a F_o value corresponding to a selected reference temperature. Different temperature/time combinations can be employed to achieve any desired level of sterility and the process time (t) at any temperature (T) can be obtained based on a F value (F_r) at a reference temperature (T_r) by the following relation:

$$t_{(TDT)} = F_r\, 10^{(T_r-T)/z} \qquad [32]$$

The parallel relationship using the Arrhenius method is:

$$t_{(ARH)} = F_r \exp\left[-(E_a/R)\,(1/T_r - 1/T)\right] \qquad [33]$$

Any discrepancy between the two methods can thus be determined by calculating a relative sterilization ratio [$t_{(TDT)}/t_{(ARH)}$ ratio or its reciprocal (Cleland and Robertson, 1985)] and the ratio can be used to compare the two techniques for an ideal or "square" process in which the product is raised instantaneously to the process temperature at time zero and cooled instantaneously at the end of the process.

Table 16 summarizes the relative sterilization ratios for ideal processes at various reference and process temperatures based on a z value of 8.5 C^o and an E_a value of 343 kJ/mole in the temperature range of 111-125^{o}C (*B. stearothermophilus* reported by Jonsson et al., 1977). The results indicate that within the actual temperature range of calculated z and E_a values, the discrepancy between the two methods is only $\pm$ 4%, but when using a broader processing temperature range of 105 to 135^{o}C, the discrepancy can reach $\pm$ 23% depending on the reference temperature and which parameter (TDT or Arrhenius) is used as the basis for the analysis. The relative sterilization ratios, calculated on the basis of kinetic parameters given in Table 14 for the respective temperature ranges, varied from 0.94 to 1.06 for ascorbic acid and 0.9 to 1.1 for *S. uvarum*. These results indicate that within the temperature range in which the kinetic parameters were calculated, the TDT and Arrhenius approaches produce reasonably similar results. There is insufficient proof in the literature to suggest which of the two methods is a better predictor of a process. For process holding time calculations, Manji and van de Voort (1985) found the Arrhenius technique was a better indicator of process times, although they concluded that the differences observed may not be of any practical significance in process calculations. Figure 26 shows the variation in the relative sterilization ratio over a broader process temperature range of 50-135^{o}C based on average z

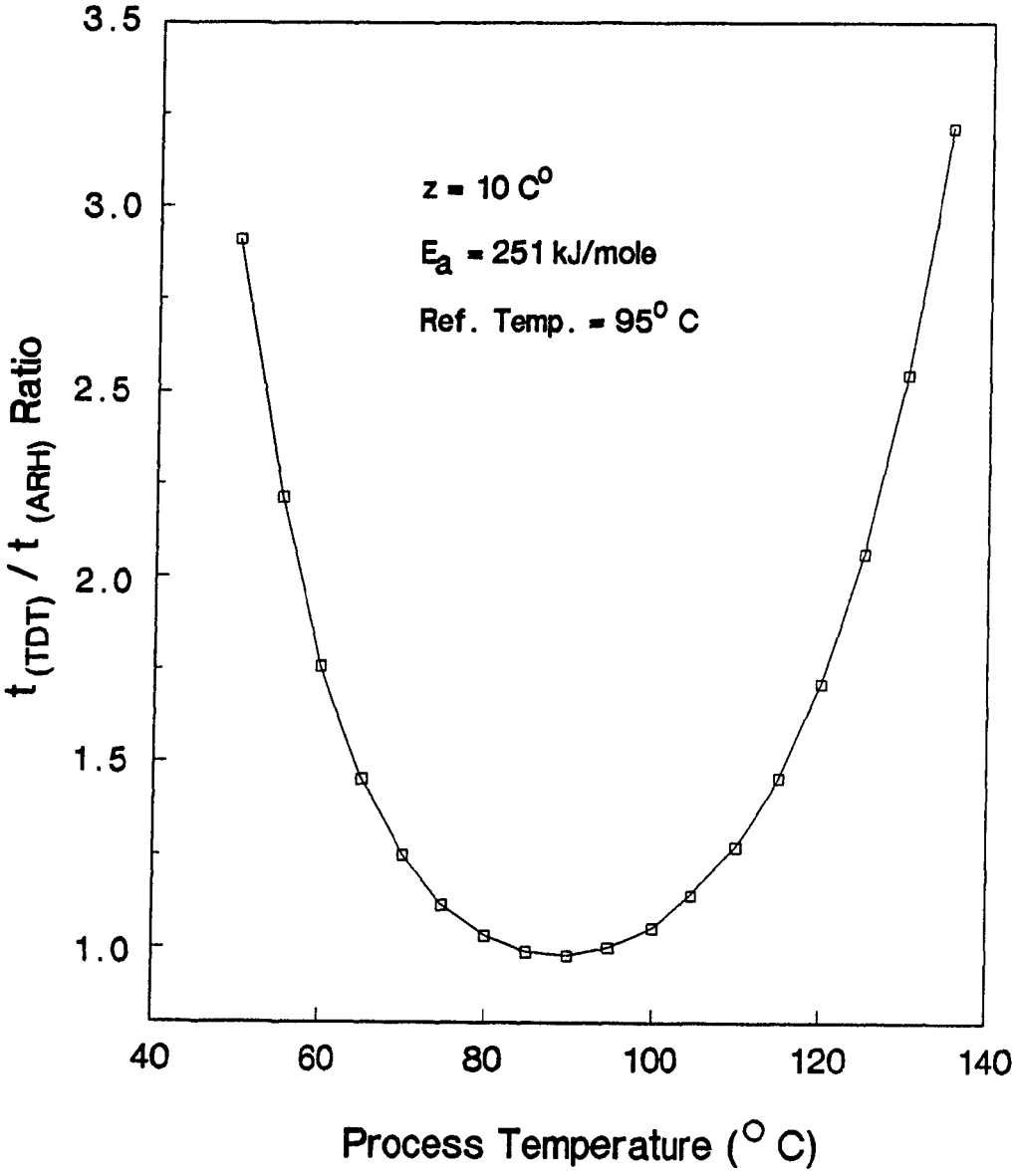


Figure 26. Relative sterilization time [$t_{(TDT)}/t_{(ARH)}$] as influenced by process temperatures using kinetic parameters at the mid-temperature (95°C).

(10 C^0) and E_a (251 kJ/mole) and a midpoint reference temperature (95°C) which demonstrates that the discrepancy between the TDT and Arrhenius methods increases as the process temperature deviates from the reference with sterilization ratios as high as 2.2 to 3.2 at the two extreme temperatures. Furthermore, should the kinetic parameters from either end of the range be the base for calculating relative sterilization ratios, the discrepancy between the two methods increases dramatically as process temperatures deviate from the reference (Figure 27 using an E_a value of 318 kJ/mole at 135°C).

Table 16. Relative sterilization ratios [$t_{(TDT)}/t_{(ARH)}$] for ideal processes (E_a = 343 kJ/mole, z = 8.5 C^0)

Process Temp (°C)	Reference Temp (°C) 105	110	120	125	135
105	1.00	1.07	1.11	1.07	0.90
110	0.93	1.00	1.03	1.00	0.84
115	0.90	0.97	1.00	0.96	0.81
120	0.90	0.97	1.00	0.97	0.82
125	0.93	1.00	1.04	1.00	0.85
130	1.00	1.07	1.11	1.07	0.91
135	1.11	1.19	1.23	1.18	1.00

The TDT method gave longer process times than the Arrhenius method for processes below the reference temperature with the converse being observed at processes above the reference temperature, resulting in a sterilization ratio as large as 165. It is important to recognize that the possibility of large errors exist because processes such as UHT sterilization and accelerated shelf-life testing are carried out at temperatures well beyond the range in which the original kinetic data were obtained. Further, in actual practice, the product within a container can not be heated or cooled instantaneously and in these real processes where temperature changes with time, the lethal effects of temperature have to be integrated

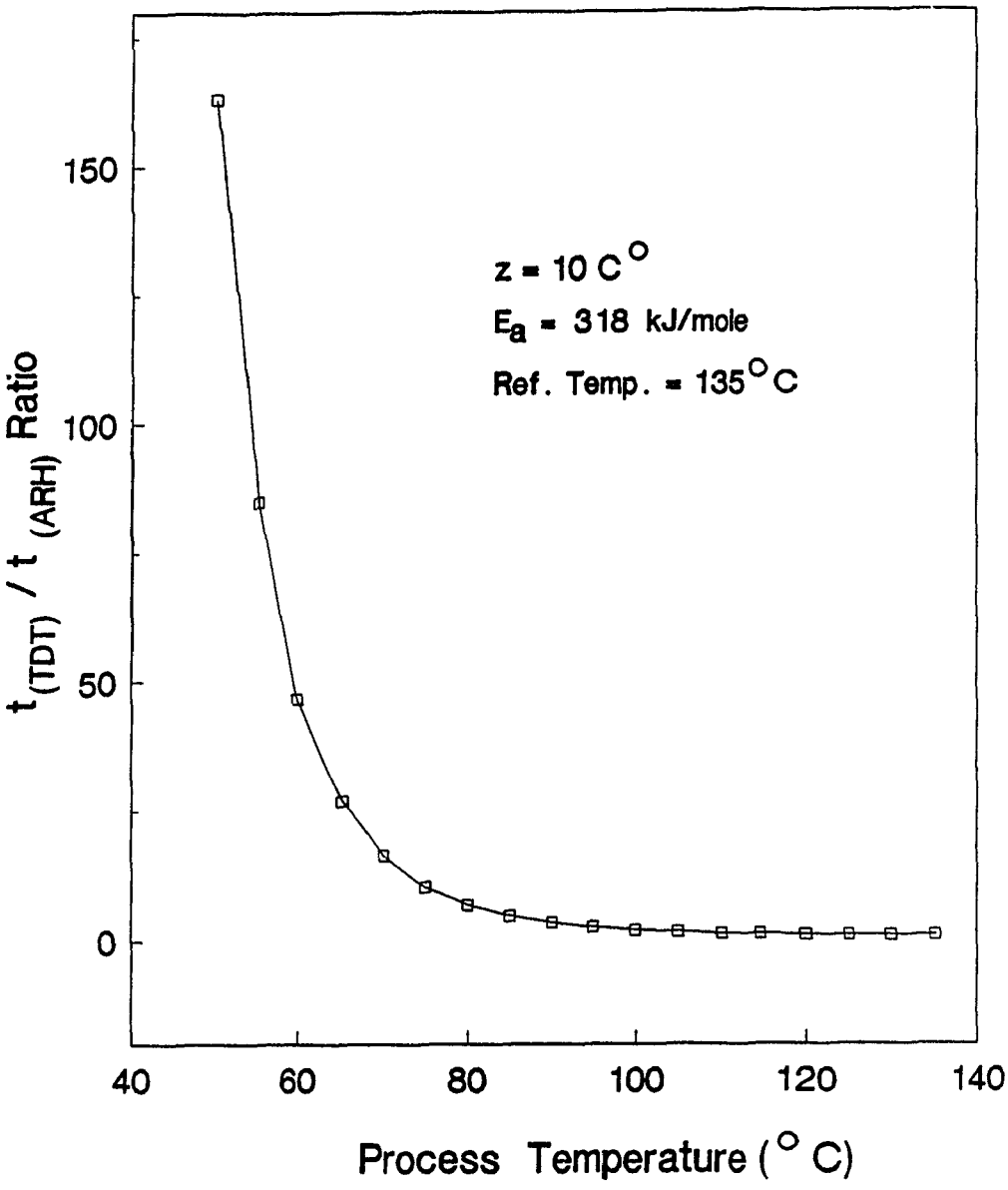


Figure 27. Relative sterilization time [$t_{(TDT)}/t_{(ARH)}$] as influenced by process temperatures using kinetic parameters at an end temperature (135°C).

with respect to time and location. These situations are more complicated than the ideal case, usually involving a wider temperature span and have been shown to result in larger discrepancies between the two approaches to process kinetics (Cleland and Robertson, 1985). The experimental determination of kinetic data on the basis of the Arrhenius kinetic theory and the subsequent conversion of E_a to z based on equation [31] for each temperature would provide appropriate z values for the calculation of the process, which should eliminate the discrepancy between the two techniques.

4.8 Summary of Kinetic Conversions

The determination of z and E_a can be carried out accurately from the original kinetic data by regression of log (D) vs T or log (k) vs 1/T. This procedure automatically defines the range and conditions under which kinetic data were obtained. In cases where such detailed information is not readily available, Lund's approach to conversion is limited by an arbitrary selection of a reference temperature and a range, both of which have been shown to influence the conversion result. By obtaining E_a and defining the temperature limits over which kinetic data were obtained, the z value can be calculated and the changes in z assessed by keeping E_a constant and deriving new z values for the temperature range or each specific temperature. This determination was initially carried out independently of our own experimental data to avoid limiting any conclusions solely to our experimental situation. The implication of the analysis presented is that conversion of factors from one system to the other outside the temperature limits over which the original data were obtained can lead to major discrepancies because only one of the two constants can in fact be a constant independent of temperature range, as indicated mathematically by trying to relate a linear function (TDT) to an asymptotic function (Arrhenius). Hence, for mechanistic reasons (i.e., the form of the functions) using temperature limits other than under which the original kinetic data were obtained will necessarily result in values which can deviate from those obtained experimentally, regardless of which kinetic factor is considered the true constant. These conclusions and the potential of defining z for individual temperatures over a process are

important and fundamental to understanding the relationship of the two kinetic models, and to making the most effective use of their predictive capabilities.

4.9 Conduction Heating

4.9.1 Heating Characteristics of Celite

The thermal characteristics of the model conduction system using the test solutions incorporated into celite showed a characteristic unbroken conduction heating behavior during thermal processing (Figure 28) and its heat penetration characteristics are summarized in Table 17. The f_h values for celite retorted in 211 x 400 cans at selected temperatures ranged from 25.0 to 30.3 min with a mean value of 26.9 min and a standard deviation of 1.56 min, while the f_c values during cooling in water ranged from 33.9 to 36.6 min, with a mean value of 35.1 min and a standard deviation of 1.55 min. The mean values of the heating rate lag factor (j_h) and the cooling rate lag factor (j_c) were 2.22 and 2.66, respectively. For more detailed information and results related to the heat penetration parameters the reader is referred to Appendix [4].

Table 17. Heat penetration parameters for the celite food model.

Parameter	Mean[1]	SD	CoV
Heating rate index (f_h), min	26.86	1.56	6.0
Cooling rate index (f_c), min	35.12	1.55	4.4
Heating rate lag factor (j_h)	2.22	0.0759	3.5
Cooling rate lag factor (j_c)	2.66	0.0688	2.6

[1] based on 96 observations; SD = Standard deviation; CoV = Coefficient of variation (%)

An average thermal diffusivity (α) was calculated the factors presented above using equation [16]:

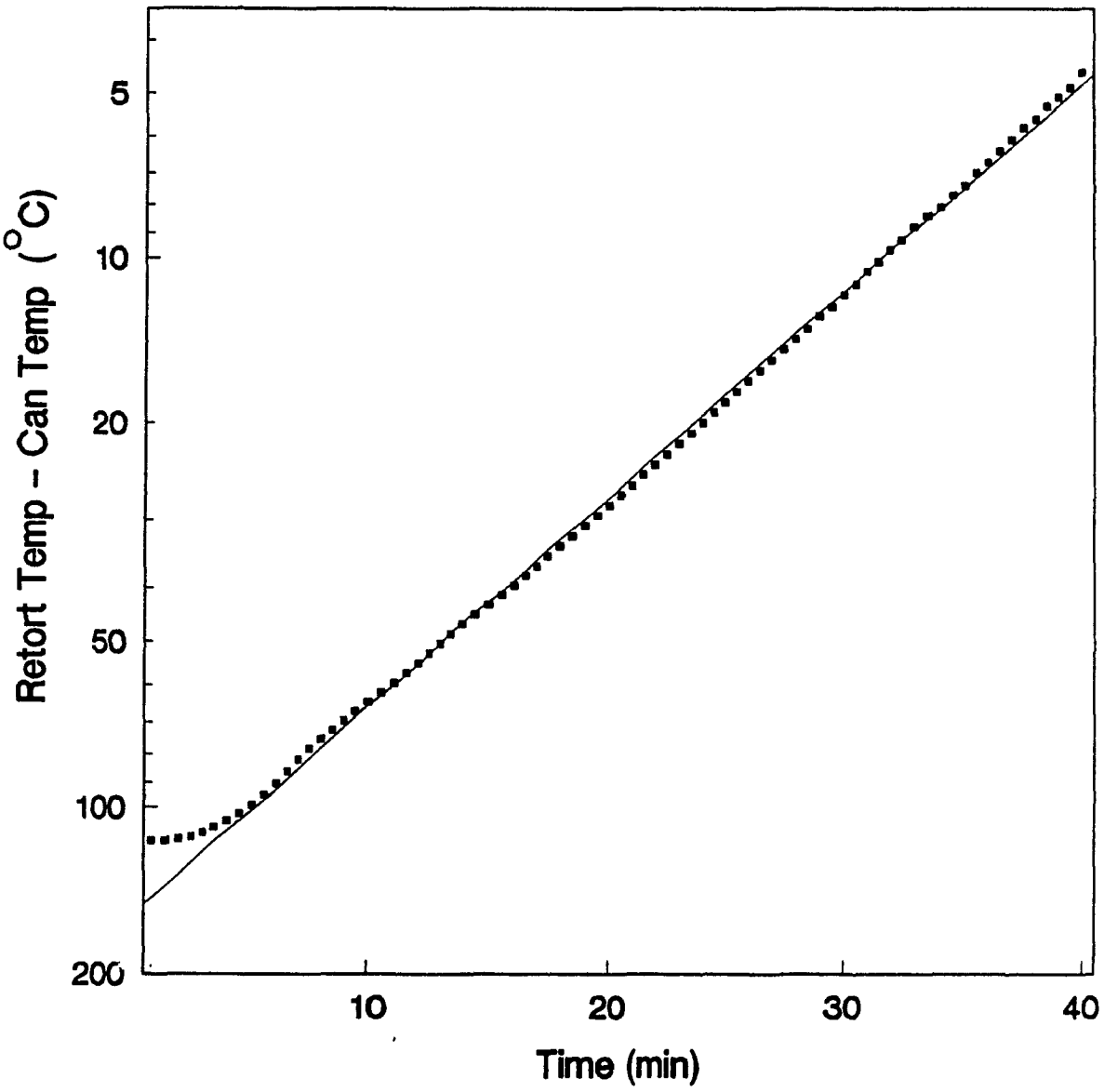


Figure 28. Typical heat penetration curve for a can filled with celite.

$$\alpha = 0.398/[f_h(1/a^2+0.427/L^2)] \quad [16]$$

where a and L are the radius and half the height of the can, respectively. Employing the inside diameter of the can (6.5 cm) and the actual fill height (9.5 cm), the mean thermal diffusivity value of the celite sample was calculated to be 2.06×10^{-7} m^2/s. This diffusivity value was somewhat higher than the range normally associated with more common conduction heating foods (Mohsinin, 1980) and is be considered more characteristic of a pureed food product (Mulley et al., 1975b).

4.9.1.1 Recovery Characteristics

The celite model permitted the dispersion of the nutrient medium in the test can from which it could subsequently be recovered (Table 18). The mean recovery of ascorbic acid from the celite preparation prior to processing was 91.5% with a coefficient of variation of 0.35% (n=32). The marginal loss of about 8.5% ascorbic acid was of minor concern since the test values following processing were always compared with the ascorbic acid content of unheated (control) samples. The recovery of the nutrient following heat treatment was also consistent with a maximum coefficient of variation of 6% (Appendix [5]) between the triplicate samples within each experimental condition.

When thiamine was studied in the same manner, the mean recovery prior to processing was only 30.6% with a coefficient of variation of 3.06% (n=32). The loss of about 69.4% thiamine was a problem because at these low recovery levels (30.6%) prior to heating and the 8% coefficient of variation (Appendix [6]), left little room for obtaining accurate results, as the relative error increases for subsequently lower recoveries following the thermal treatment. Analyses however were carried out in the hope that some useful data would result as we could not change our formulation at this stage of the work. Experiments carried out later on, indicated that for concentrations above 0.8g/L, the nutrient recovery from the celite improved and stabilized (Table 19).

Table 18. Recovery (%) of ascorbic acid (AA/DDW) and thiamine (B1/DDW) from the celite food model prior to processing.

Recovery (%) of AA*	Recovery (%) of B1**
90.8	28.1
90.9	28.6
91.0	28.9
91.1	29.2
91.1	29.7
91.1	29.8
91.1	29.9
91.1	30.0
91.2	30.0
91.3	30.0
91.3	30.0
91.3	30.1
91.3	30.1
91.4	30.4
91.4	30.4
91.4	30.4
91.4	30.4
91.4	30.5
91.4	30.7
91.4	30.8
91.5	30.9
91.6	30.9
91.6	31.0
91.6	31.1
91.7	31.4
91.7	31.6
91.7	31.7
91.8	31.9
91.9	32.1
91.9	32.2
92.0	32.4
92.0	32.5

* based on average original concentration of ascorbic acid of 0.9970 g/L.
** based on average original concentration of thiamine of 0.0999 g/L.

Recovery of AA from Celite		Recovery of B1 from Celite	
Number of Observation=	32	Number of Observation=	32
Mean Recovery (%)=	91.5	Mean Recovery (%)=	30.6
CoV =	0.35	CoV =	3.06

Table 19. Recovery (%) of thiamine (B1/DDW) from the celite food model prior to processing.

Original B1 Concentration (g/L)	Recovery (%) of B1/DDW
0.0999	30.59
0.1999	57.47
0.3998	77.67
0.7996	88.81
1.1994	89.94
1.5992	91.44
1.9990	91.48
2.3988	91.46
2.7986	91.36
3.1984	91.52
3.5982	91.43
3.9980	91.49

In terms of color, celite did not affect the reaction medium either before or after browning had been induced independently of celite. Passing the solution which had browned through celite did not cause any measurable changes to the chromaticity coordinates (%Y, x,y), however once actual processes were carried out, it was observed that a brown pigment was present in the celite, lighter in the center and darkening toward the can walls, being more apparent with more severe processes. It was clear that some of the pigment formed was adhering to or trapped in the celite and the assumption was made that this loss might be be consistent enough to provide a good relative measure of the color formation in the product.

4.9.2 Quality Factor Retention in Celite

Ascorbic acid retention in celite was studied using the two systems, alone in distilled water and as a mixture including thiamine, glucose and glycine. The retention results following processing at various retort operating temperatures over the range of 110.0 to 126.7^{o}C are shown as a function of heating time in Appendix [7], and Figures 29 and 30 respectively. In both systems, within the range of experimental conditions, ascorbic acid retention was found to decrease linearly with time at each temperature, and as indicated by the steeper slopes of their regression lines, the temperature effect was more pronounced at

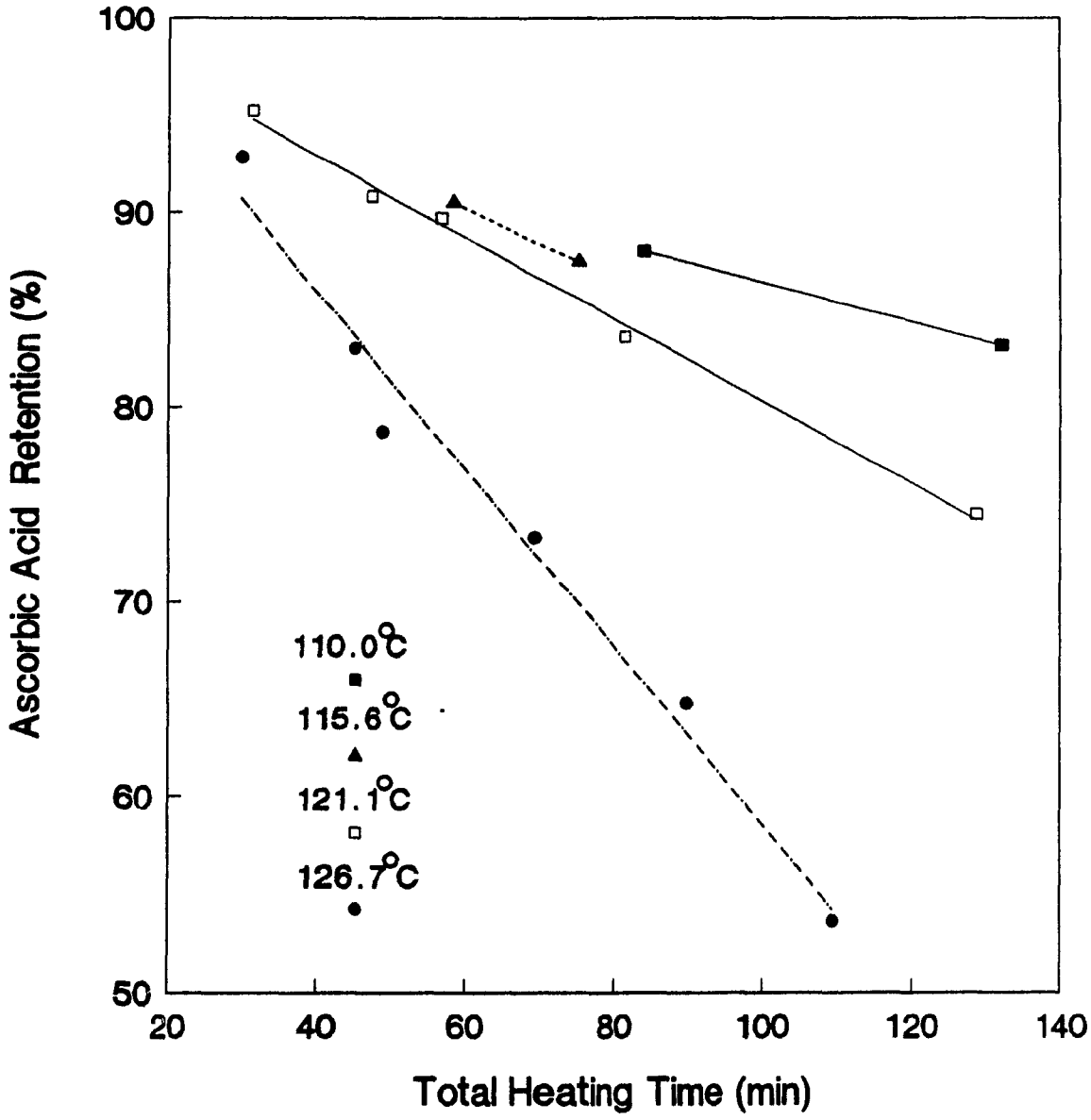


Figure 29. Ascorbic acid retention in celite following thermal processing for various periods at selected temperatures (AA/DDW system).

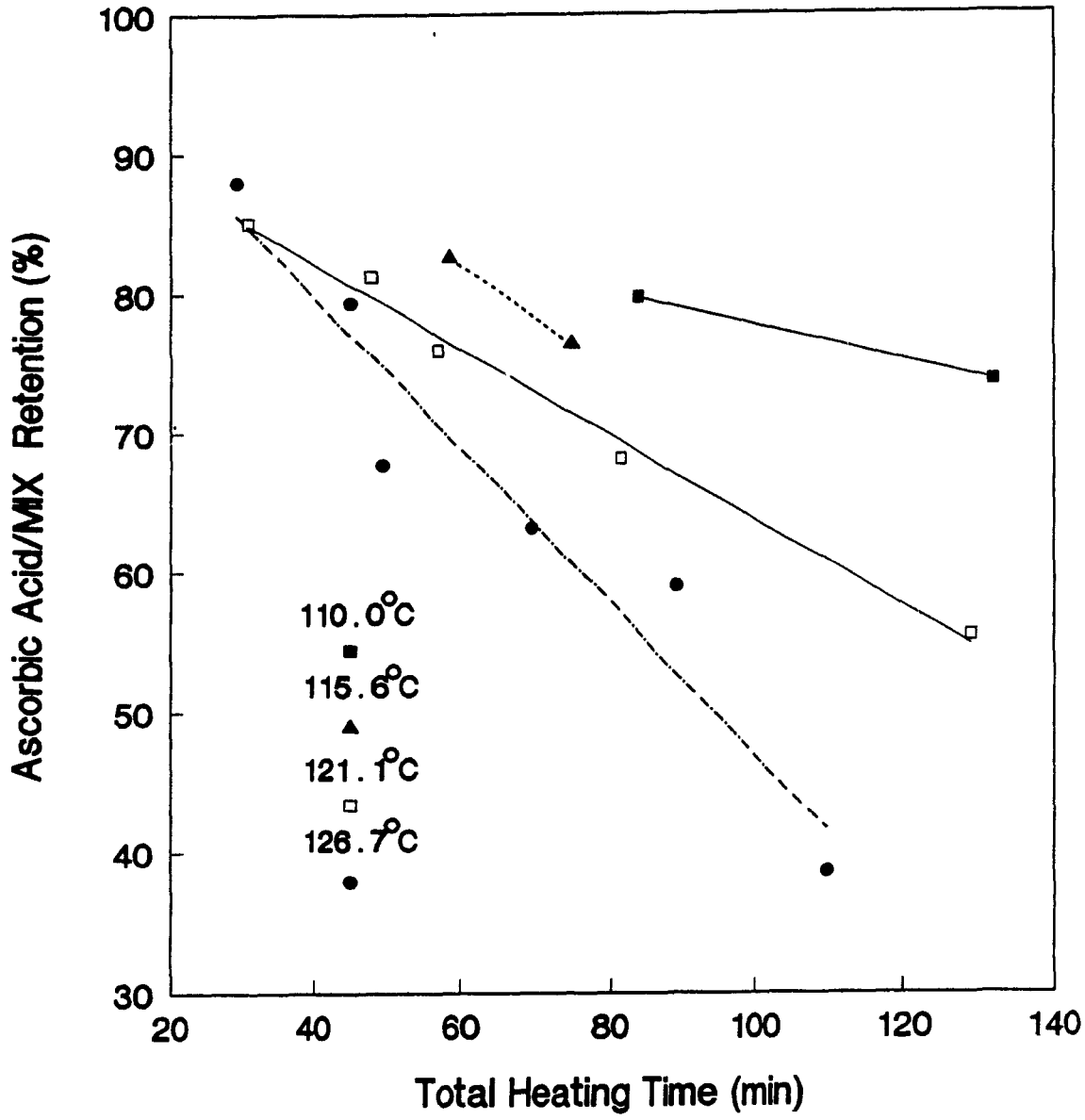


Figure 30. Ascorbic acid retention in celite following thermal processing for various periods at selected temperatures (AA/MIX system).

higher temperatures. The retention data also showed a somewhat larger scatter at higher processing temperatures. In order to compare the retention of ascorbic acid in these two systems following thermal processing, the retention data in both systems were plotted against the accumulated centerpoint lethality (based on $z = 10C^{0}$). As shown in Figure 31 (Appendix [8]), the ascorbic acid retention could be described as a linear function of accumulated process lethality alone ($R^2 = 0.93$, $p<0.05$) and as a mixture ($R^2 = 0.88$, $p<0.05$) systems. There was a progressive destruction of ascorbic acid process lethalities as increased and the retention was higher in the pure system than in the mixture. Following a given thermal process, ascorbic acid retention was found to be about 10% higher alone than in the mixture. These results are consistent with the trend of the kinetic data originally derived using the ampoules and capillaries.

Equivalent lethality process experiments, numbers 1 to 8, with their conditions listed in Table 1, were carried out to establish process conditions for optimizing the retention of ascorbic acid. In these experiments, the ascorbic acid retentions varied from 78.7 to 90.8% (Appendix [7]). For calculated lethalities of both 3 and 8 min, processing at the intermediate temperatures of 115.6 and 121.1^{o}C resulted in a slightly higher retention of ascorbic acid (Appendix [3]) than at the other temperatures. The resulting data however, was insufficient to determine an optimized thermal processing schedule for maximizing the retention of ascorbic acid. The higher processing times at 121.1 and 126.7^{o}C in the subsequent runs, with process lethalities substantially larger than normally employed in commercial applications, were primarily included for the purpose of estimating the severity of heat induced destruction of ascorbic acid. These results are shown in Figure 31 and the lethality-destruction relationship was estimated using a linear function, with the scatter in the data attributed to differences in the magnitude of nutrient destruction at different temperatures.

Color formation was measured for the glycine/glucose systems and the four component mixture after processing as a function of time over the operating temperature range of 110.0 to 126.7^{o}C (Figures 32, 33 and Appendix [9]). The color formation at a given temperature was linear, increasing with

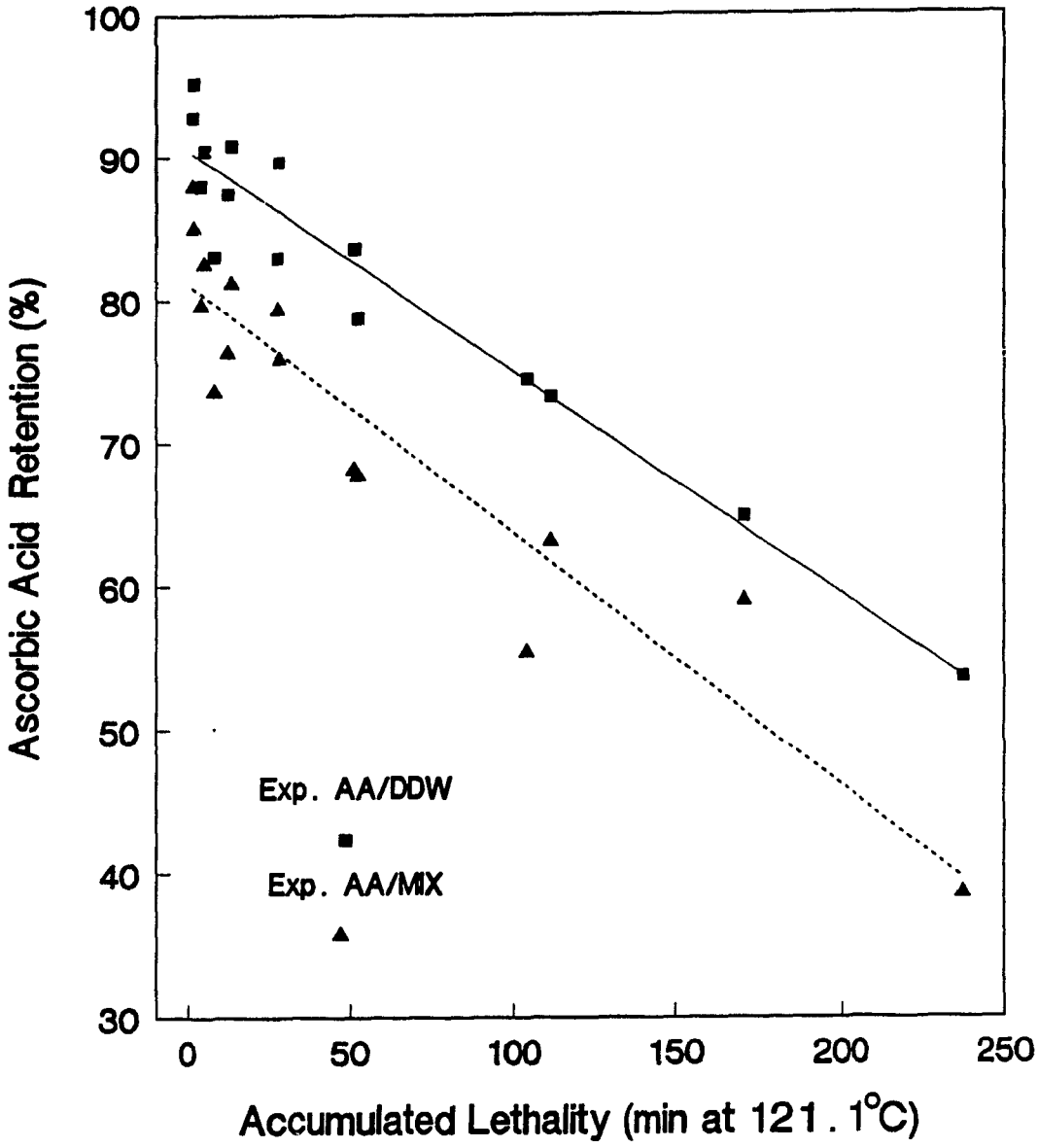


Figure 31. Ascorbic acid retention in thermoprocessed celite as a function of accumulated lethality.

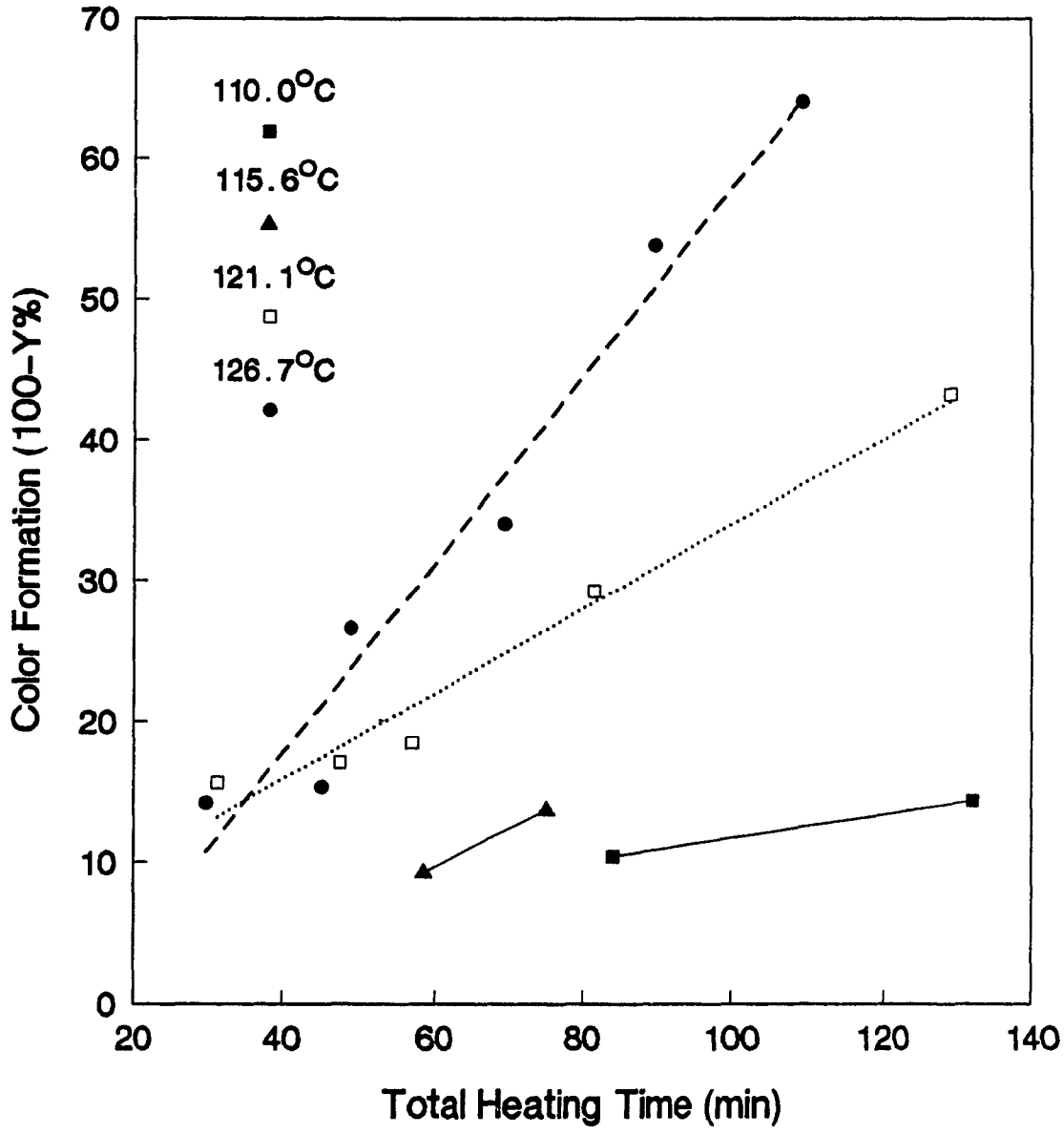


Figure 32. Color formation in celite following thermal processing for various periods at selected temperatures (Color/DDW system).

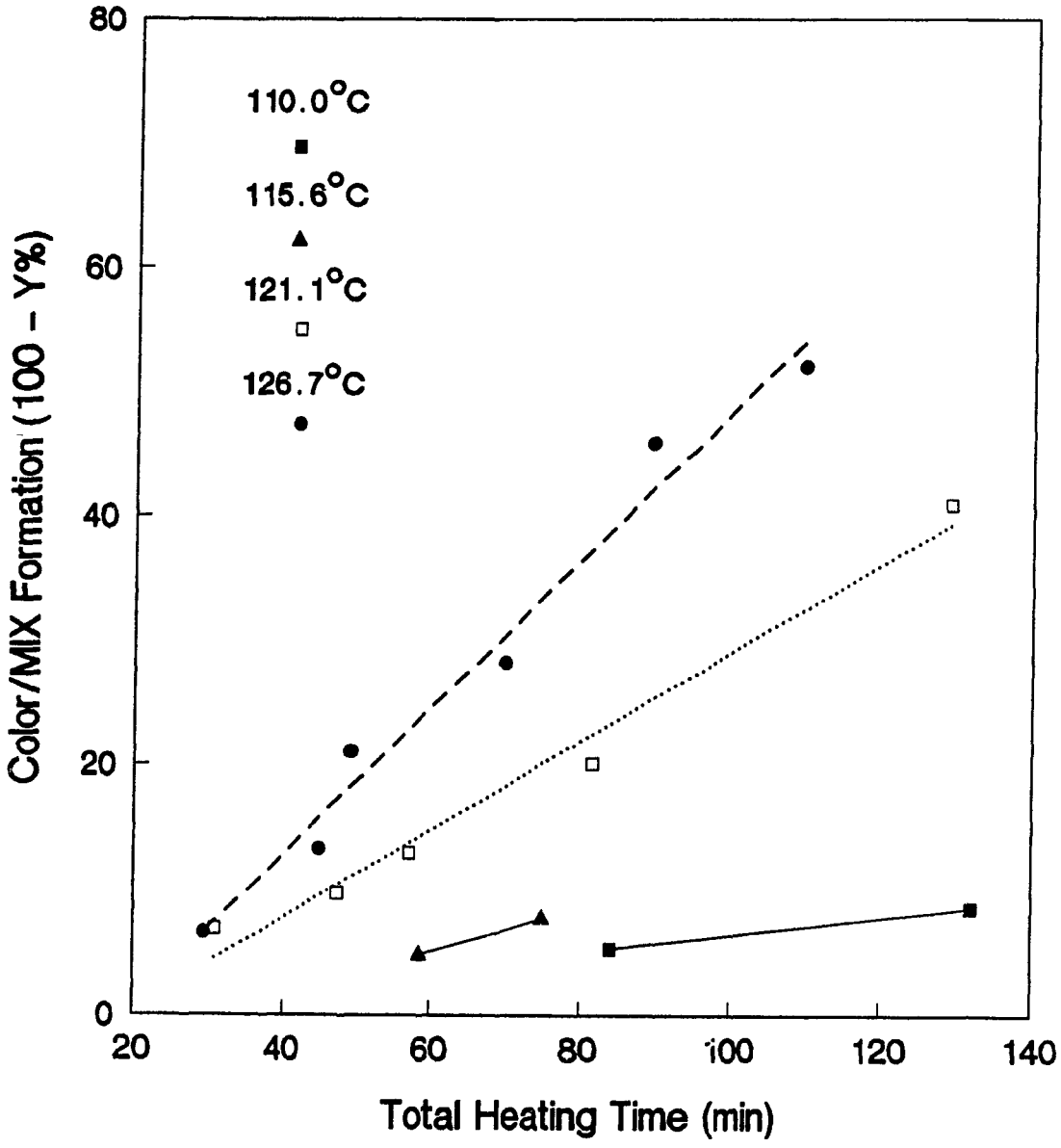


Figure 33. Color formation in celite following thermal processing for various periods at selected temperatures (Color/MIX system).

processing time and became much more pronounced at higher temperatures. The color formation was ~10% lower in the four component mixture than for the glucose/glycine system. The color formation-lethality relationships for both systems were also linear (R^2 = 0.96, $p<0.05$) and (R^2 = 0.94, $p<0.05$) respectively as shown in Figure 34 (Appendix [10]).

4.9.3 Centerpoint Nutrient Retention in Celite

The centerpoint retention of ascorbic acid and thiamine following thermal processing at three temperature-time combinations, 115.6°C for 80 min; 121.1°C for 50 min and 126.7°C for 30 min, are shown in Table 20. Four replicates were run of each sample at the three operating conditions and the results obtained had standard deviations ranging from 0.91 to 2.42% with an overall coefficient of variation of less than 3%, indicating that the technique for centerpoint nutrient determination was reproducible. Because of the small size of the stainless steel capsules, the high thermal conductivity of steel and the use of minute quantities (75 μL) of sample, the temperature within the capsule was assumed to be uniform and representative of the centerpoint temperature of the can. Since, it was not possible to simultaneously place a capsule and insert a thermocouple at the center of the same test can, temperatures were measured in separate cans undergoing the same process. A large number of replicates of temperature measurement tests were carried out in order to obtain reliable estimates of the heat penetration data for prediction of centerpoint temperature-times.

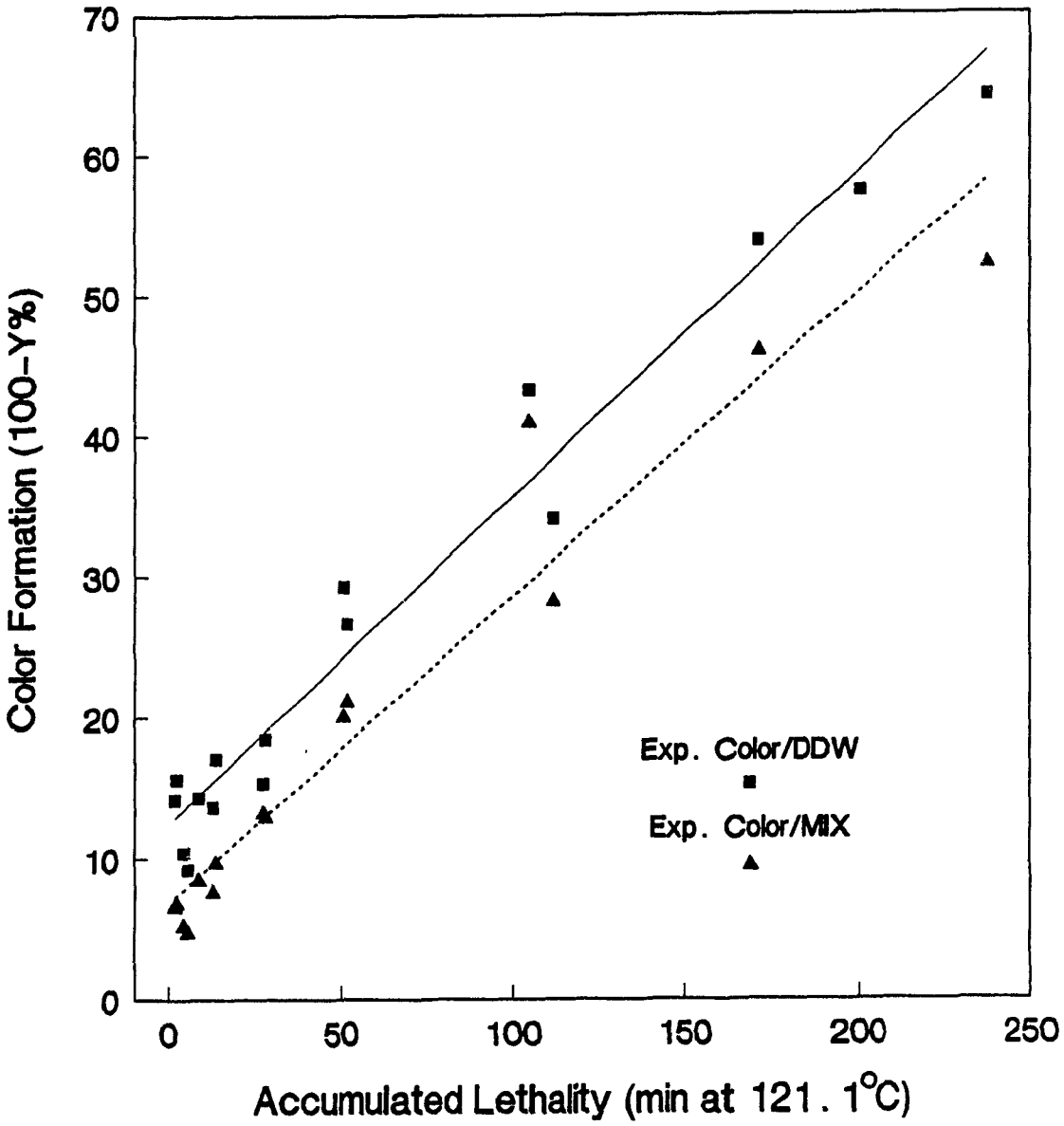


Figure 34. Color formation in thermoprocessed celite as a function of accumulated lethality.

Table 20. Centerpoint nutrient retention in a thermoprocessed food model.

Sample type	Capsule number	Centerpoint Nutrient Retention (%) Process Temperature, °C/(Time, min) 126.7 (30)	121.1 (50)	115.6(80)
AA/DDW	1	95.7	93.1	87.2
	2	97.5	96.0	82.6
	3	95.0	94.3	83.6
	4	97.5	94.1	84.6
	Mean	96.4	92.1	84.5
	SD	1.10	0.62	1.71
	CoV	1.14	0.67	2.03
B1/DDW	1	84.2	84.4	79.7
	2	86.6	88.2	84.7
	3	84.9	88.6	78.2
	4	85.8	88.9	81.5
	Mean	85.4	88.8	81.0
	SD	0.91	0.44	2.42
	CoV	1.06	0.49	2.99

SD = Standard deviation; CoV = Coefficient of variation (%)

4.10 Verification of Quality Factors for the Conduction System

4.10.1 Centerpoint Models (Ball, Teixeira)

Centerpoint nutrient retentions (100 - % destroyed), were determined employing our kinetic data, heat penetration parameters and processing conditions using three predictive models, Ball's original method, a modification of Ball's original method (Finnegan, 1984) and Teixeira's approach (Teixeira et al., 1969b). The predictions obtained by Ball's method and its modification were based on the computer program developed by Finnegan. Ball's model was based on the experimental heat penetration parameters, f_h and j_h with the assumption that $f_h = f_c$ and $j_c = 1.41$. Finnegan (1984) extended Ball's original method by including a hyperbolic function to predict the early portion of cooling

curve to determine the f_c and j_c values. Teixeira's approach is based on solving the heat transfer equation using a finite difference approximation and requires an f_h value and assumes that $f_h = f_c$.

A comparison of the experimental centerpoint nutrient retention results and the predicted values (Table 21) showed excellent agreement, with less than 4% discrepancy between experimental and predicted values for all models, with the exception of thiamine at 126.7°C. These processes were chosen to represent a high temperature process (126.7°C for 30 min), a more conventional process (121.1°C for 50 min) and lower temperature process (115.6°C for 80 min). Nutrient retention was highest for the higher temperature, shorter time process and decreased as temperatures dropped and time increased. All the models appear to provide similar predictions for the centerpoint retention value. The predicted values were based on centerpoint temperature-time response while the experimental values (Figure 35, Appendix [11]) were from test capsules placed at the centerpoint.

Table 21. Comparison of experimental centerpoint retention values with prediction from various models.

Particulars	Nutrient Retention, % (deviation, %) Process Temperature, °C		
	126.7	121.1	115.6
Ascorbic acid			
Experimental	96.4	92.1	84.5
Ball	97.2 (+0.8)	92.1 (0.0)	87.1 (+3.0)
Teixeira	95.9 (-0.5)	92.3 (+0.2)	87.9 (+3.9)
Finnegan	95.8 (-0.7)	90.1 (-2.2)	86.5 (+2.3)
Thiamine			
Experimental	85.4	88.8	81.0
Ball	96.7 (+11.7)	89.5 (+0.8)	83.2 (+2.6)
Teixeira	94.7 (+9.8)	89.7 (+1.0)	84.4 (+4.0)
Finnegan	95.0 (+10.1)	86.8 (-2.2)	82.2 (+1.4)

The temperature response in the small volume surrounding the centerpoint was assumed to be similar on the actual centerpoint temperature response, based to the geometrical symmetry associated with the transfer of heat toward the center. This assumption was tested mathematically using Teixeira's

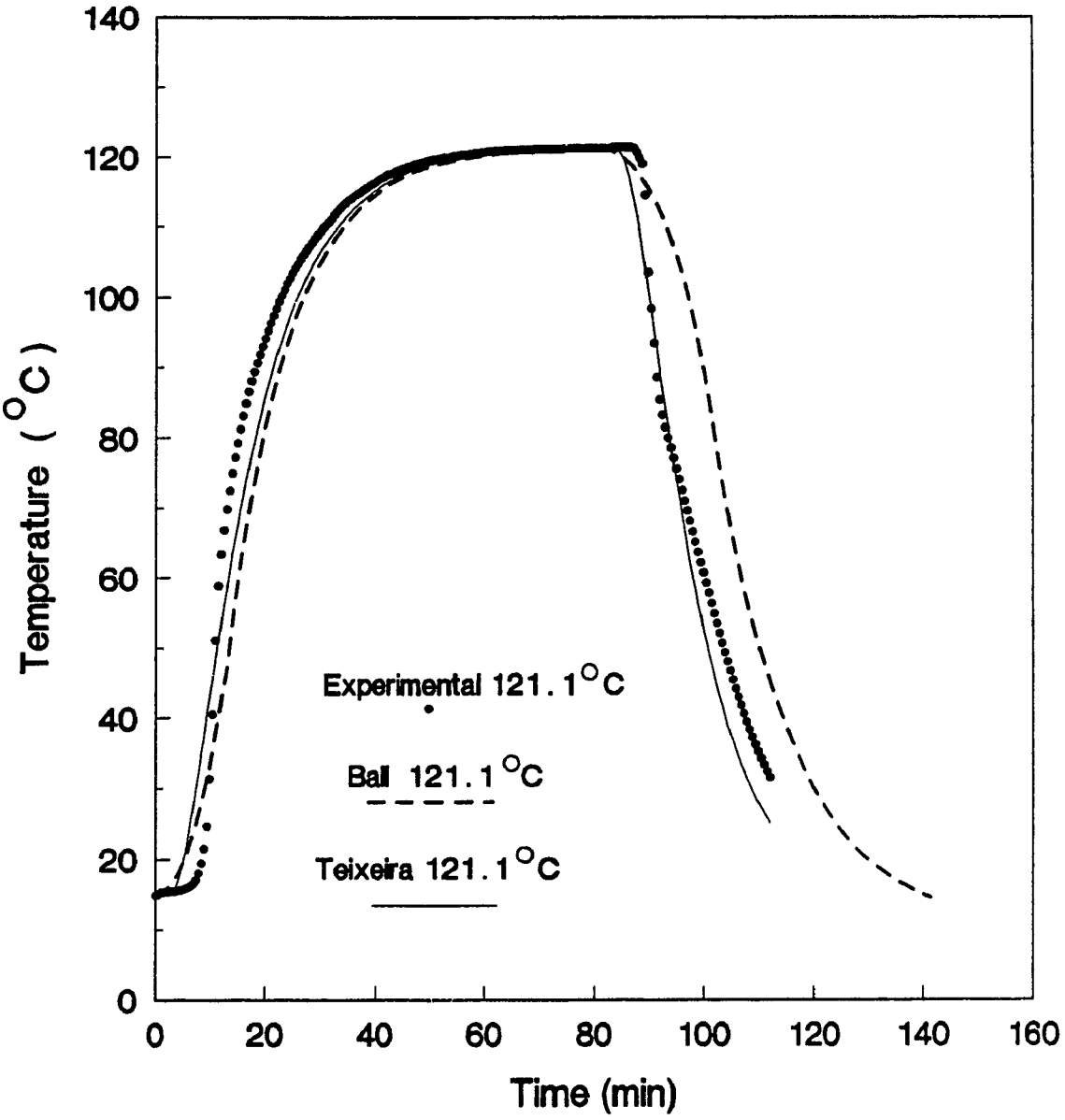


Figure 35. Comparisons of predicted versus experimental centerpoint temperature-time response at retort temperature of 121.1 °C.

finite difference program considering a 10 x 10 space grid for a can of radius 3.25 cm and 9.52 cm height. Based on these geometrical considerations, the size of the test capsule fits within the space occupied by the adjoining nodes in the radial and longitudinal directions. Temperatures at the center [T(NR, NH)] as well as the two other nodes [T(NR-1, NH), T(NR, NH-1)] were predicted using conditions matching one of the test runs (Table 22).

Table 22. Predicted nodal temperatures at the center and two adjoining nodes (radial and longitudinal) using Teixeira's program.

Time (min)	Nodal Temperature (^{o}C)		
	Central T(NR,NH)	Radial T(NR-1,NH)	Longitudinal T(NR,NH-1)
0	15.0	15.0	15.0
2	15.0	15.0	15.0
4	16.3	16.7	16.3
6	22.0	22.7	22.0
8	30.9	31.9	31.1
10	41.2	42.2	41.4
12	51.4	52.4	51.7
14	61.0	61.8	61.3
16	69.5	70.3	69.9
18	77.1	77.7	77.5
20	83.7	84.2	84.0
22	89.4	89.8	89.7
24	94.3	94.6	94.5
26	98.4	98.7	98.7
28	102.0	102.2	102.2
30	105.0	105.2	105.2
32	107.5	107.7	107.7
34	109.7	109.8	109.8
36	111.5	111.6	111.6
38	113.1	113.2	113.2
40	114.4	114.5	114.4
42	115.5	115.5	115.5
44	116.4	116.5	116.4
46	117.2	117.2	117.2
48	117.8	117.9	117.9
50	118.4	118.4	118.4

Retort Temperature, 121.1^{o}C; 10 x 10 spatial matrix, time step, 0.125 min.
(NR, NH): Radial and longitudinal nodal coordinates at the can center.

The results indicate that the maximum difference between the three temperatures were 1.0°C for the first 12 min of the process when the product temperature was below 60°C and ~0.2°C after 28 min onward. These small differences, especially after temperatures became higher, suggest that our assumption of similar temperatures for the capsule and centerpoint were valid.

4.10.2 The Modified Ball Method (Finnegan Program)

The centerpoint retention of ascorbic acid in the celite conduction system (DDW) based on 16 temperature/time processes (Table 1) were compared with the retention values (Figure 36) predicted by Finnegan's modification of Ball's original method using Finnegan's computer program and assessed by linear regression. A significant relationship (R^2 = 0.72; $p<0.05$) was found between the predictions and the experimental results and could be described by the following relation:

$$AA_{pre} = 0.939\ AA_{exp} + 1.22 \qquad [34]$$

where:

AA_{pre} = Ascorbic acid retention predicted by the model

AA_{exp} = Experimental ascorbic acid retention.

These comparisons are based on centerpoint destruction as predicted by Finnegan's model on the one hand and average destruction based on experimental values on the other. At the high process lethalities employed in the study, the difference between the centerpoint and average destruction can be expected to be small because the differences between the centerpoint temperature and distribution temperature will be minimal. Furthermore, as recognized by Lund (1975) the predicted retention values at the centerpoint serve as indicators of maximum of nutrient retention possible in any particular process.

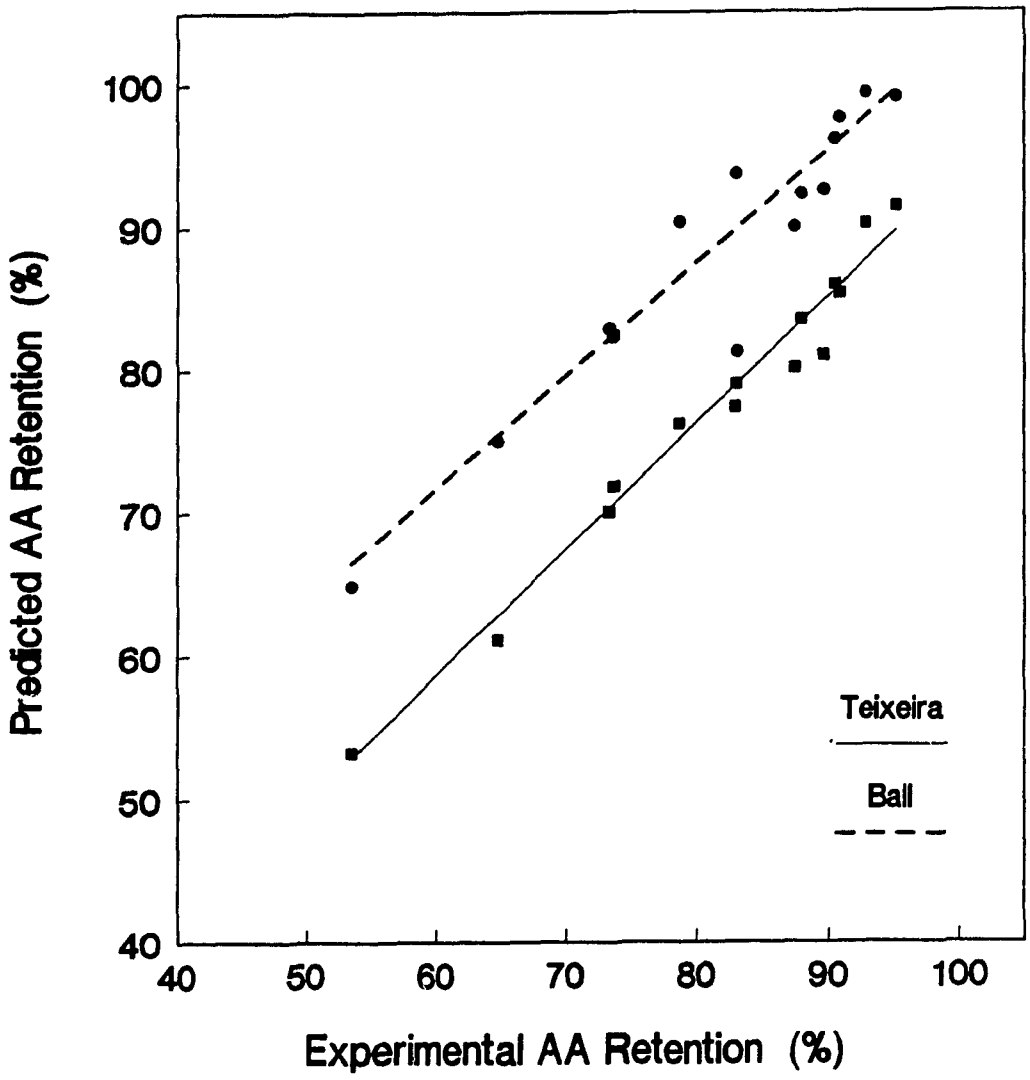


Figure 36. Comparisons of predicted versus experimental ascorbic acid (AA/DDW) retention in thermoprocessed cellte.

Color formation (100 -Y%) under the same conditions was also predicted according to Finnegan's model and program (Figure 37). The predictions relative to the experimental data as assessed by linear regression (R^2 = 0.74; $p<0.05$) indicated that the results were similar to those obtained for ascorbic acid and could be represented by the following relation:

$$Y\%_{pre} = 0.269\ Y\%_{exp} + 2.27 \qquad [35]$$

where:

$Y\%_{pre}$ = Color formation predicted by the model

$Y\%_{exp}$ = Experimental color formation.

4.10.3 The Teixeira Program

The retention of ascorbic acid (DDW) using the 16 temperature/time conditions as assessed by linear regression (R^2 = 0.94; $p<0.05$) compared well (Figure 36) and were significantly better than those predicted by the modified Ball method. The relation derived between the experimental and predicted data can be estimated by the following relation:

$$AA_{pre} = 1.107\ AA_{exp} - 10.04 \qquad [36]$$

As can be seen from Figure 36, the predicted ascorbic acid retention by Finnegan's model was about 20% higher. This discrepancy is a result of the Finnegan's predictions being based on the temperature at the slowest heating region of the can, while Teixeira's predictions are based on the temperature distribution throughout the can at any time better representing the true conditions.

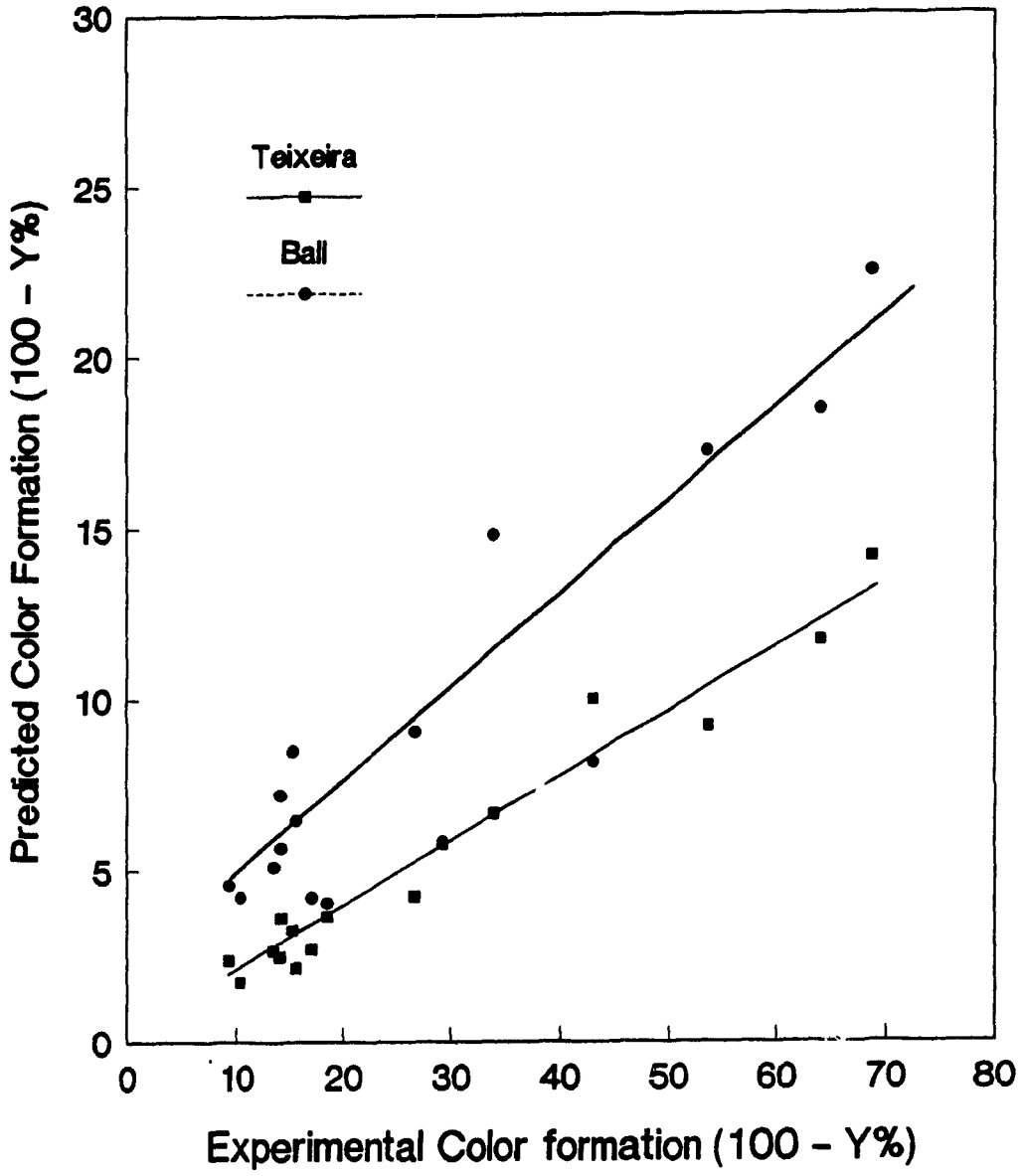


Figure 37. Comparisons of predicted versus experimental color formation (100 - Y%) in thermoprocessed cellite.

In the case of color (100 -Y%) similar results were obtained for Teixeira's predictions vs experimental results (Figure 37), the predictions were lower than the modified Ball method and the regression equation had an R^2 value of 0.94 ($p<0.05$) and was described by the following relation:

$$Y\%_{pre} = 0.189\ Y\%_{exp} + 0.199 \qquad [37]$$

Overall, it would appear that Teixeira's predictions are better than Ball's, especially in the cooling portion of the process.

4.10.4 Retentions vs Accumulated Lethalities

In order to validate Finnegan's and Teixeira's computer models in terms of lethalities, the experimentally determined retentions of the quality factors were compared with the predictions of these computer models. The predictions were based on the experimental kinetic parameters derived for nutrient retention and color formation, combined with the heat penetration parameters (i.e., f_h, f_c, j_h, j_c and the thermal diffusivity) for the 16 processes (Table 1). A complete table of Teixeira's predictions for ascorbic acid retention, thiamine retention, and color formation based on the kinetic parameters determined experimentally are presented in Appendix [12]. The experimental and predicted retentions were plotted against the accumulated lethality based on a z of 10°C for *Cl. Botulinum* (Figure 38). Based on linear regressions of retention vs lethality, Finnegan's and Teixeira's predictions are parallel to each other but differ in slope relative to the experimental data. This results in both models underpredicting at lower accumulated lethalities and overpredicting at higher lethalities. Over the whole lethality range, the predicted values from both models are roughly within 10% of the experimental data. Most processes accumulate lethalities of 100 min or less at 121.1°C, and under these conditions, the predictions are reasonable. Although less accurate, the higher lethalities were primarily included to assess the ability of these programs to predict more severe processes.

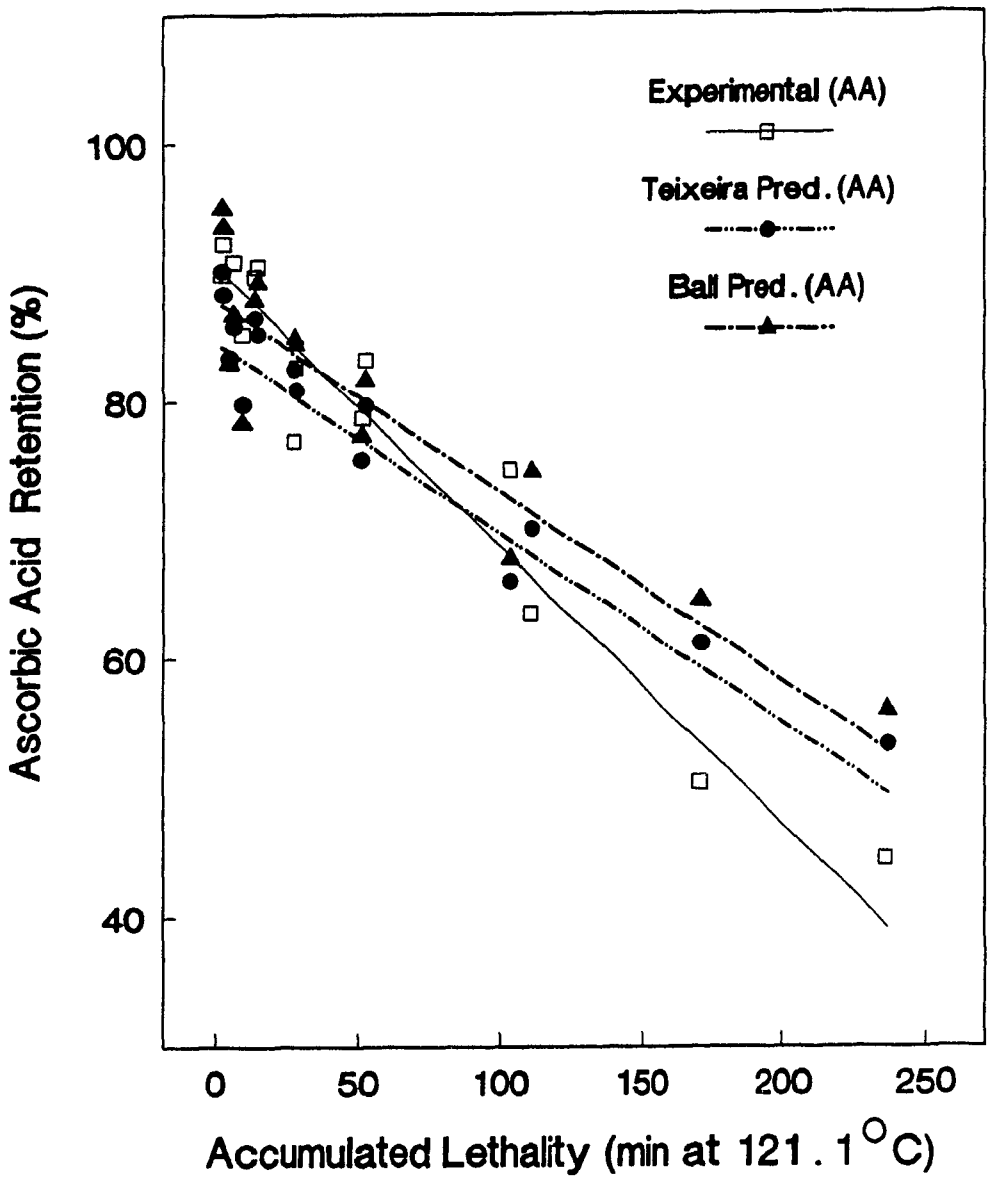


Figure 38. Comparisons of predicted and experimental ascorbic acid retention in thermoprocessed celite as a function of accumulated lethality.

Figure 39 shows the predictions of thiamine retention for the B1/DDW system from both computer models vs the accumulated lethalities also based on z = 10°C. Since the experimental thiamine retention values were inconsistent due to low recoveries, these experimental values were not used for comparison. Even without the comparison, however, the same parallel trend is observed and Finnegan's predictions are about 5% higher than Teixeira's as a result of using the centerpoint measurement as the basis for calculation.

The experimental and predicted results in terms of accumulated lethality for color development (100 - Y%) are presented in Figure 40. Color formation was considered linear, although the variability in the experimental results was much more than the predictions. The predictions for color are significantly different than the experimental data and are not representative, although once again Finnegan's predictions were higher as was the case for the calculated ascorbic acid and thiamine results. The poor concurrence of these results is attributed to the adherence of the color compounds to celite, resulting in less residual color being measured than is actually formed. The slope difference indicates that the rate of color formation is slower for the real system, which would be expected if more color were lost as a function of temperature. It is likely, based on the lethality results obtained for ascorbic acid, that the predictive values for color are in fact a better reflection of color formation than the actual experimental data.

4.11 Convection Heating

4.11.1 Kinetic Parameter Determinations

The basic kinetic data was gathered using ampoules and capillaries, however it was also of interest to determine the kinetic parameters directly from convection heating retort-processed cans. The retort TDT data was gathered in a manner similar to that of the ampoules, with the exception that for any one temperature, the retort had to be re-run for each sample, since it could not be opened and closed to recover additional samples without disturbing the process, a problem not encountered in the ampoule

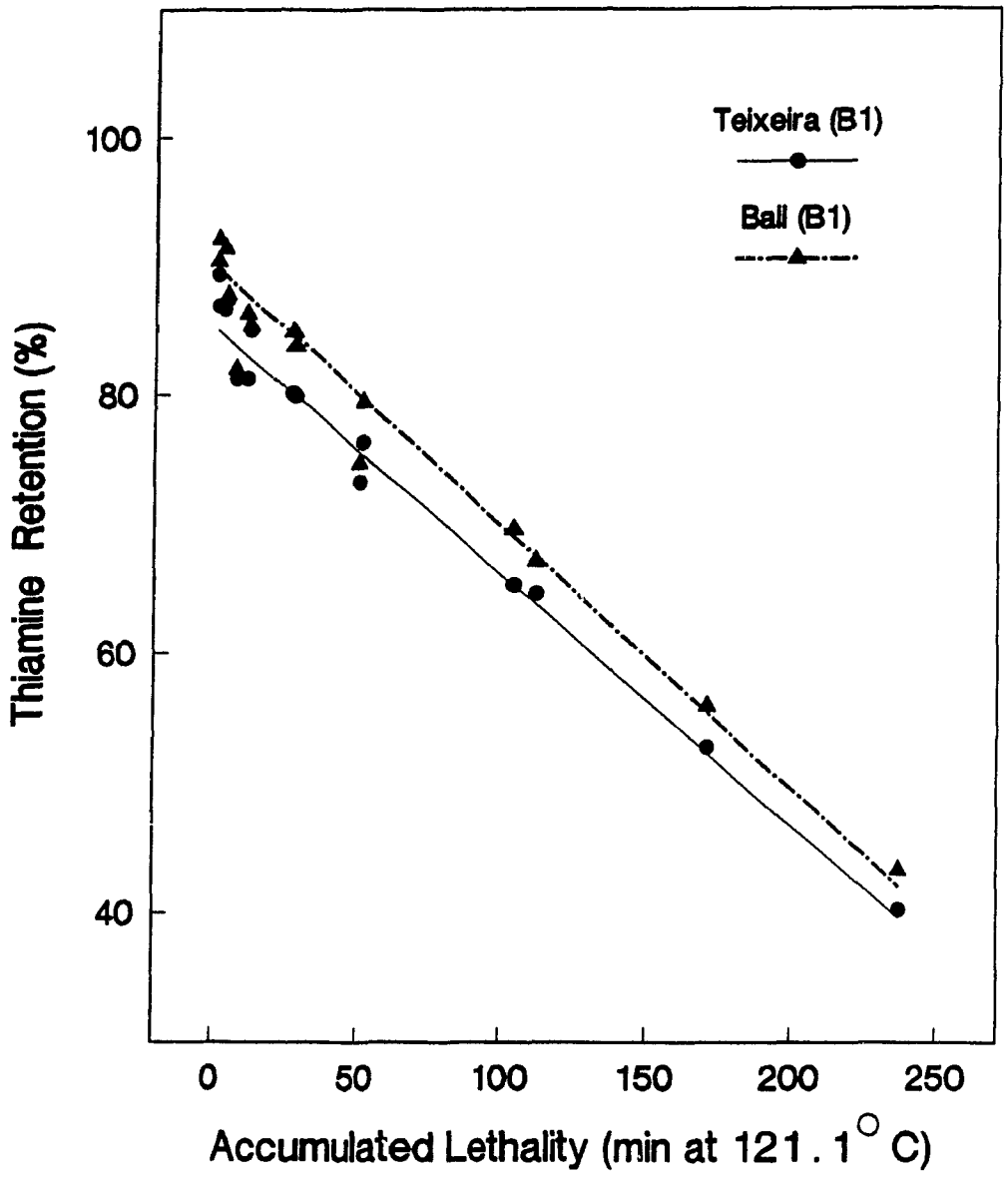


Figure 39. Predicted thiamine retention in thermoprocessed celite as a function of accumulated lethality.

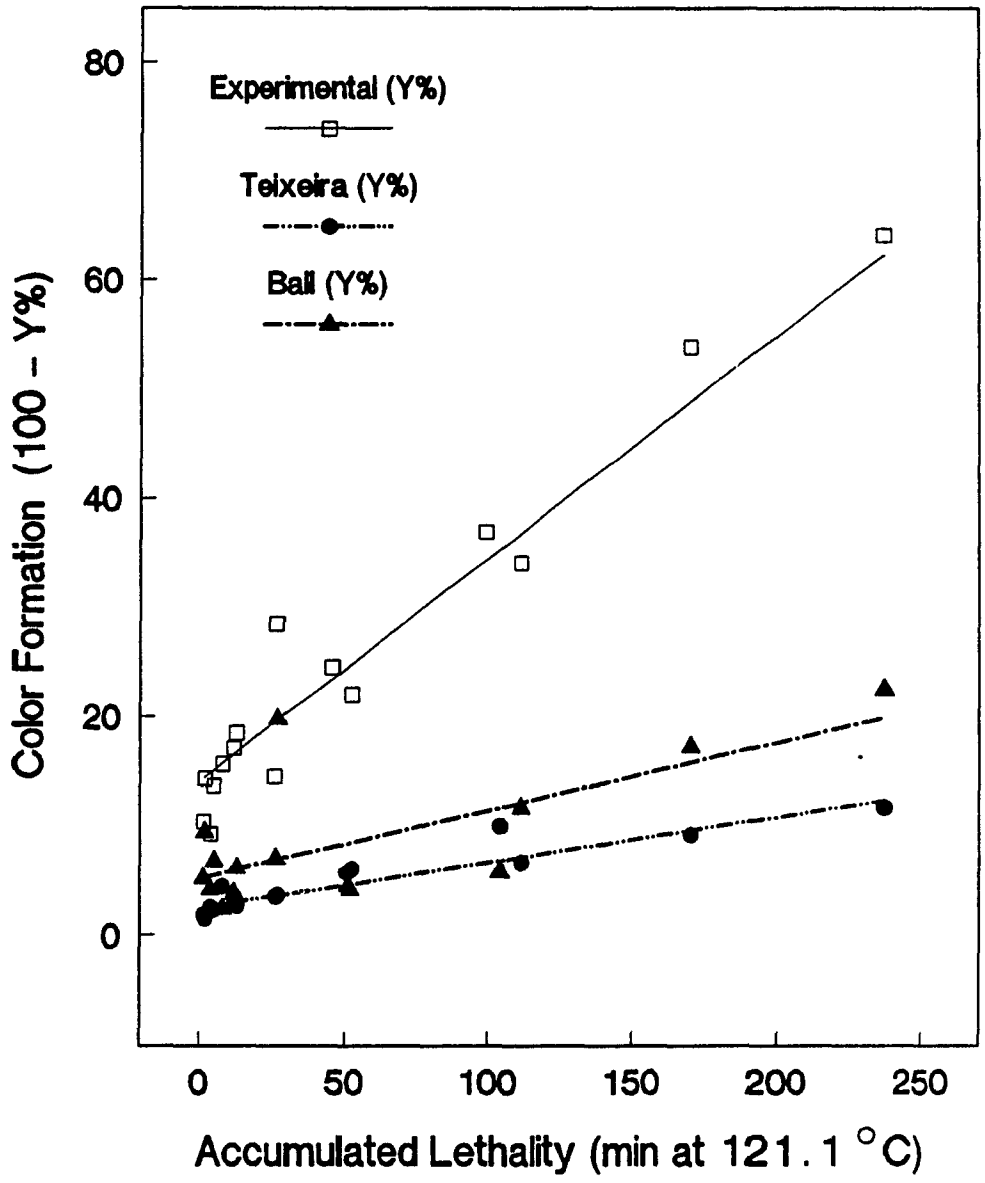


Figure 40. Comparisons of predicted and experimental color formation in thermoprocessed celite as a function of accumulated lethality.

technique. The heat penetration profile was very consistent for the retort in all cases, and excepting some error contributed by the come-up and come-down contributions to the process, there is little to differentiate the processes between the ampoules and the cans. The kinetic parameters, k, D, E_a and z for the can were determined for ascorbic acid, thiamine and color (Tables 23 and 24), and the associated plots derived (Figures 41-46 for log Retention (%) vs time, and Figures 47-49 for the Arrhenius-plot) for ascorbic acid, thiamine, and color formation in the distilled water and in the mixture, respectively. Most of the plots look reasonable and had good statistical characteristics in terms of their fit to the kinetic models considering the magnitude of the complete experiment.

If one compares the can kinetic data to that of the ampoules (Tables 4, 9, and 12), there appears to be very little relation between the results, with the exception of thiamine, which has some semblance to the ampoule data. It was expected that these two approaches would result in basically the same data, giving a consistent activation energy, although one could expect z to change somewhat considering that the temperature range was somewhat different (110-126.7°C vs 110-150°C). The thermal processes and their evaluation were very carefully carried out and the incongruous data obtained appeared difficult to resolve. In an attempt to make a scientific judgment about these major discrepancies, predictive calculations were carried out using both ampoule and can kinetic parameters and compared to the experimentally measured residual concentrations in the cans. Experimental retention values of thiamine, color and ascorbic acid in the two systems following the processes listed in Table 2 are listed in Tables 25-27. The calculated retention is based on the original heat penetration data using the kinetic parameters (z and D values) obtained from 4 mL ampoules or derived from the can data. Regressions were carried out comparing the actual measured concentrations in the can vs the predictions based on the two z values to obtain the relationship between the predictions relative to the experimental data and the results are presented below for thiamine and color, individually and as a mixture.

Table 23. Kinetic parameters for quality factor degradation using can data.

Sample Description	Method	Temperature (°C)	R^2	k value (min^{-1})	D value (min)
AA/DDW (pH 4.05)	Can	110.0	na	0.00041	5517.7
		115.6	na	0.0007	3527.8
		121.1	0.9966	0.0010	2260.0
		126.7	0.9745	0.0015	1537.5
AA/MIX (pH 5.60)	Can	110.0	na	0.0017	1346.8
		115.6	na	0.0021	1099.2
		121.1	0.9978	0.0023	986.3
		126.7	0.9587	0.0055	420.0
B1/DDW (pH 4.11)	Can	110.0	na	0.0032	712.4
		115.6	na	0.0055	419.5
		121.1	0.9722	0.0093	247.1
		126.7	0.9968	0.0135	170.0
B1/MIX (pH 5.60)	Can	110.0	na	0.0044	523.1
		115.6	na	0.0056	413.4
		121.1	0.9960	0.0106	216.3
		126.7	0.9963	0.0158	145.9
Y%/DDW (pH 5.73)	Can	110.0	na	0.0003	6670.0
		115.6	na	0.0007	3472.3
		121.1	0.9221	0.0009	2435.2
		126.7	0.9871	0.0020	1147.6
Y%/MIX (pH 5.60)	Can	110.0	na	0.0003	6981.1
		115.6	na	0.0005	4674.9
		121.1	0.9936	0.0008	2911.7
		126.7	0.9864	0.0015	1546.3

na = not applicable because only two points were used in calculations.

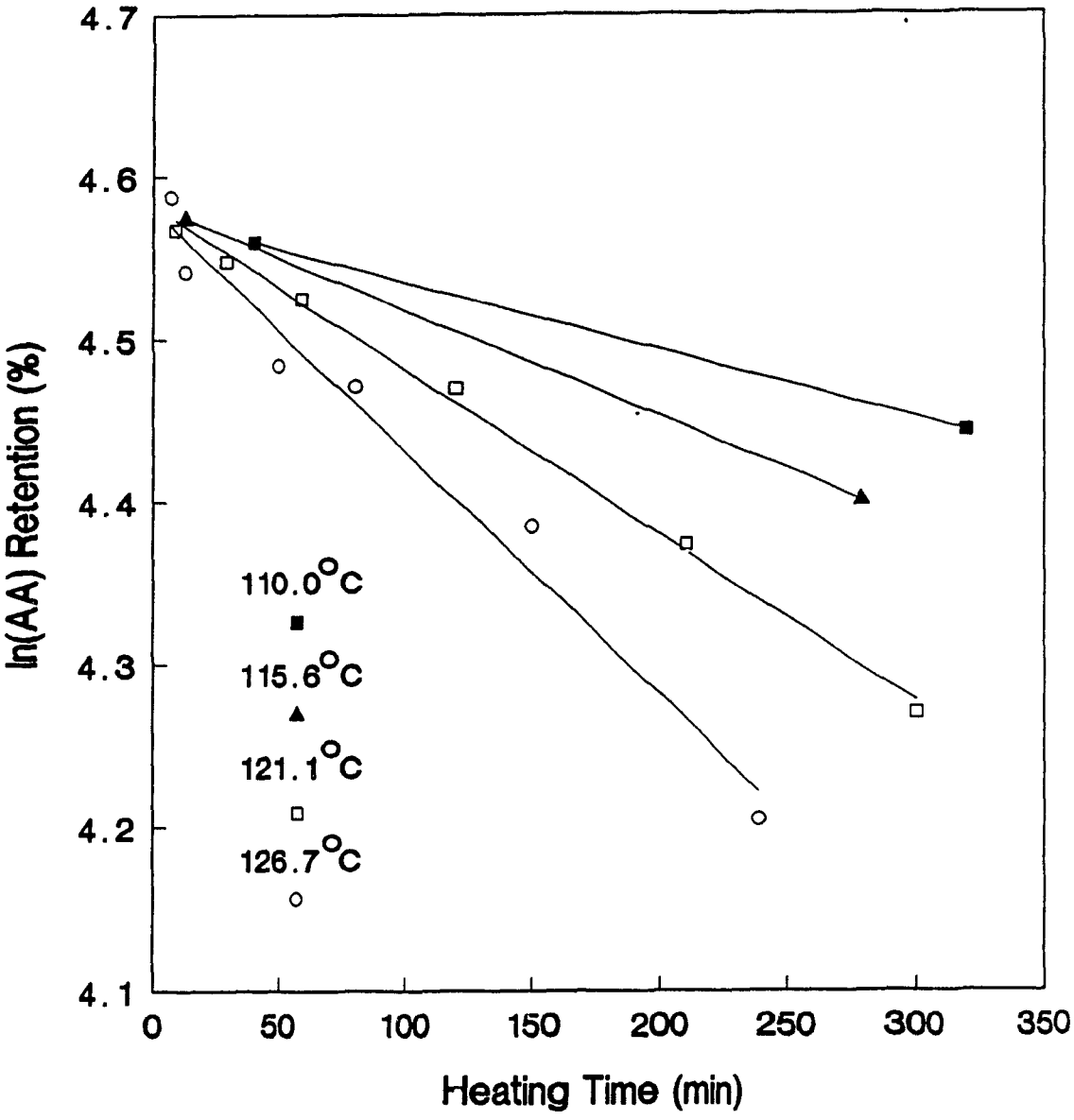


Figure 41. Ascorbic acid retention in convection heated cans following thermal processing for various periods at selected temperatures (AA/DDW).

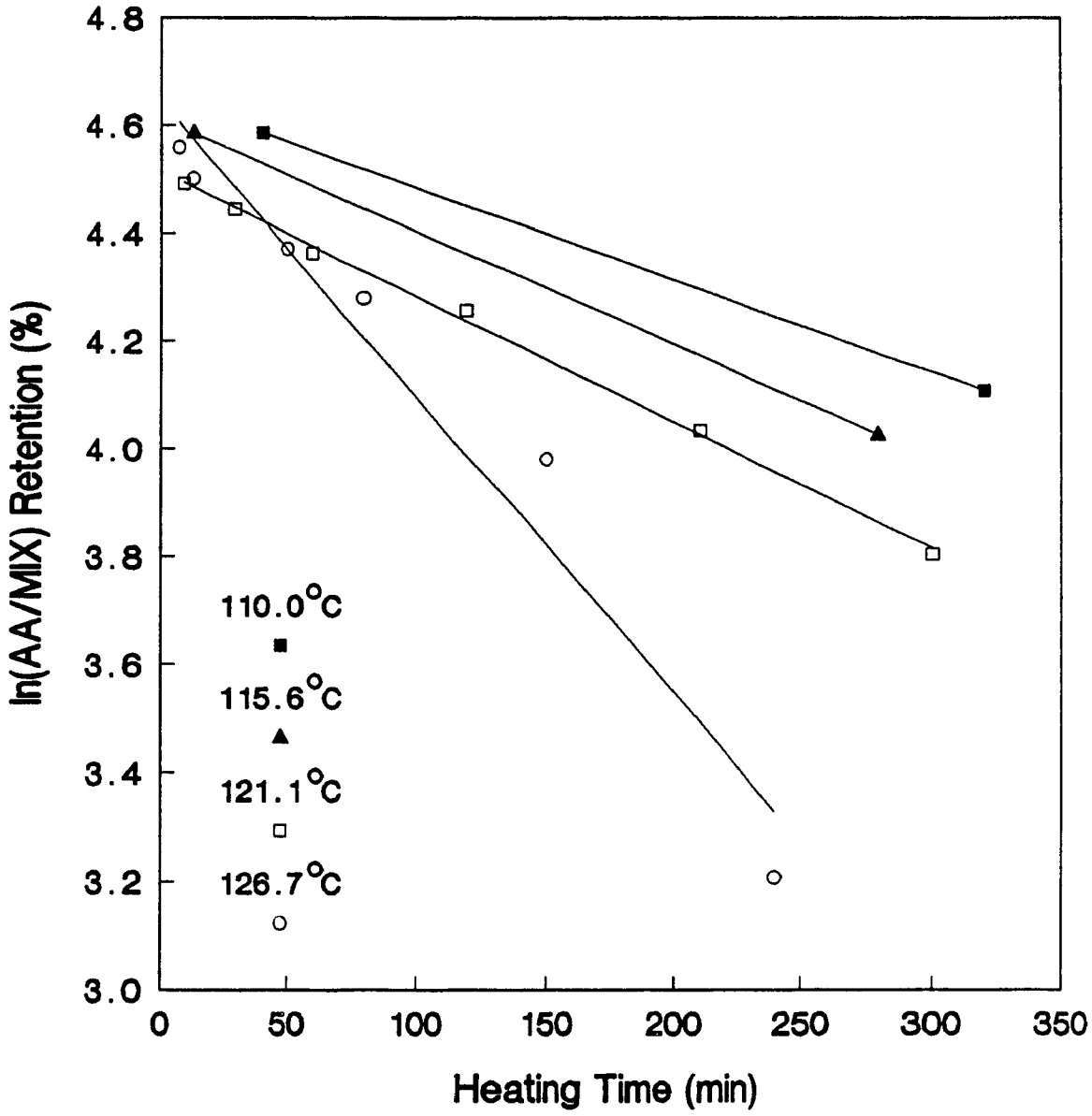


Figure 42. Ascorbic acid retention in convection heated cans following thermal processing for various periods at selected temperatures (AA/MIX).

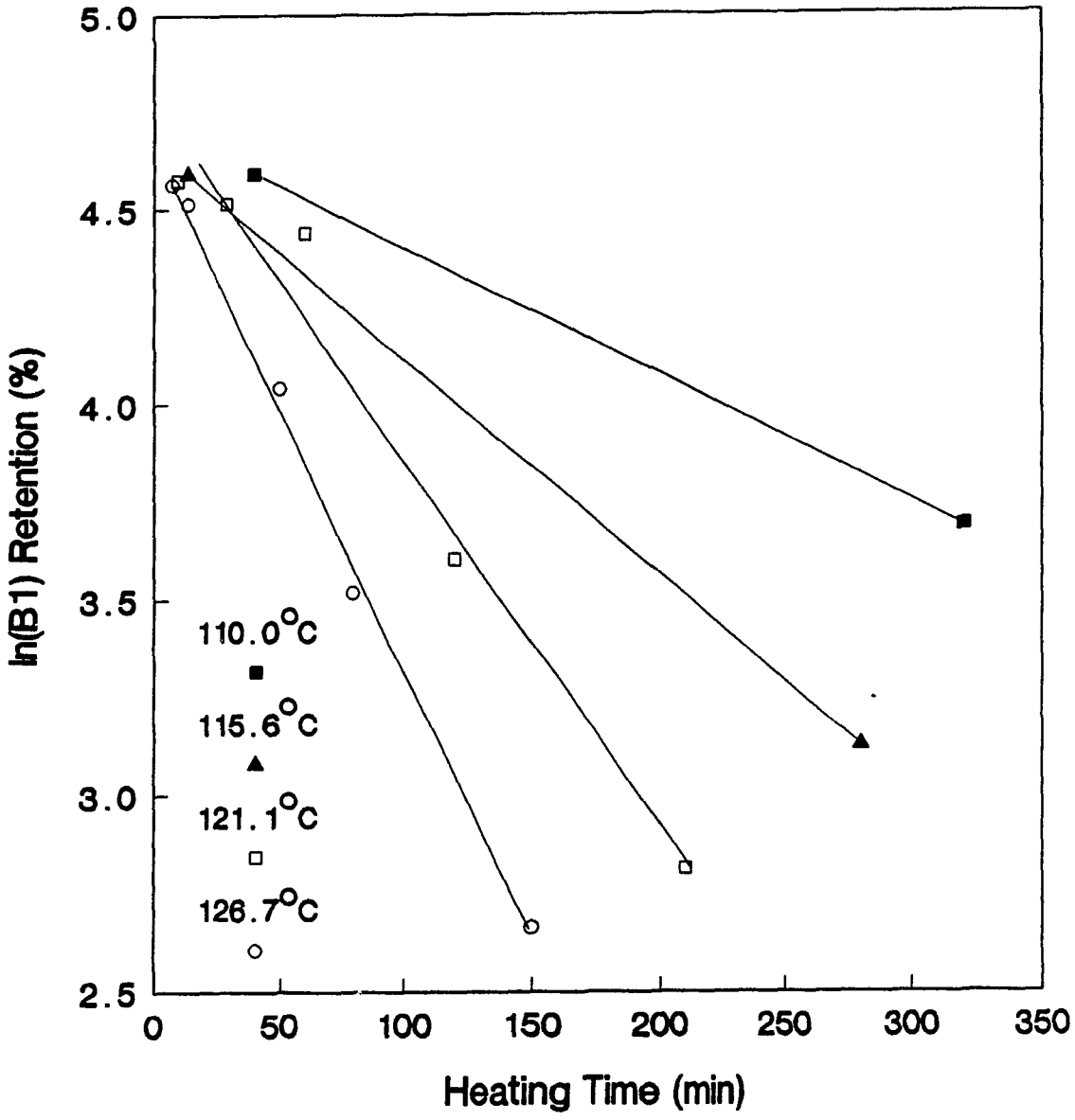


Figure 43. Thiamine retention in convection heated cans following thermal processing for various periods at selected temperatures (B1/DDW).

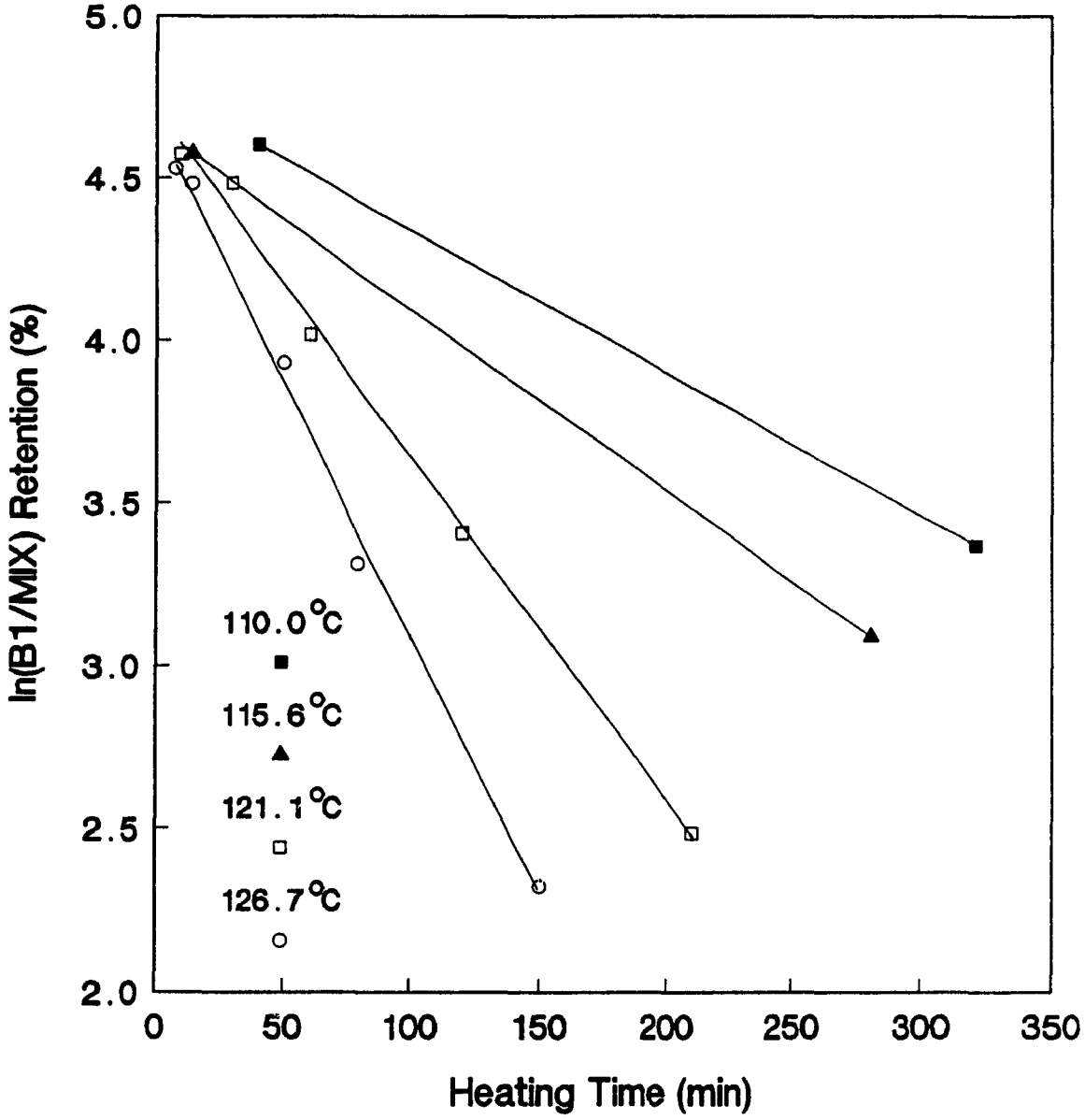


Figure 44. Thiamine retention in convection heated cans following thermal processing for various periods at selected temperatures (B1/MIX).

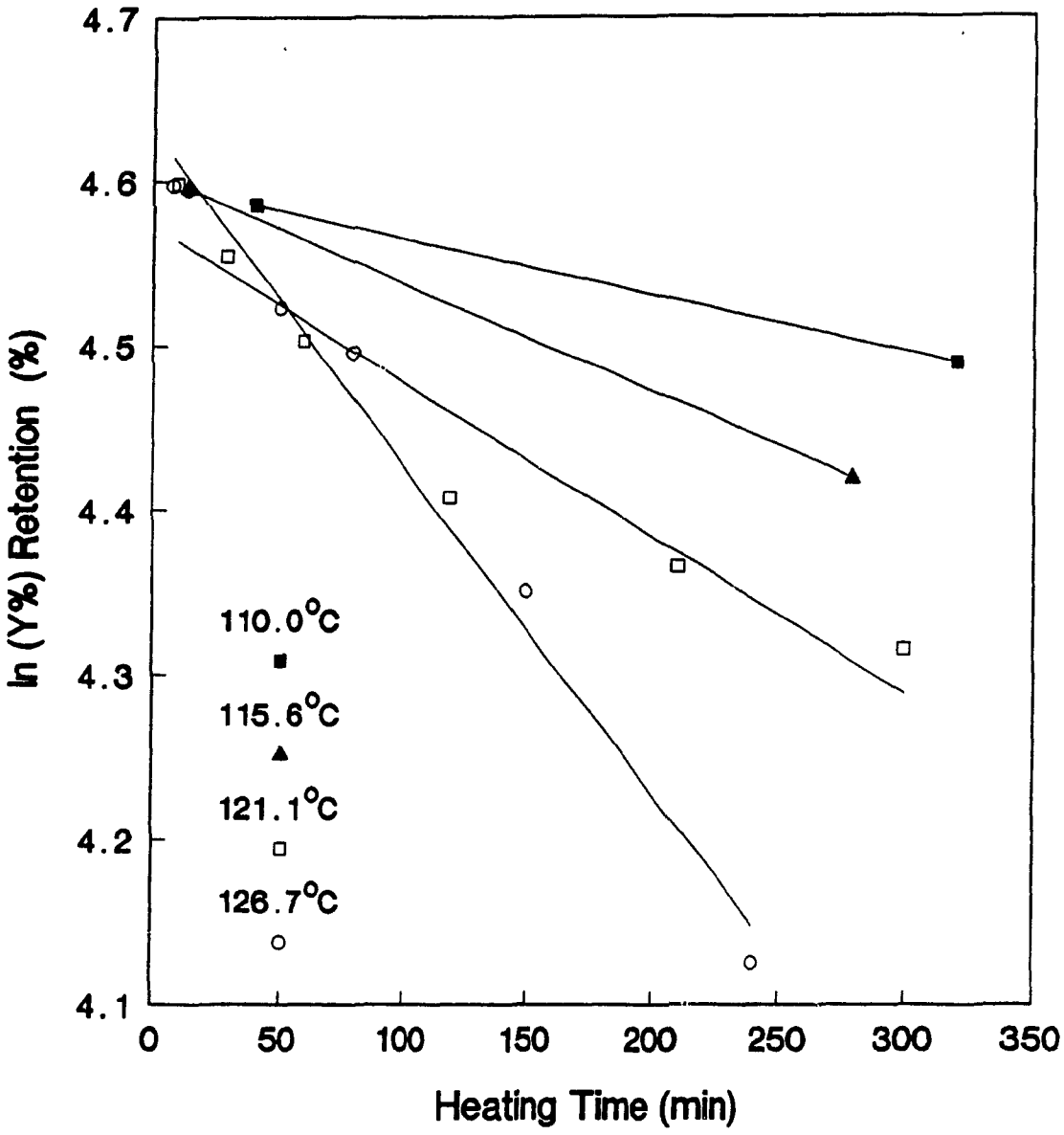


Figure 45. Retention of luminance factor, Y% (Color/DDW system) in convection heated cans following thermal processing for various periods at selected temperatures.

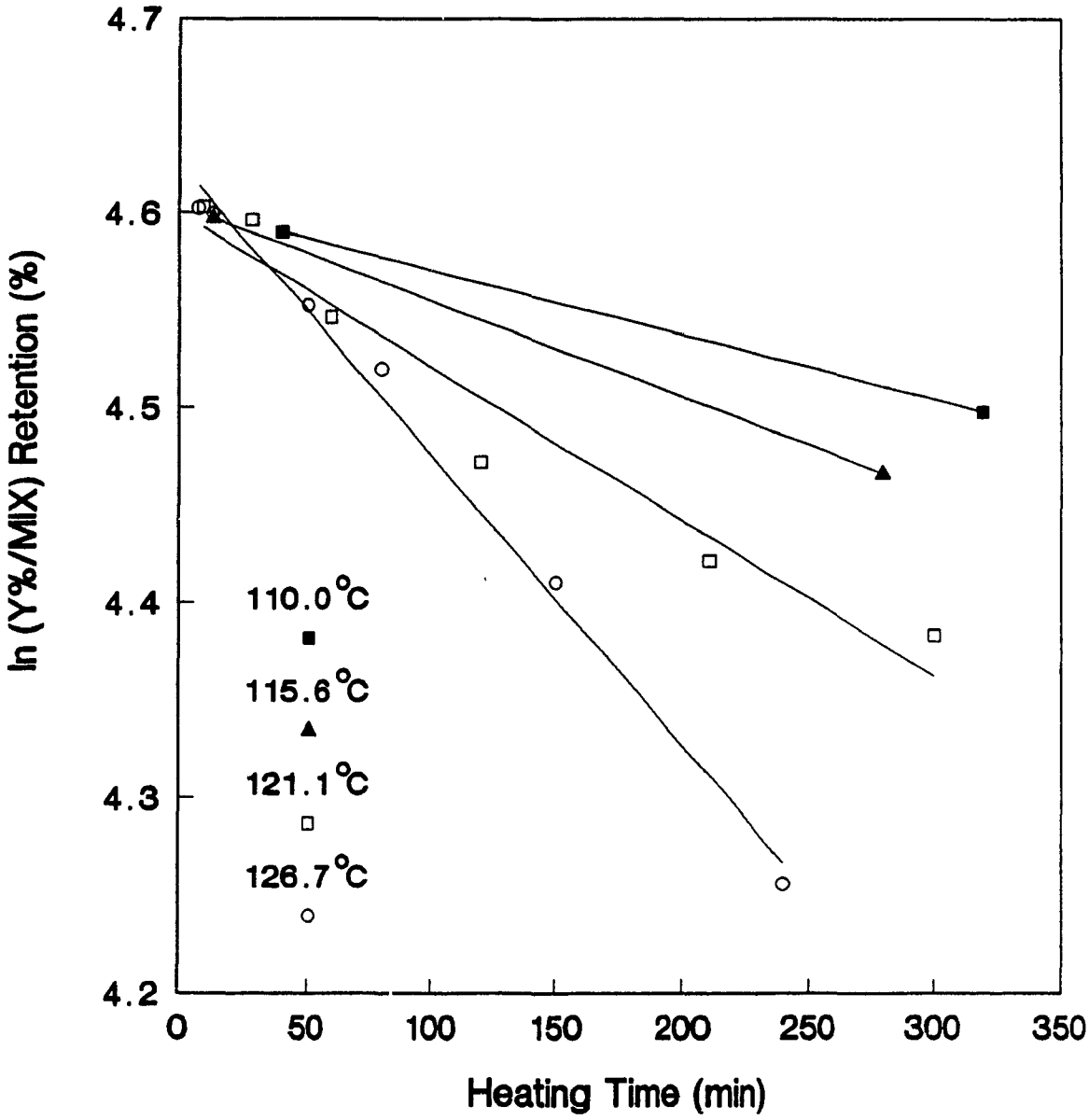


Figure 46. Retention of luminance factor, Y% (Color/MIX system) in convection heated cans following thermal processing for various periods at selected temperatures.

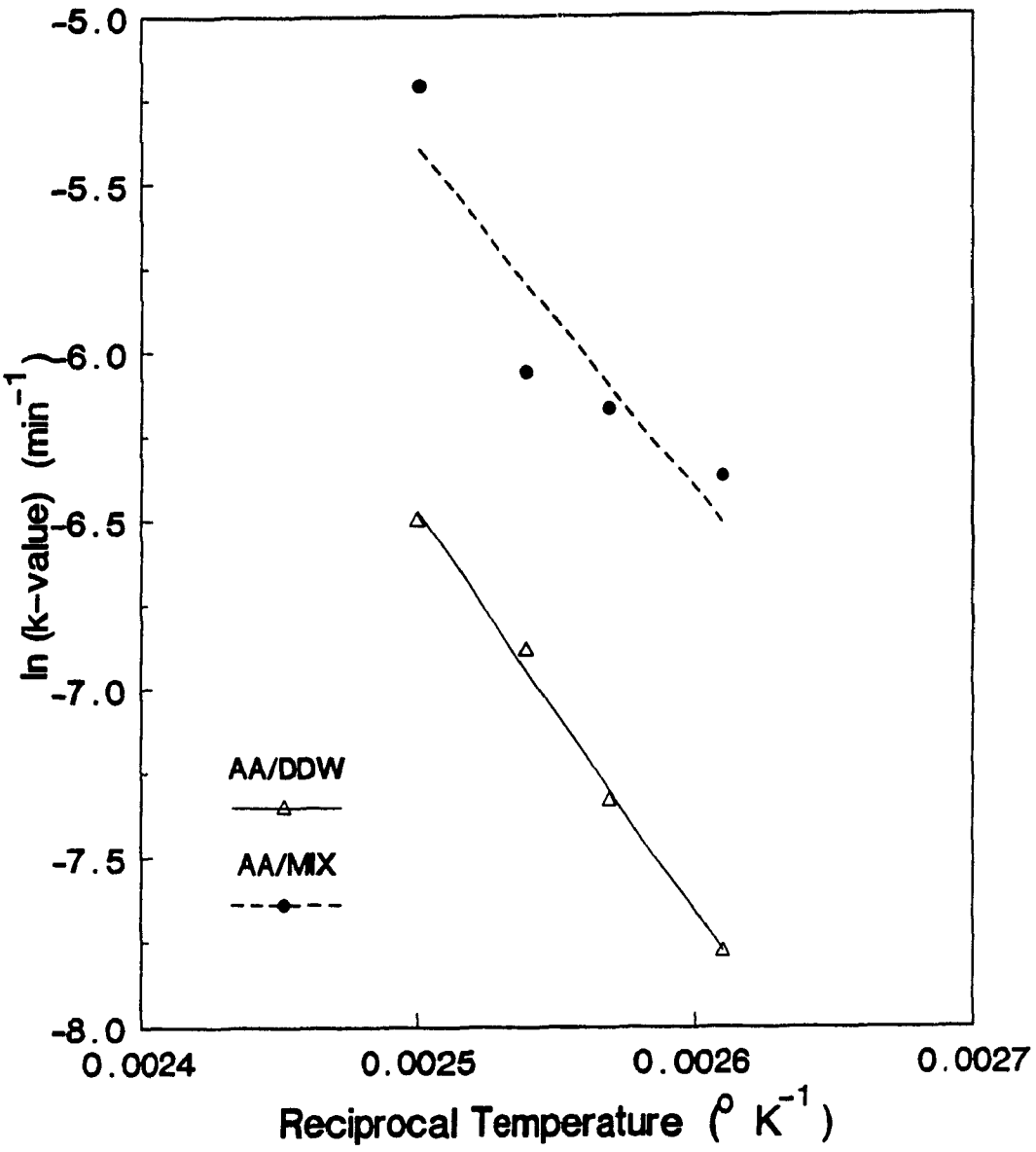


Figure 47. Arrhenius-plot of ascorbic acid destruction (AA/DDW and AA/MIX) employing convection heated cans.

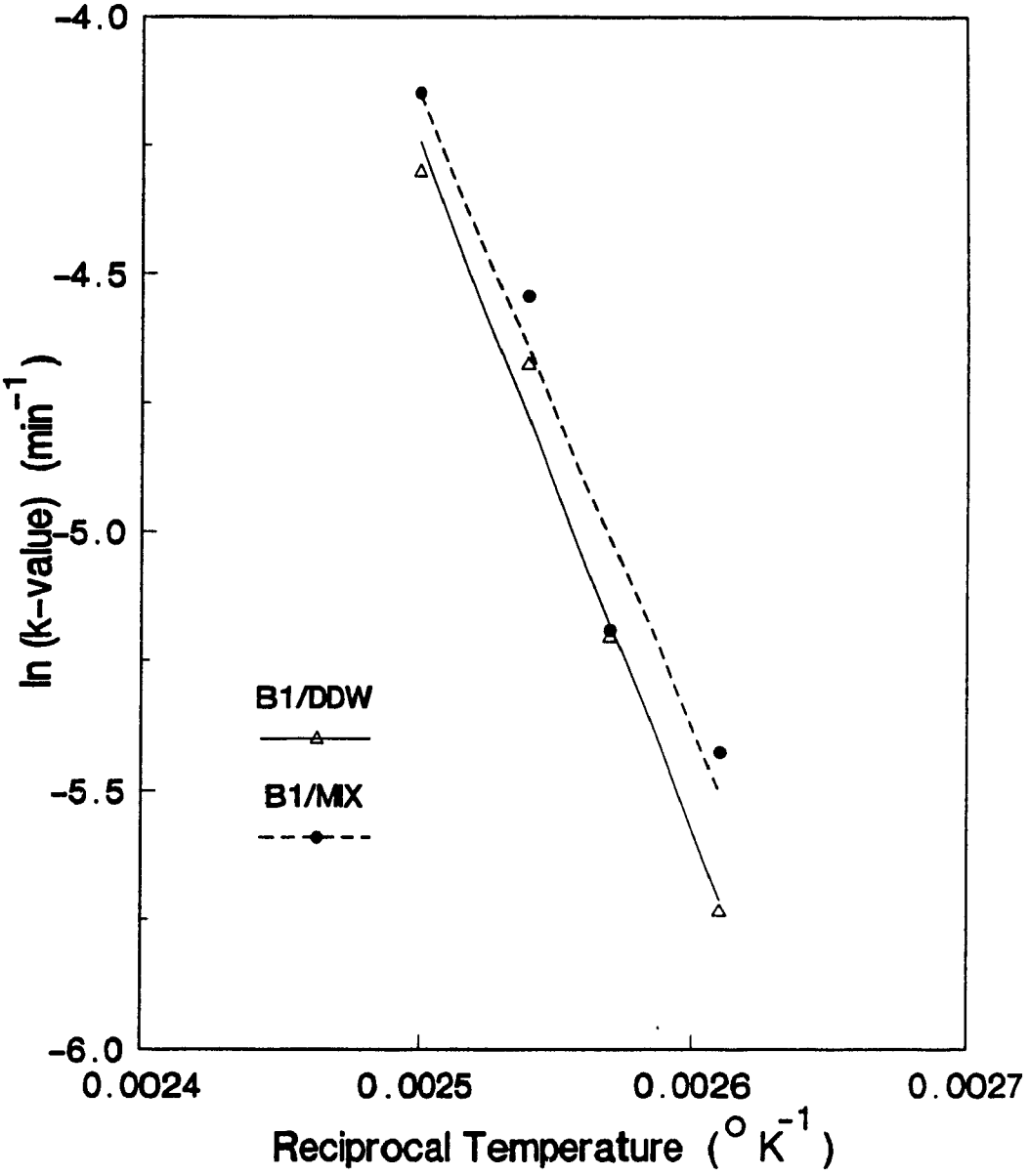


Figure 48. Arrhenius-plot of thiamine destruction (B1/DDW and B1/MIX) employing convection heated cans.

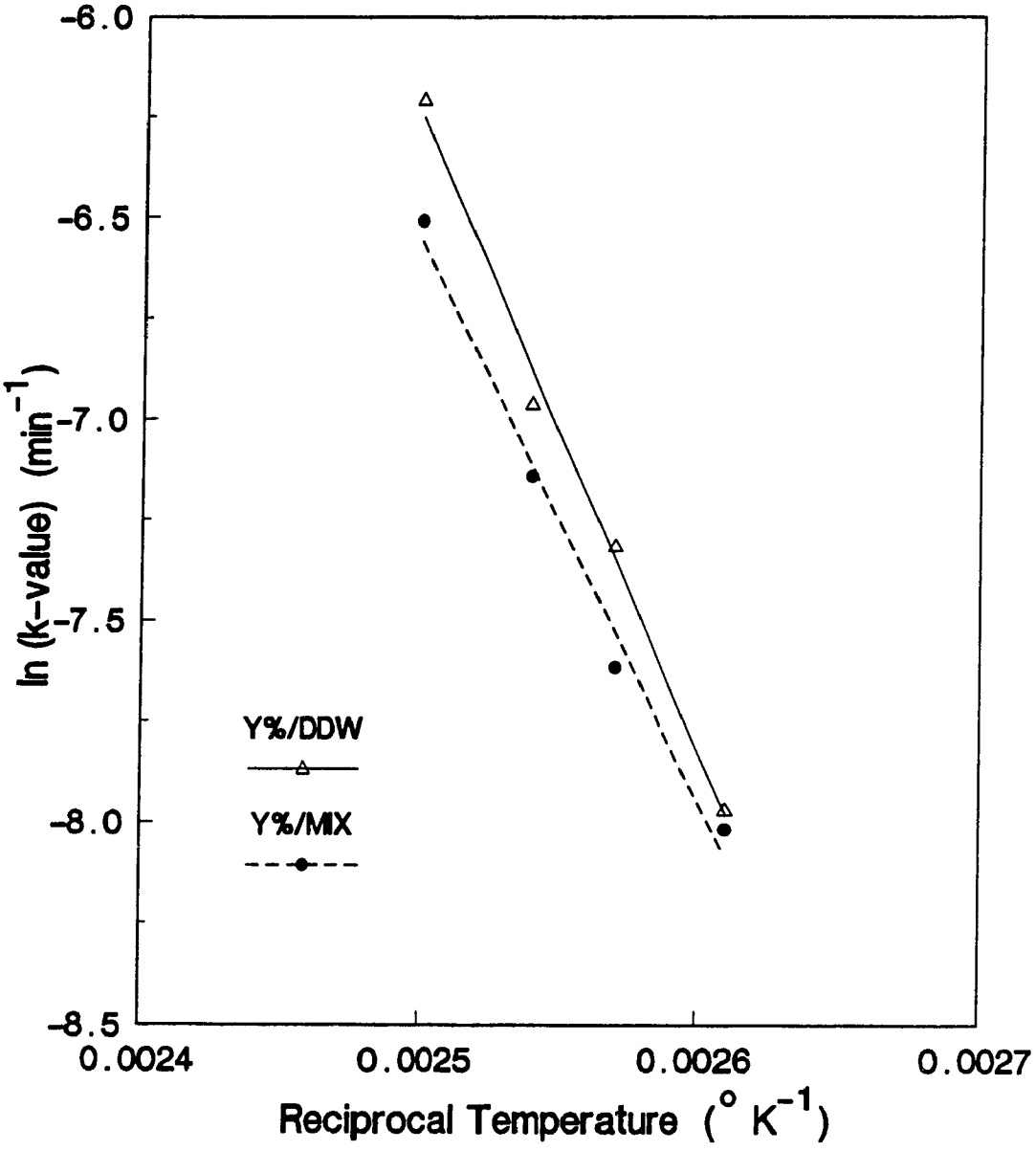


Figure 49. Arrhenius-plot of luminance factor, Y% (Color/DDW and Color/MIX) employing convection heated cans.

Table 24. Arrhenius and thermal death time (TDT) parameters for quality factor destruction using can data.

Sample Description	Method	Temperature Range (^{o}C)	E_a (kJ/mole)	R^2	z (C^{o})	R^2	D_o (min)	k_o (min^{-1})
AA/DDW (pH 4.05)	Can	110-127	206.4	0.999	29.9	0.999	2320.8	0.0010
AA/MIX (pH 5.60)	Can	110-127	173.1	0.814	35.5	0.823	740.3	0.0023
B1/DDW (pH 4.11)	Can	110-127	233.0	0.995	26.5	0.994	263.6	0.0093
B1/MIX (pH 5.60)	Can	110-127	215.6	0.969	28.6	0.971	230.4	0.0106
Y%/DDW (pH 5.73)	Can	110-127	271.7	0.983	22.7	0.984	2146.3	0.0009
Y%/MIX (pH 5.60)	Can	110-127	240.6	0.986	25.6	0.989	2719.0	0.0008

(1) B1/DDW - Actual vs predicted using can z:

$$y = 1.6775 + 1.0457x \qquad R^2 = 0.9854 \qquad [38]$$

(2) B1/DDW - Actual vs predicted using ampoule z:

$$y = -20.5451 + 1.2290x \qquad R^2 = 0.9791 \qquad [39]$$

(3) B1/MIX - Actual vs predicted using can z:

$$y = 1.2783 + 1.1189x \qquad R^2 = 0.9143 \qquad [40]$$

(4) B1/MIX - Actual vs predicted using ampoule z:

$$y = -18.7248 + 1.1953x \qquad R^2 = 0.8472 \qquad [41]$$

(5) Y%/DDW - Actual vs predicted using can z:

$$y = 0.4813 + 0.9846x \qquad R^2 = 0.8834 \qquad [42]$$

(6) Y%/DDW - Actual vs predicted using ampoule z:

$$y = -12.7019 + 1.1194x \quad R^2 = 0.8587 \qquad [43]$$

(7) Y%/MIX - Actual vs predicted using can z:

$$y = 4.6445 + 0.9629x \quad R^2 = 0.9587 \qquad [44]$$

(8) Y%/MIX - Actual vs predicted using ampoule z:

$$y = 16.4838 + 0.8515x \quad R^2 = 0.9475 \qquad [45]$$

Table 25. Comparisons of thiamine retention values obtained from experimental convection heating cans together with the calculated values.

Retort Temp. (oC)	Process Time (min)	Experimental Retention (%)		Calculated Retention (%)			
				Can		Ampoule	
		B1/ DDW	B1/ MIX	B1/ DDW	B1/ MIX	B1/ DDW	B1/ MIX
110.0	40.0	98.80	99.86	87.87	83.86	91.79	86.56
115.6	13.0	96.96	97.98	93.11	91.26	94.16	93.65
121.1	9.0	97.03	97.13	93.22	91.92	95.50	94.88
126.7	7.0	96.03	92.91	91.78	90.70	94.55	94.74
110.0	320.0	39.96	29.11	38.90	27.63	42.98	29.93
115.6	280.0	81.45	56.00	78.73	50.07	75.77	61.98
121.1	29.0	91.50	88.78	87.34	73.58	84.49	82.81
126.7	13.0	91.32	88.66	86.54	84.65	90.98	90.88
121.1	60.0	74.70	55.73	66.95	51.27	69.14	66.84
126.7	50.0	56.91	51.06	57.72	52.90	69.79	69.37
121.1	120.0	36.77	30.19	34.06	27.67	49.34	45.70
126.7	80.0	33.73	27.55	33.71	29.22	49.14	51.24
121.1	210.0	16.64	12.01	14.61	10.12	28.32	24.98
126.7	150.0	14.34	10.20	12.24	9.34	25.36	27.89
121.1	300.0	0.0	0.0	6.26	3.70	16.26	13.64
126.7	240.0	0.0	0.0	3.33	2.16	10.83	12.75

Table 26. Comparisons of color retention (Y%) values obtained from experimental convection heating cans together with the calculated values.

Retort Temp. (oC)	Process Time (min)	Experimental Retention (%)		Calculated Retention (%)			
				Can		Ampoule	
		Y%/ DDW	Y%/ MIX	Y%/ DDW	Y%/ MIX	Y%/ DDW	Y%/ MIX
110.0	40.0	98.10	98.49	96.68	98.73	98.45	98.13
115.6	13.0	99.08	99.23	99.23	99.28	99.19	99.03
121.1	9.0	99.37	99.81	99.19	99.28	99.26	99.11
126.7	7.0	99.28	99.74	98.96	99.11	99.15	98.97
110.0	320.0	89.06	89.80	88.80	89.25	87.30	84.89
115.6	280.0	81.45	56.00	82.98	56.14	75.77	54.81
121.1	29.0	95.07	99.12	97.05	97.39	97.33	96.78
126.7	13.0	99.03	99.46	98.27	98.51	98.55	98.24
121.1	60.0	90.32	94.28	93.62	94.36	94.29	93.13
126.7	50.0	92.13	94.87	93.62	94.46	94.56	93.44
121.1	120.0	82.06	87.51	88.21	89.51	89.30	87.21
126.7	80.0	89.65	91.82	87.50	89.27	89.76	87.73
121.1	210.0	78.68	83.21	79.89	82.04	81.74	78.35
126.7	150.0	77.54	82.29	77.23	80.30	81.22	77.71
121.1	300.0	74.83	80.08	72.36	75.19	74.81	70.38
126.7	240.0	61.89	70.52	65.78	70.08	71.41	66.49

Table 27. Comparisons of ascorbic acid retention values obtained from experimental convection heating cans together with the calculated values.

Retort Temp. (oC)	Process Time (min)	Experimental Retention (%)		Calculated Retention (%)			
				Can		Ampoule	
		AA/ DDW	AA/ MIX	AA/ DDW	AA/ MIX	AA/ DDW	AA/ MIX
110.0	40.0	95.56	98.14	98.39	95.59	90.08	60.99
115.6	13.0	96.96	97.98	99.16	97.84	94.16	83.49
121.1	9.0	96.34	89.34	99.23	98.15	95.44	88.79
126.7	7.0	98.31	95.51	99.11	97.99	95.43	90.67
110.0	320.0	85.02	60.80	86.86	68.07	32.44	3.84
115.6	280.0	81.45	56.00	83.85	58.05	75.77	31.18
121.1	29.0	94.48	85.17	97.23	93.49	84.61	68.48
126.7	13.0	93.88	90.16	98.49	96.54	91.96	75.59
121.1	60.0	92.31	78.53	94.06	86.47	70.13	48.43
126.7	50.0	88.60	79.18	94.33	87.38	72.68	46.35
121.1	120.0	87.34	70.53	88.89	75.48	50.11	23.72
126.7	80.0	87.45	72.24	89.35	77.63	56.24	35.98
121.1	210.0	79.31	56.46	81.06	60.66	29.48	8.81
126.7	150.0	80.24	53.55	80.50	61.51	33.42	15.85
121.1	300.0	71.52	44.88	73.93	48.74	17.33	3.24
126.7	240.0	66.99	24.72	70.40	45.61	17.12	5.52

This result indicates that the can data is slightly a better fit than the ampoule data in terms of prediction (R^2). The predicted can data has the advantage of being a result of a direct back-calculation from the retention data, hence the correspondence should be better. Closer statistical scrutiny of the ampoule and can kinetic data indicated that the predicted retention data were not significantly different from the experimental data, nor were the ampoule and can predictions significantly different from each other. The implication of this analysis is that z and E_a of the ampoules vs the can were not significantly different from each other for thiamine and color. This data brings into question which set of kinetic data is correct, the ampoule or can. Although there is no direct way to prove which is more representative, the fact that ampoule and capillary were a good match gives credence to the smaller containers. In addition, the ampoule kinetic data worked well in the predictive models, while if these can values are used in Teixeira's computer model, the predictions are poor.

In contrast to the thiamine and the color data, ascorbic acid produced a poor correspondence between the experimental and calculated retention data in both systems (Table 27), was significantly different in this regard and the experimental data clearly indicated that ascorbic acid was degrading much more slowly in the can than the ampoule. After considering all the possible reasons which might contribute to this discrepancy, no mechanistic answer seemed reasonable. Once again, the ampoule kinetic data is unlikely to be the cause, since good predictions were obtained in the conduction system for ascorbic acid. Based on these facts, our only explanation is that inhibition of ascorbic acid degradation was taking place in the can. The only cause that can be suggested is that low concentrations of components from the can wall varnish went into solution and may have acted as an electron donor, possibly stabilizing the dehydroascorbic acid and reducing the overall rate of ascorbic acid destruction. This effect would not be observed in the conduction system since the leaching of inhibitory components would be limited to the immediate surroundings of the can wall. Although this mechanism is conjecture on our part, without proof, it is a reasonable possibility. No published reports were found in the literature of any attempts to determine nutrient kinetic data from retort cans involving convection cans. Our attempt to reproduce ampoule kinetic data from a real processing system did not produce the results expected. Although the results should match in theory, this was not the case, even though the experiment was very carefully carried out.

4.12 Summary of Process Verification

Celite appears to be a workable conduction matrix having thermal characteristics similar to pureed foods. Quality factors as assessed by computer models indicated that Ball's method is workable for centerpoint predictions, while Teixeira's model was applicable for both centerpoint and integrated destruction. The centerpoint capsule is a useful tool for recovering the components after thermal processing and implies that the technique could be expanded to be used at other locations also.

4.13 Optimization of Quality Factors

As discussed in the materials and methods section, the approach used to choose the optimal batch sterilization conditions first required the calculation of the "equal lethality" data, i.e., the process times required to obtain a given process lethality at various retort temperatures from 110 to 144^{o}C calculated in 2^{o}C temperature increments. The process times were obtained from Stumbo's centerpoint model and a typical curve is shown in Figure 50 and indicates that any point on the curve represents a process producing a process lethality of 6.0 min, which in turn is associated with a certain nutrient destruction. Knowing the F and z for a specified nutrient and the process conditions, the nutrient retention can be predicted through the use of a program such as that developed by Teixeira's. Furthermore, one can also consider several nutrients simultaneously and can optimize the process graphically or by using an objective function. Nine nutrients were tested and the predictions are listed in Appendix [13]. A sample optimization curve for selected nutrients is presented in Figure 51 and the quality factors are clearly distinguishable from each other based on their kinetic parameters. Note that the optimum process is very close to a conventional batch process, and contrary to what one would expect, the optimum condition does not favor the high temperature-short time (HTST) combinations. The shapes of the majority of the curves in fact indicate that nutrient retention actually decreases as the process temperatures increase. Determining an optimum from such a complex system as shown in Figure 51 solved graphically results in an optimum of ~120^{o}C for 52 minutes, however, for more accurate results, it is better to handle such an evaluation by an objective function.

Teixeira's program requires substantial computational effort and it was of interest to determine whether simpler models such as Ball's model based on centerpoint method would also work. Figure 52 compares the two methods for ascorbic acid (AA) and thiamine (B1) out of the 9 factors tested and all others followed the trend demonstrated in Figure 52, which shows that Ball's model always predicts higher retentions at higher temperatures. There is no optimum obtainable from Ball's model since the

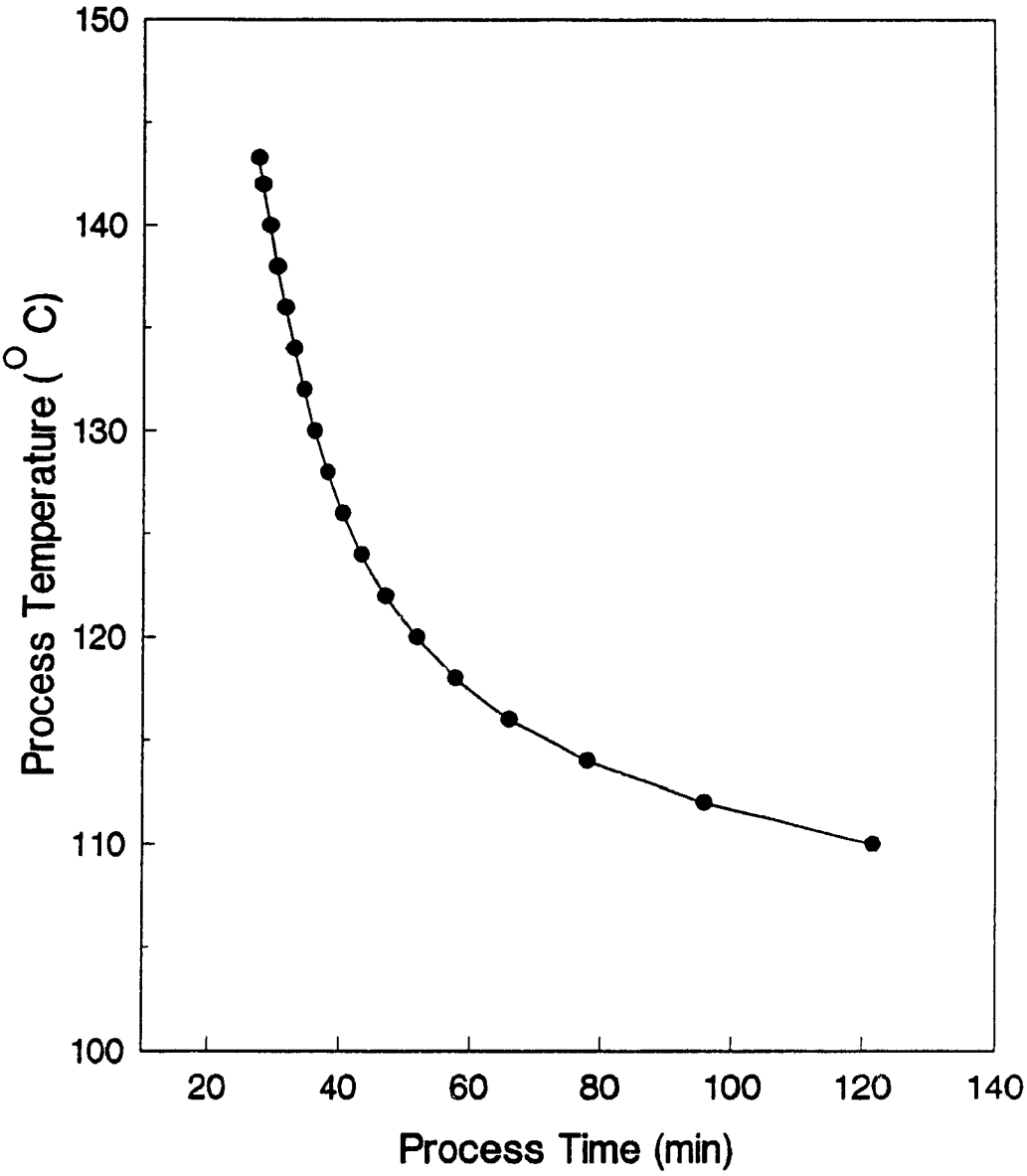


Figure 50. Equal lethality curve: Process temperatures versus process times.

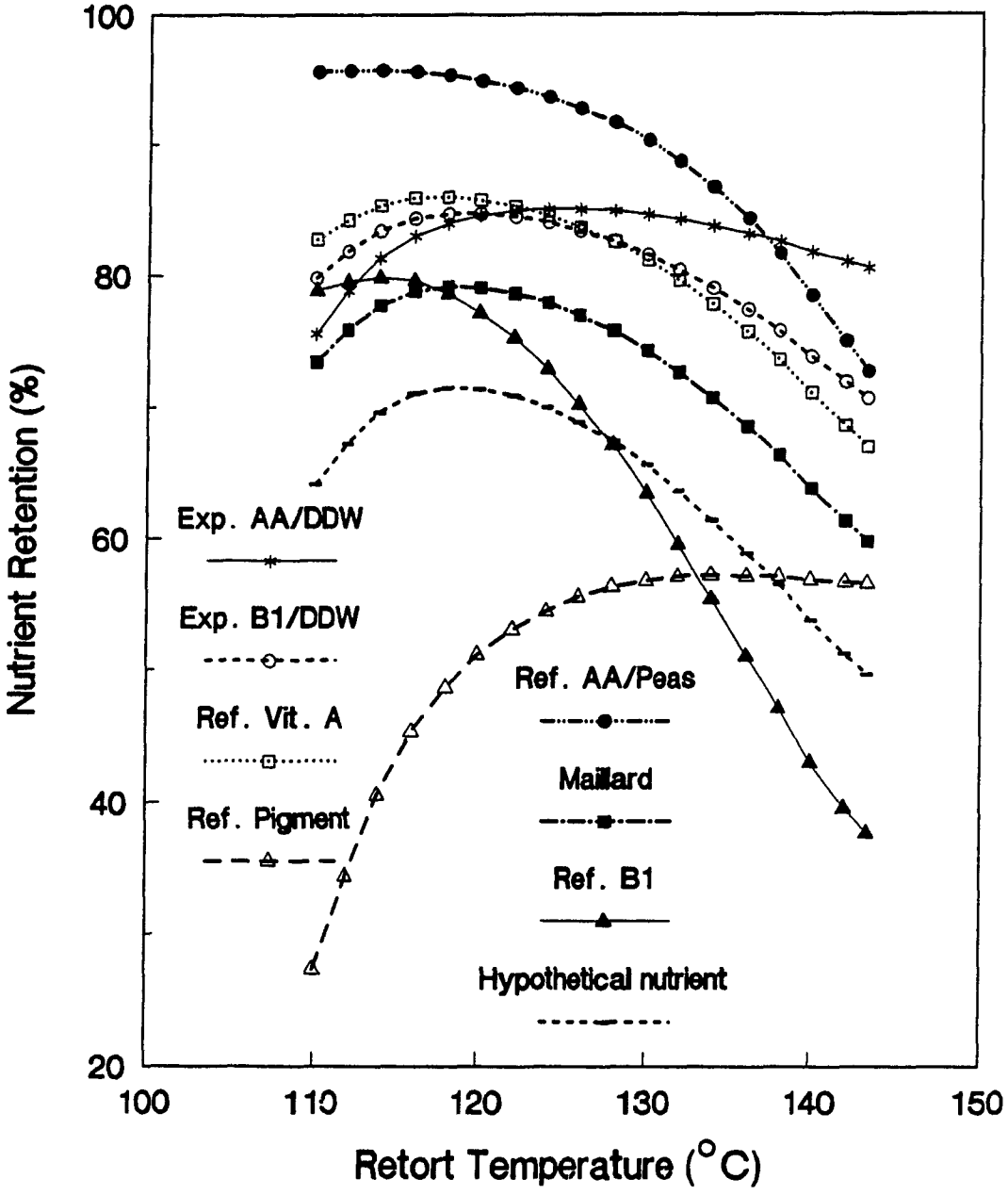


Figure 51. Multi-nutrient optimization, different quality factor retentions versus retort temperatures.

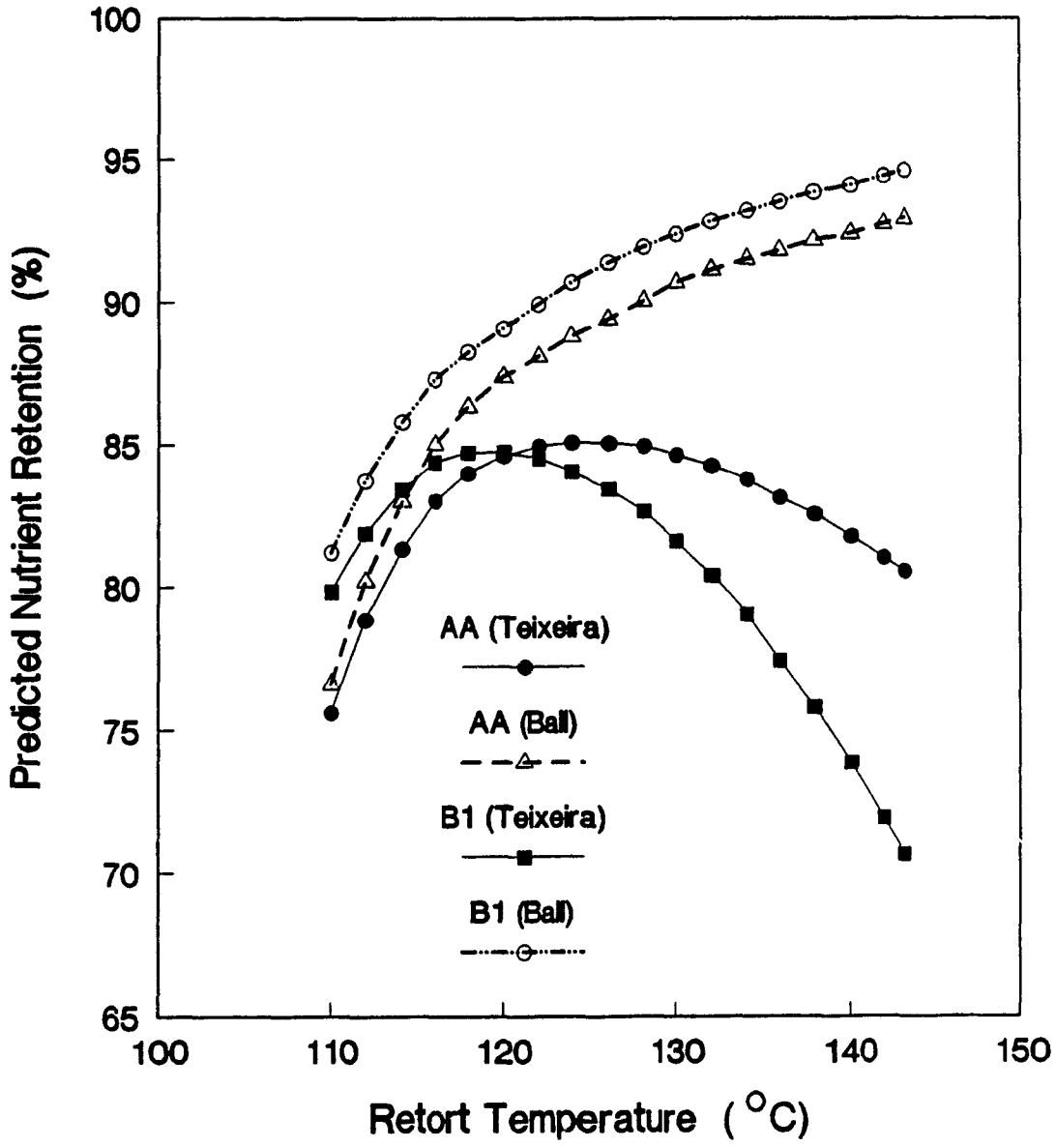


Figure 52. Verification of ascorbic acid and thiamine retentions as predicted by both Ball and Teixeira models.

values always continue to increase. Therefore, Ball's method is not useful for determining an optimal process.

4.13.1 The Objective Function

An multi-factor objective function, which relates the importance of each factor was defined in equation [28], and was used to obtain the optimum batch process. Several quality factors, i.e., those determined in this study, plus some from the literature (Appendix [13]) were assessed for optimization by the objective function. Ascorbic acid and thiamine data from this study, plus Maillard data from published literature were used to determine the objective function illustrated in Figure 53. The optimal value, which is obtained graphically from Figure 53 is about 82.67 for the three quality factors chosen and corresponds to a process time of 49 min at 121°C. At this temperature the nutrient retentions are: ascorbic acid (84.80%), thiamine (84.61%), and the reference Maillard reaction (78.88%) based on a weight factor of 1.0 for each. The individual optima for all the 9 quality factors are given in Appendix [13] and are based on the objective functions given in Table 28. To demonstrate the effect of increasing the quality factors to five, by adding a pigment and vitamin A (Figure 54), an optimal value of 79.20 is obtained (weight factor = 1). This optimum objective function corresponds to a process time of 42 min and 125°C and gives retentions of 85.07% for ascorbic acid, 83.74% for thiamine, 77.46% for the Maillard data, 55.08% for the pigment, and 93.24% for vitamin A.

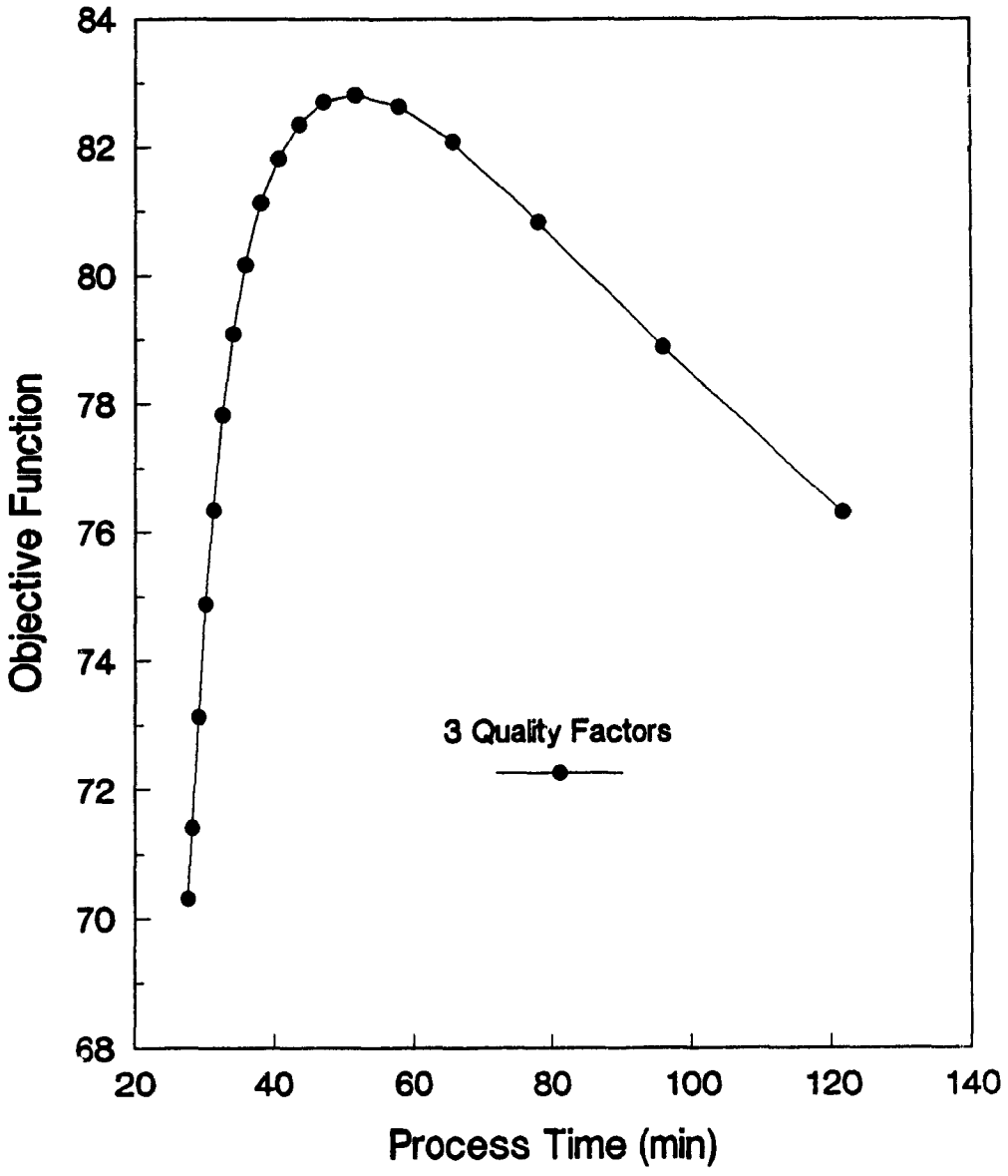


Figure 53. Objective function values versus process times for three quality factors with no weight factors.

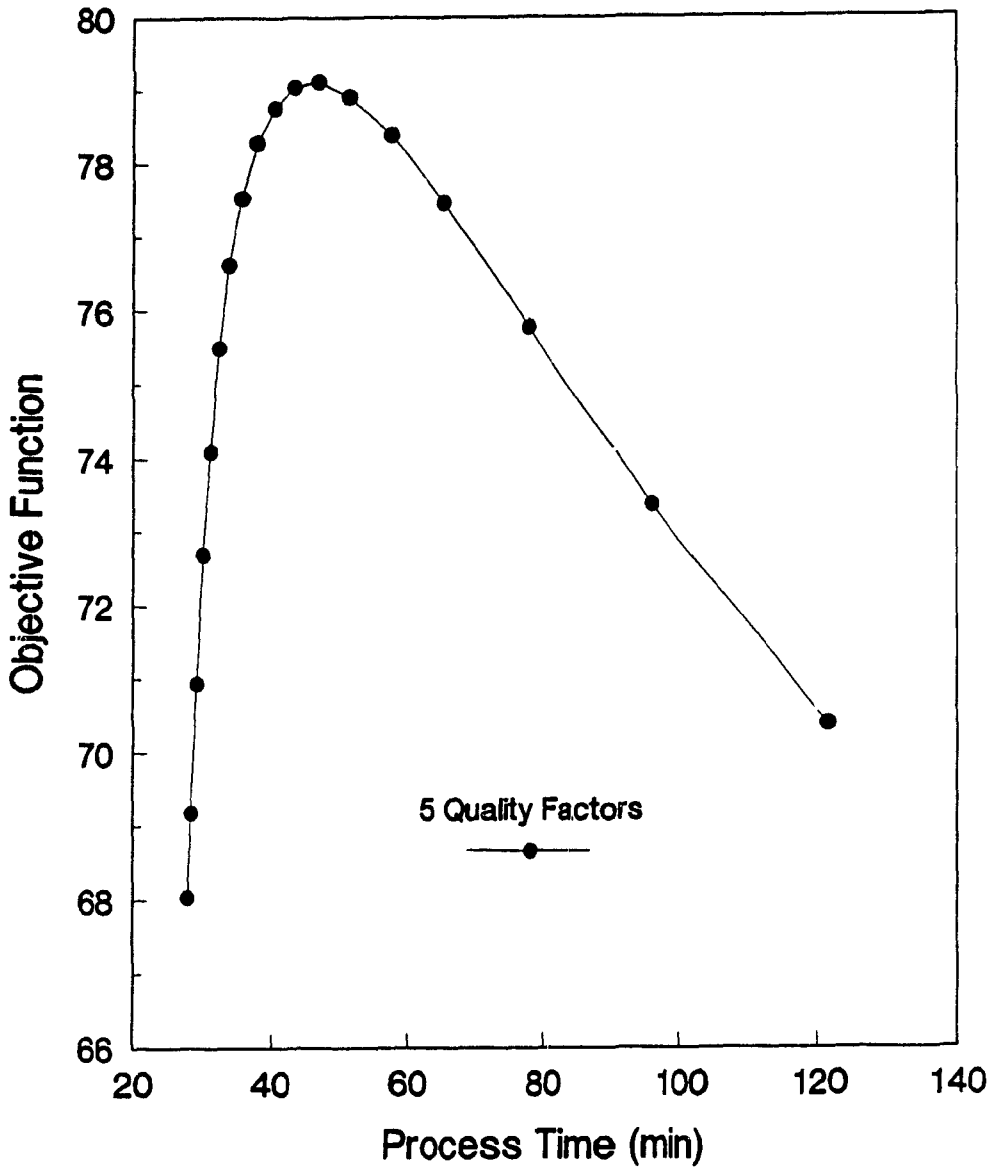


Figure 54. Objective function values versus process times for five quality factors with no weight factors.

Table 28. Various objective functions obtained by varying the number of quality factors and/or having weight factors or not.

Retort Temperature (oC)	Process Time (min)	Objective Functions			
		3 Factors[1]	5 Factors[2]	Objective [3] (+ve.wt.factor)	Objective [4] (-ve.wt.factor)
110	121.5	76.30	70.38	40.96	14.02
112	95.8	78.88	73.35	42.46	14.63
114	77.9	80.83	75.76	43.61	15.10
116	65.8	82.08	77.45	44.37	15.45
118	57.7	32.63	78.39	44.76	15.72
120	51.7	82.81	78.91	44.96	15.96
122	47.1	82.70	79.12	45.02	16.18
124	43.5	82.35	79.04	44.96	16.39
126	40.5	81.82	78.76	44.82	16.60
128	38.0	81.13	78.29	44.61	16.82
130	35.9	80.17	77.53	44.29	17.04
132	34.2	79.09	76.62	43.90	17.28
134	32.7	77.83	75.49	43.45	17.53
136	31.4	76.34	74.09	42.89	17.78
138	30.2	74.88	72.69	42.36	18.04
140	29.2	73.13	70.94	41.69	18.30
142	28.2	71.41	69.18	41.03	18.55
144	27.6	70.31	68.04	40.61	18.70

[1] = Exp. AA/DDW+ Exp. B1/DDW+ Ref. Maillard, with no weight factors.
[2] = Exp. AA/DDW+ Exp. B1/DDW+ Ref. Maillard+ Ref. Pigment+ Ref. vitamin A, with no weight factors.
[3] = Exp. AA+ Exp. B1+ Ref. Maillard, with positive weight factors.
[4] = Exp. AA+ Exp. B1+ Ref. Maillard, with negative weight factors.

Note: Refer to Appendix [13] for the values of kinetic parameters (z and D) used to predict the retention of selected quality factors from Teixeira model. These retentions are included in the values of objective function tabulated above.

The data for the balance of the objective functions is also presented in Table 28. By maintaining all process and the quality factor (F and z) parameters constant and varying the weight factors, new objective function values result. The choice of the weight factors depends on the process requirements (economic and/or nutritional reasons), and their values may be positive or negative.

By changing the weight factors, the optimum value of the objective function will change, causing corresponding changes in the optimum temperature-time combinations. To illustrate such a case,

selected positive weight factors were assigned to each the three original quality factors, using values of 1.0 for ascorbic acid, 0.5 for thiamine, and 0.1 for the Maillard data. Figure 55 shows the plot of the objective functions versus process time with one curve with no weight factors and the other with positive weight factors. The maximum value for the objective function with no weight factors is ~82.67 while the other is ~45.00 which corresponds to a process time of 42 min at 125^{o}C.

It would initially be difficult to envision a situation where the amount of component increases or one wishes it to increase, since nutrient loss has dominated this discussion. However, color for example can develop, and may be desirable in certain circumstances, i.e., toffee. In these circumstances optimization would require negative weights, and such an effect is illustrated in Figure 56 using 1.0 for ascorbic acid, 0.5 for thiamine, and -1.0 for Maillard data. In this case no maximum is obtained, although this does not imply one does not always exist, as the objective function is a result of the interaction of at least three components. Minimization of undesirable color development is another instance where one would assign a negative weight factor. In order to make the comparisons between different objective functions, Figure 57 includes the last two cases (i.e., objective functions with positive and negative weight factors, Figures 55-56), as well the objective function with no weight factors.

4.14 Summary of Optimization

The concept of process optimization using objective functions was suggested by Teixeira (1969b) and has been implemented in this study. Clearly the end users have to have in mind what weights they wish to give to the components they are interested in, balance these against all other factors contributing to product quality, plus include the practical limits associated with the processes available and food product under consideration. The results indicate that multi-factor optimization may well be useful in fine tuning processes, assuming that the kinetic parameters for each component are representative for the food system.

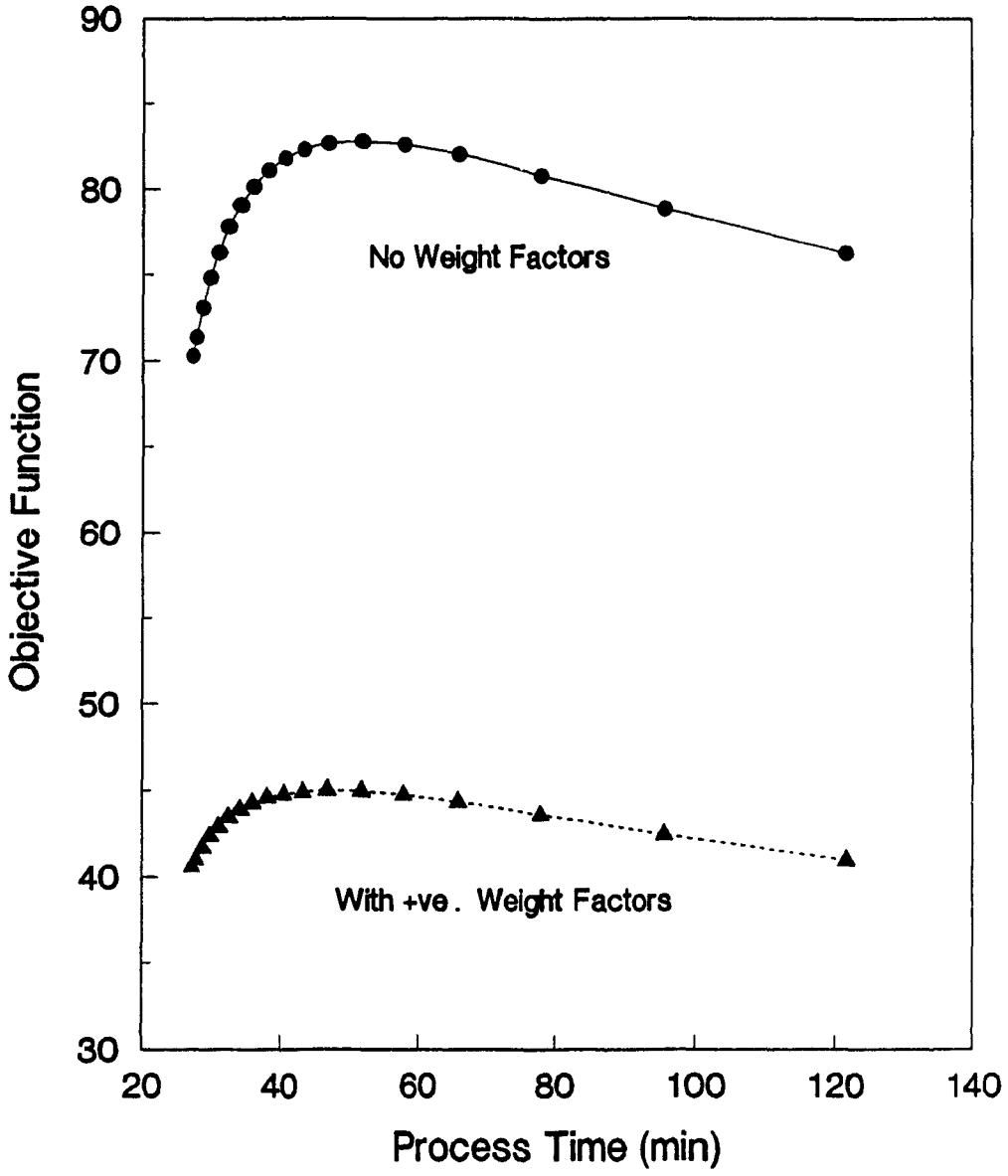


Figure 55. Objective function values versus process times for three quality factors with positive weight factors.

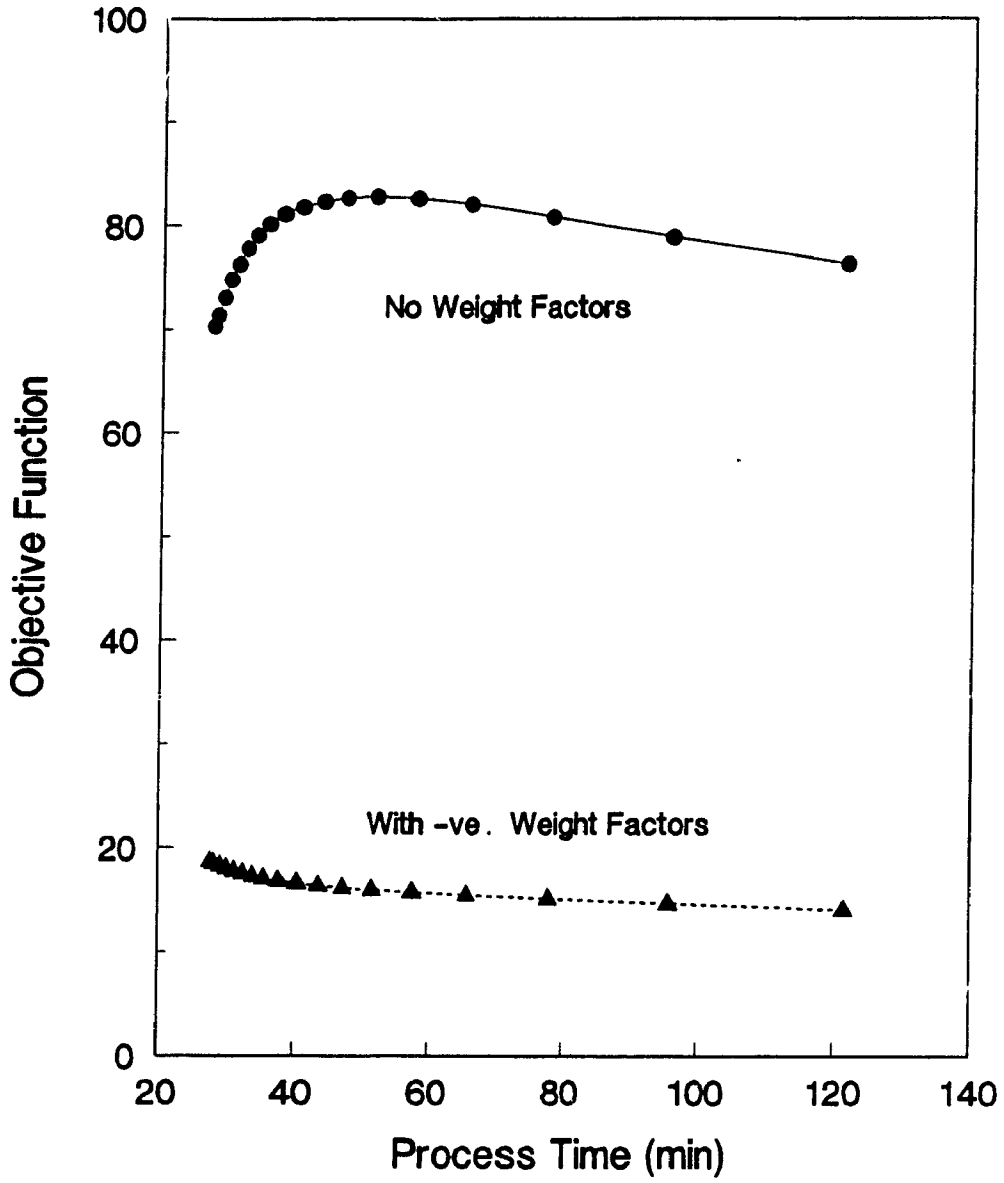


Figure 56. Objective function values versus process times for three quality factors with negative weight factors.

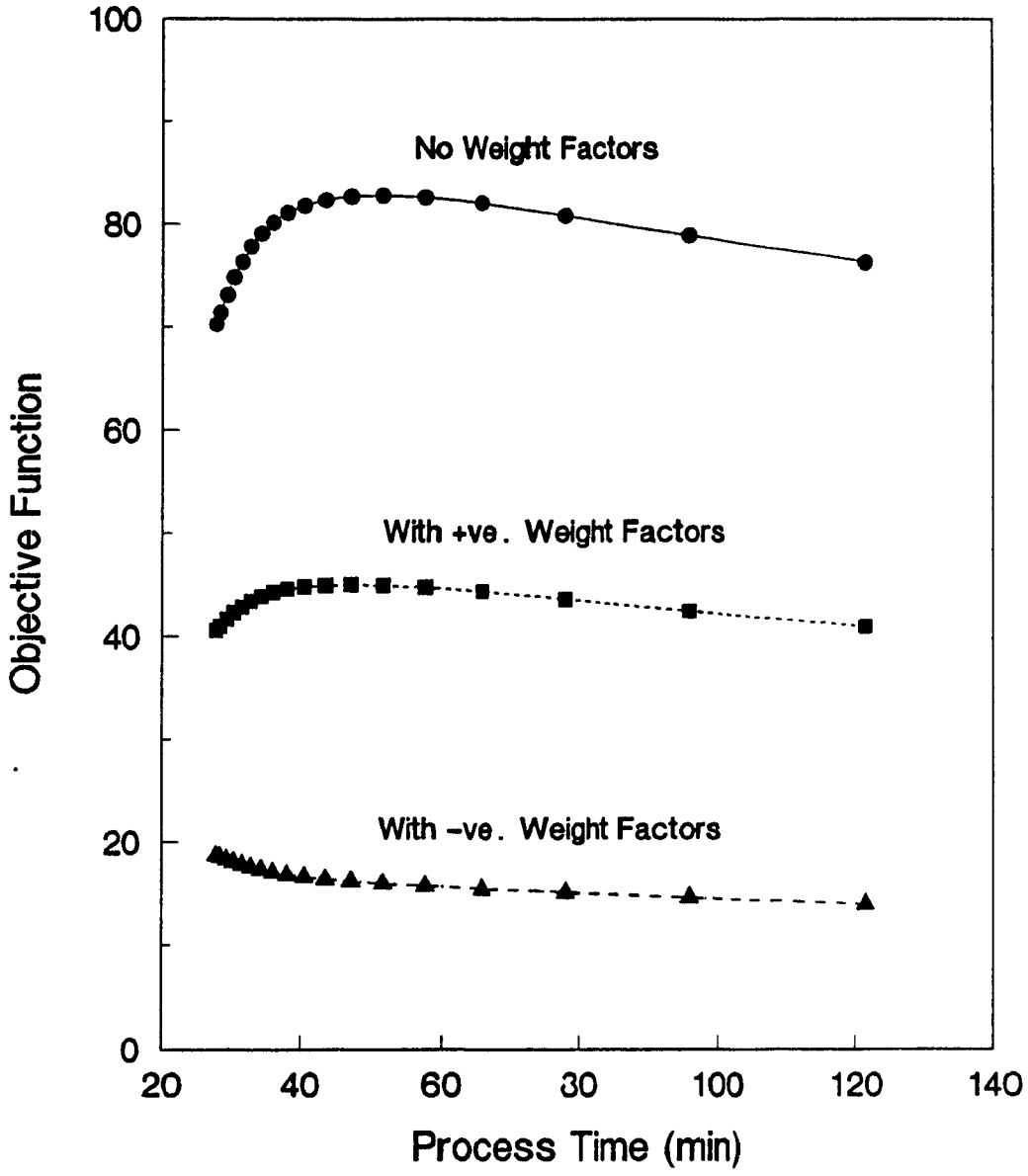


Figure 57. Objective function values versus process times for three quality factors with positive and negative weight factors.

V. SUMMARY AND CONCLUSIONS

Thermal processes can be designed to produce a safe product of optimal quality, having desirable attributes for both the processor and the consumer. The main objective of this work was to study the kinetics of nutrients/quality factors and incorporate this information into computer models and verify their predictions. Extrapolating this objective and assuming it to be workable in any process situation, the impact would be higher quality canned foods having greater retained nutrient levels, better color with minimized operating costs for food processors. The complexity of food systems obviates this extrapolation from becoming a reality in the foreseeable future.

Although the global objective of improving nutrient/quality factor retention for all food systems cannot be met in the short term, small steps taken by researchers in the field of thermal processing continue to make headway toward this global objective. Such steps were taken in this work, (a) resulting in the assessment of a novel conduction system, (b) a reconciliation between the TDT and Arrhenius methods, (c) introducing the concept of using centerpoint conduction capsules, (d) the verification of Teixeira's method as opposed to Ball's method and (e) demonstrating the basic validity of objective function optimization.

Although minor contributions in the context of the vast field of thermal processing, these results will provide data for other researchers to consider and a basis to build upon in moving toward the goal of improving the nutrient/quality factor retention in food products.

VI. LIMITATIONS OF STUDY AND FUTURE WORK

One of problems encountered in the conduction portion of this study was the selection of the appropriate medium for simulating conduction heating. The conduction model must embody inertness, allow the recovery of the components of interest and simulate typical conduction heating behavior. The celite model worked reasonably well, certainly better than any other material used to date, however is still limited in having some reactivity and recovery problems, especially if low concentrations of components are used.

In relation to the components used to simulate the "quality factors", there are obvious limitations associated with this approach as the system was artificial. Clearly every food system is different and the data obtained is limited in terms of extrapolating it to any "real" system. However, it has served a useful purpose by allowing the verification of important computer models and brining to light the relation between the TDT and Arrhenius techniques.

The conditions under which most kinetic studies have been carried out vary greatly and as a consequence need to be assessed individually. Thus the establishment of predictive kinetic models is an area that requires a great deal of effort. It is not only important to determine order of reaction, rate constants, energies of activation, and the influence of compositional parameters on rate constants, but it is also important to be able to correlate all kinetic information in such a way that general kinetic models can be established rather than using empirical correlations with limited applicability. Information on heat and mass transfer for the individual processes needs to be collected accurately and compared to be able to minimize and resolve discrepancies between experimental and predicted values. The institution of constraints such as minimum levels of vitamin retention or organoleptic requirements and the search for ideal conditions constitute the final stages of an optimization process. There is little information available in the literature on nutrient/quality factor degradation and in many instances conflict, so better information is required if the goal of optimizing quality is to be met. On the other hand, monitoring of

organoleptic properties such as color and texture presents added complications because of the lack of single and representative ways to evaluate these parameters.

In view of the many problems associated with nutrient /quality factor assessment in relation to thermal processing and based on the experiences obtained in the course of this research, the following recommendations are made in terms of areas which need further development:

1. The conduction medium can still be improved and glass powder or teflon may be workable, however it would require careful definition in terms of its thermal characteristics and uniformity of particle size. A workable medium would go a long way toward further to testing the more sophisticated computer models for processing predictions.

2. Review of the literature indicates that studies which monitor quality factor changes as a function of processing conditions are very limited. Although this study has made a contribution to this area, there is still a great deal of work needed in order to establish general kinetic models which should be applicable to wide range of quality factors.

3. The basic relationship between the Arrhenius and TDT methods requires further exploration. The hypothesis put forward in this work has illustrated that mathematically the two approaches can be related unambiguously. Proof can be obtained through a careful study of a very well characterized chemical reaction by both methods. The consequences of this concept being correct would be significant, as it implies that chemical engineers and food processors can use conventional kinetics to characterize their reactions and calculate their processes using the TDT approach which is more practical for process determinations.

4. The multi-factor objective function applied for the first time in this study indicates that nutrient optimization may be feasible. The original manual procedure can be made into a computer

module and incorporated into Teixeira's program to directly provide accurate optimum temperature-time combinations without the attendant time presently required. Acceptance of computer simulations is an area which must be developed and honed to the point where processors have the confidence to base their calculations on such predictions rather than always having to carry out heat penetration studies.

As is usual, research, although it tries to provide answers to specific problems, generally produces more questions than it answers. This is the case with this work, however, the results obtained have contributed something tangible to the field of thermal processing.

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APPENDICES

Appendix [1]

Bali's first model

The heated curve for a conduction heating food can be plotted on an inverted semi-logarithmic axis, with the ordinate axis representing the difference between the retort temperature and the container centre temperature, and with the abscissa representing time. Theoretically, the equation for the heating curve is derived from the asymptote of the curve; in practice the straight-line approximation is drawn as a tangent one or two log cycles from the origin (Stumbo, 1973). The equation for the straight-line approximation of the heating curve is given by Ball and Olson (1957) formula:

$$\log [(T_r - T_{pi}) / (T_r - T)] = (1 / f_h)\, t \qquad (1)$$

where

T_r = processing or retort temperature

T = calculated temperature at the centre of the can

t = time passed since exposure to the heat source

T_{pi} = pseudo-initial temperature

$1 / f_h$ = slope of the heating curve

The pseudo-initial temperature (T_{pi}) can be determined from the plot of the straight-line approximation of the heating curve. It represents the initial food temperature that would need to be present to yield the temperature/time curve, if there was no initial lag in the heating rate of the food. The value of f_h is the time necessary to reduce the temperature difference (T_r-T) by one log cycle.

Equation (1) can be rewritten as:

$$\log (j_h / u) = (1 / f_h)\, t \qquad (2)$$

where

u = temperature ratio $(T_r - T_{pi}) / (T_r - T)$

j_h = heating curve lag factor

The general formula for the temperature ratio is given by the following formula:

$$u = (T_a - T) / (T_a - T_o) \quad (3)$$

where

T_a = environmental temperature (= T_r in this case)

T = calculated temperature (centre temperature)

T_o = equivalent to the initial temperature (T_i) of food for this case

j_h is defined as:

$$j_h = (T_r - T_{pi}) / (T_r - T_i) \quad (4)$$

Equations 2, 3 and, 4 can be combined to yield the logarithmic heating curve equation in the form used in model one:

$$T = T_r - (T_r - T_i)\ j_h\ 10^{(-t / f_h)} \quad (5)$$

The cooling curve of model one is considered as described by Ball to be comprised of first a hyperbolic section and then a logarithmic part. The hyperbolic section is given by Ball (1923):

$$T = T_{cmax} - a_c [\sqrt{1 + (t^2_{cool} / b^2_c)} - 1] \quad (6)$$

where

T_{cmax} = maximum cooling temperature

t_{cool} = time passed since exposure to the cooling water

a_c and b_c = fitting constants for the hyperbola

Ball (1923) determined, graphically, that suitable values for the a_c and b_c constants can be derived from the following:

$$a_c = 0.3 \, (T_{cmax} - T_w) \tag{7}$$

$$b_c = 0.173 \; f_c \tag{8}$$

where

T_w = cooling water temperature

f_c = reciprocal of the slope of the cooling curve

The temperature at which the cooling curve switches from a hyperbolic shape to a logarithmic one is given by:

$$T^*_c = T_{cmax} - 0.343 \; (T_{cmax} - T_w) \tag{9}$$

where

T^*_c = temperature at which the switch will occur.

This switch temperature (T^*_c) will occur at time (t^*_c)

$$t^*_c = f_c \log [j_c \, (T_{cmax} - T_w) / (T_c - T_w)] \tag{10}$$

Equation 10 can be simplified (using equation 9) to give:

$$t^*_c = f_c \; \log (j_c / 0.657) \tag{11}$$

After time t^*_c has passed, the cooling curve is calculated using the general logarithmic equation:

$$T = T_a - (T_a - T_o) \; j_c \; 10^{(-t / f_c)} \tag{12}$$

where

t = time equivalent to t_{cool} in this case.

Equation 12 can also be written as:

$$T = T_w + (T_{cmax} - T_w) \; j_c \; 10^{(-t_{cool} / f_c)} \tag{13}$$

Ball (1923) determined, graphically, that the value of 1.41 for j_c would yield the equations which closely approximate the empirical heat penetration data.

Ball's second model

In this model, the heating curve is modeled as a hyperbolic and then a logarithmic section. This modification of the heating equation will not affect subsequent lethality calculations, since the early temperatures do not contribute significantly to the magnitude of the lethality accumulated. The hyperbolic portion of the heating curve is calculated by:

$$T = T_i + a_h \left[\sqrt{(1 + t^2 / b^2_h)} - 1 \right] \qquad (14)$$

where

a_h and b_h = fitting constants.

The logarithmic heating section is calculated similar to model one (equation 5). The two fitting constants in the hyperbolic heating equation (a_h and b_h) can be determined by imposing the two following conditions:

A- The point of intersection of the hyperbolic and logarithmic heating curve sections occurs at T^*_h (similar to Ball's intersection point for the cooling curves in model one):

$$T^*_h = T_i + 0.343 (T_r - T_i) \qquad (15)$$

B- At the point of intersection the slopes of the two heating curve sections must be the same, as plotted on Cartesian coordinates. This ensures a smooth transition from hyperbolic to logarithmic heating.

From these two conditions it is possible to determine the expression for the fitting constants a_h and b_h, in terms of the independent variables T_r, T_i, j_h and, f_h. The following steps are followed:

1- The coordinates of the point of intersection of the two heating section are determined.

2- These coordinates are substituted into the hyperbolic equation (equation 14) to obtain the first relationship between a_h and b_h.

3- The derivatives of the equations for the hyperbolic and logarithmic heating sections are found.

4- The coordinates of the point of intersection are substituted into these two different equations.

5- By equating the two differential equations, the second relationship between a_h and b_h is determined.

6- The equations for a_h and b_h are found from the two relationships.

The calculation of the steps of the solution for a_h and b_h (steps 1-6) are now examined in detail:

a- Calculation of step 1

At the point of intersection the temperature is equal to T^*_h, as defined in equation 15, and is also equal to T in equation 5. Setting equation 15 equal to equation 5, one obtains the following expression:

$$T_i + 0.343 (T_r - T_i) = T_r - (T_r - T_i) j_h \; 10^{(-t^*h / f_h)} \qquad (16)$$

The x-coordinate, time, can be determined from equation 16. The equation for the time coordinate is given by:

$$t^*_h = f_h \log(j_h / 0.657) \qquad (17)$$

Thus, from equation 15 and 17, the coordinates of the point of intersection (T^*_h and t^*_h) are found.

b- Calculation of step 2

At the point of intersection the expression for T^*_h, from equation 15, is equal to the temperature calculated by the hyperbolic heating equation (equation 5), at time = t^*_h:

$$T_i + 0.343 (T_r - T_i) = T_i + a_h \left[\sqrt{(1 + t^{*2}_h / b^2_h)} - 1 \right] \quad (18)$$

From this equation, the first relationship between a_h and b_h can be obtained:

$$0.343 = (a_h / (T_r - T_i)) \left[\sqrt{(1 + t^{*2}_h / b^2_h)} - 1 \right] \quad (19)$$

c- Calculation of step 3

The time derivation of the hyperbolic heating equation (equation 14) is given by:

$$\delta T / \delta t = (a_h / b_h^2) \left[t / \sqrt{(1 + t^2 / b^2_h)} \right] \quad (20)$$

The time derivative of the logarithmic heating equation (equation 5) is:

$$\delta T / \delta t = -(T_r - T_i) j_h (-\ln 10 / f_h) e^{(-\ln 10 \ t / f_h)} \quad (21)$$

Equation 21 can also be written as:

$$\delta T / \delta t = - (T_r - T_i) j_h (-2.30259 / f_h) 10^{(-t / f_h)} \quad (22)$$

d- Calculation of step 4

The differential equation of the hyperbolic heating section, at the point of intersection is as follows:

$$\delta T / \delta t = (a_h / b^2_h) \left[t^*_h / \sqrt{(1 + t^*_h / b^2_h)} \right] \quad (23)$$

The differential equation of the logarithmic heating section, at the point of intersection, is given by:

$$\delta T / \delta t = -(T_r - T_i) j_h (-2.30259 / f_h) 10^{(-t^*_h / f_h)} \quad (24)$$

e- Calculation of step 5

At the point of intersection, the slopes of the two heating equations are equal. Thus, the two differential equations can be set equal to each other, to obtain the second relationship between a_h and b_h:

$$a_h / b_h \left[t^*_h / \sqrt{(1+t^{*2}_h / b^2_h)} \right] = -(T_r - T_i)\, j_h\, (-2.30259 / f_h)\; 10^{(-t^*_h / f_h)} \qquad (25)$$

f- Calculation of step 6

By mathematical manipulation of the two relationships between a_h and b_h, given in equations 19 and 25, the expressions for a_h and b_h can be derived:

$$a_h = 0.343 \left[(S - 0.22673) / (0.45346 - S) (T_r - T_i) \right] \qquad (26)$$

where

$$S = \log(j_h / 0.657) \qquad (27)$$

$$b_h = Z(S)\; f_h^2 \qquad (28)$$

where Z is the axial coordinate.

$$Z(S) = [\, 1 - (0.45346 / S) + (0.0514065 / S^2)] / [(0.45346 / S^3) - (1 / S^2) \,] \qquad (29)$$

In model two, the cooling curve is also comprised of a hyperbolic and then logarithmic sections. The cooling curve equations are the same as those described in the cooling section of model one, with the fitting constants a_c and b_c and the switch time and temperature being calculated similarly.

Ball's third model

In this model, the heating curve is represented as being first hyperbolic and then logarithmic, as is the case with the cooling curve. The heating curve is calculated in the same manner as that of model two, with the derived hyperbolic fitting constants a_h and b_h. The cooling curve differs from model one and two, however, in that the hyperbolic fitting constants are calculated, the values for a_c and b_c that Ball (1923) derived graphically are not used. Also, user-supplied j_c values are taken, instead of a constant value of 1.41.

The hyperbolic cooling curve section is given by equation 6, and the logarithmic cooling section by equation 13. The hyperbolic- to- logarithmic switch time t^*_c from equation 10 and the switch temperature T^*_c from equation 9. The j_c value, rather than being assumed to be 1.41, is supplied by the user. Another difference between the hyperbolic cooling curve section of model three, and those of models one and two, is in the way a_c and b_c are calculated. These hyperbolic cooling curve fitting constants are derived by the method used to find the hyperbolic heating curve fitting constants (a_h and b_h) of model two.

Appendix [2]

Program listing of Teixeira's model for the determination of lethality and nutrient retention in conduction-heated foods in cylindrical containers.

```
**********************************************************************************************
C       **** Dimensioning ****
      DIMENSION TA(50,50)
      DIMENSION TB(50,50)
      DIMENSION T(50,50)
      DIMENSION D(50,50)
      DIMENSION CA(50,50)
      DIMENSION TV(50,50)
      DIMENSION PR(50,50)
      INTEGER COOL, NUMBER, SET
      CHARACTER * 8 DATE
C     **** GET  NMBER OF DATA SETS ****
      PRINT *, 'Enter the Number of data sets: '
      READ *, NUMBER
      PRINT *,NUMBER
      PRINT *, 'The number of data sets:  ', NUMBER
      DO 1000 SET= 1,NUMBER
C **** OPEN FILE INPUT FOR INPUT DATA ****
      OPEN(UNIT = 3, FILE = 'B:INPUT1', FORM = 'FORMATTED',
     1 ACCESS = 'SEQUENTIAL', STATUS = 'OLD')
C
C       **** READ AND PRINT EACH RECORD ****
      READ (UNIT = 3, FMT = 1) A,DO,TO,Z
      READ (UNIT = 3, FMT = 2) RO,HO,U
      READ (UNIT = 3, FMT = 3) TI,TR,TC,FH,TCF
      READ (UNIT = 3, FMT = 4) NR,NH,DU
 1    FORMAT(4F10.5)
 2    FORMAT(3F10.5)
 3    FORMAT(5F10.1)
 4    FORMAT(2I10,F10.5)
      PRINT *, '   A      DO      TO      Z'
      PRINT 1, A,DO,TO,Z
      PRINT *,'   RO      HO      U'
      PRINT 2, RO,HO,U
      PRINT *,'   TI      TR      TC      FH      TCF'
      PRINT 3,TI,TR,TC,FH,TCF
      PRINT *,'      NR      NH      DU'
      PRINT 4,NR,NH,DU
C **** OPEN FILE RESULT FOR OUTPUT ****
      OPEN(UNIT = 4, FILE = 'C:SUAD_OUT', FORM = 'FORMATTED',
     1 ACCESS = 'SEQUENTIAL', STATUS = 'UNKNOWN')
      WRITE(UNIT =4, FMT = 5) NUMBER
 5    FORMAT( 'The number of  data sets is: ' ,I4,///)
      WRITE(UNIT = 4, FMT =201)
201   FORMAT(3X,'A (%)',3X,'DO (min)',3X,'TO (F)',3X,'z (F)',/)
      WRITE(UNIT = 4, FMT = 1) A,DO,TO,Z
```

```
      WRITE (UNIT = 4, FMT = 202)
  202   FORMAT(/,3X,'RO (cm)',3X,'HO (cm)',3X,'U (min)',/)
      WRITE(UNIT = 4, FMT = 2)RO,HO,U
      WRITE(UNIT = 4, FMT = 203)
  203   FORMAT(/,3X,'TI (F)',5X,'TR (F)',3X,'TC (F)',3X,'Fh (min)',3X,'
     1TCF (F)',/)
      WRITE(UNIT = 4, FMT = 3)TI,TR,TC,FH,TCF
      WRITE(UNIT = 4, FMT = 204)
  204  FORMAT(/,8X,'NR',8X,'NH',7X,'DU (min)',/)
      WRITE(UNIT = 4, FMT = 4)NR,NH,DU
C         **** EVALUATE CONSTANTS ****
      FI=NR
      FJ=NH
      DRO=RO/FI
      DHO=HO/(2.*FJ)
      UT=0.0
      COOL=0
      CO=A/(HO*3.14*RO**2)
      Z=Z/2.30285
      DO=DO/2.30285
      NR1=NR+1
      NR2=NR+2
      NH1=NH+1
      NH2=NH+2
C         **** PRESET ALL POINTS TO INITIAL CONCENTRATION ****
      DO 40 I=1,NR
      DO 40 J=1,NH
      CA(I,J)=CO
C     PRINT*,'CA(I,J)'
C     PRINT *,CA(I,J)
  40  CONTINUE
C         **** PRESET BOUNDARY AND INTERIOR TEMPERATURES ****
      DO 10 I=2,NR2
      DO 10 J=2,NH2
C     TB(I,J)=TI
      TA(I,J)=TI
  10  CONTINUE
      DO 12 I=1,NR2
  12  TA(I,1)=TR
      DO 11 J=1,NH2
  11  TA(1,J)=TR
      DO 42 I=1,NR2
  42  T(I,1)=TR
      DO 43 J=1,NH2
  43  T(1,J)=TR
C     AL IS COMPUTED BY SLOPE OF HEATING CURVE GIVEN BY STUMBO
      AL=.398/(((1./RO**2)+.427/(HO/2.)**2)*FH)
C     PRINT*,'AL'
C     PRINT *,AL
C         **** SIMPLIFY COEFFICIENTS ****
      P=AL*DU/DRO**2
      Q=AL*DU/(2.*DRO)
      S=AL*DU/DHO**2
      PRINT*,'          P              Q              S'
```

```
      PRINT *,P,Q,S
C     **** CALCULATE TEMPERATURE DISTRIBUTION FOR THIS TIME INTERVAL ****
 13   DO 15 J=2,NH1
C          **** RESET INITIAL R FOR EACH NEW J ****
      R=RO
      DO 14 I=2,NR
      R=R-DRO
 14   TB(I,J)=TA(I,J)+P*(TA(I-1,J)-2.*TA(I,J)+TA(I+1,J))
     ++Q/R*(TA(I-1,J)-TA(I+1,J))+S*(TA(I,J-1)-2*TA(I,J)+TA(I,J+1))
C          *** CENTER LINE TEMPERATURE MUST BE CALC. SEPERATELY SICNE R=0 ***
      TB(NR1,J)=TA(NR1,J)+2.*P*(TA(NR,J)-2.*TA(NR1,J)+TA(NR2,J))
     ++S*(TA(NR1,J-1)-2.*TA(NR1,J)+TA(NR1,J+1))
C          **** CALC. TEMP. AT FIRST INCREMENT OPPOSIT CENTER LINE ****
      TB(NR2,J)=TB(NR,J)
 15   CONTINUE
C          **** CALC. TEMP'S IN A ROW BENEATH CENTER ****
      DO 46 I=2,NR2
      TB(I,NH2)=TB(I,NH)
 46   CONTINUE
C          **** AVEARGE TEMP./TIME, DU AT EACH POINT ****
      DO 20 I=2,NR1
      DO 20 J=2,NH1
      T(I,J)=(TB(I,J)+TA(I,J))/2.
 20   CONTINUE
      DO 22 I=1,NR
      DO 22 J=1,NH
      TV(I,J)=(T(I,J)+T(I+1,J)+T(I,J+1)+T(I+1,J+1))/4.
 22   CONTINUE
C          **** TO REPEAT, LET NEW TEMP BECOME OLD TEMP ****
      DO 52 I=2,NR2
      DO 52 J=2,NH2
      TA(I,J)=TB(I,J)
 52   CONTINUE
C          **** CALC. CONC. AT EACH POINT OVER TIME ****
      DO 75 J=1,NH
      DO 74 I=1,NR
      D(I,J)=DO*EXP((TO-TV(I,J))/Z)
      CA(I,J)=CA(I,J)*EXP(-DU/D(I,J))
 74   CONTINUE
 75   CONTINUE
      IF(T(NR1,NH1) .LE. TCF) GOTO 100
      IF(T(NR1,NH1) .GT. TCF) GOTO 103
C          **** CALCULATE ELAPSED TIME ****
 103  UT=UT+DU
       PRINT*,'          UT          T(NR1,NH1)'
       PRINT *,UT,T(NR1,NH1)
C       WRITE(UNIT = 4, FMT = 9) UT,T(NR1,NH1)
C 9     FORMAT(F14.6,12X,F14.6)
C     IF PROCESS TIME IS REACHED, SET BOUNDARY = TO TC
 8    IF(UT .LT. U) GOTO 13
      IF(COOL .EQ. 0) GOTO 100
      IF(COOL .GT. 1) GOTO 13
 130  DO 29 I=1,NR2
 29   TA(I,1)=TC
```

```
      DO 28 J=1,NH2
   28 TA(1,J)=TC
      DO 27 I=1,NR2
   27 T(I,1)=TC
      DO 26 J=1,NH2
   26 T(1,J)=TC
      PRINT*,' COOLING STARTED'
      WRITE(UNIT = 4, FMT = 206)
  206 FORMAT(' C O O L I N G     S T A R T E D')
C     PRINT*,'TA(1,1)'
C     PRINT *,TA(1,1)
      COOL=2
      GO TO 13
C          **** CALCULATE LETHALITY ****
C          **** MULTIPLY CONCENTRATION AT EACH POINT BY CORRESPONDING ****
C          ****     INCREMENTAL VOLUME, AND ADD TOGETHER     ****
  100 WRITE(UNIT = 4, FMT = 17)
   17 FORMAT(///, 'Nutrient Retention (%)',5X,'Time (min)',10X,'Centre
     1Temperature (C)'//)
      SUM=0.0
      DO 32 J=1,NH
      R=RO
      DO 32 I=1,NR
      R=R-DRO
      PR(I,J)=CA(I,J)*3.14*DHO*(2.*R*DRO+DRO**2)
   32 SUM=SUM+PR(I,J)
      BE=2.*SUM
      WRITE(UNIT = 4, FMT = 30) BE,UT,T(NR1,NH1)
   30 FORMAT(1X,F20.8,10X,F14.6,12X,F14.6)
      COOL=1
      IF (T(NR1,NH1) .LE. TCF) GOTO 110
      IF (T(NR1,NH1) .GT. TCF) GOTO 13
  110 CONTINUE
 1000 CONTINUE
      CLOSE (UNIT = 3)
      ENDFILE (UNIT = 4)
      CLOSE (UNIT = 4)
      STOP
      END
*****************************************************************************************
```

Appendix [3]

Effect of pH and volume on ascorbic acid retention (%) after thermal processing at 121.1 C and 115.6 C.

pH	Volume	Temperature (121.1 C)		Temperature (115.6 C)	
	(mL)	Time (min)	AA/DDW Retention(%)	Time (min)	AA/DDW Retention(%)
4.05 NB*	8	0	100.0	0	100.0
		24	94.31	36	96.50
		48	91.68	72	93.69
		72	80.28	108	88.72
		96	76.96	144	76.22
		120	73.14	180	70.48
		144	63.03	216	63.36
		168	60.53	252	58.78
		192	54.70	288	51.97
		216	48.26	324	45.03
		240	46.09	360	40.32
4.05 WB**	8	0	100.0	0	100.0
		24	95.91	36	98.48
		48	93.09	72	95.69
		72	84.59	108	90.45
		96	79.66	144	83.73
		120	73.25	180	74.77
		144	64.73	216	69.83
		168	61.55	252	61.39
		192	56.99	288	54.13
		216	51.07	324	49.93
		240	48.98	360	46.83
5.60 WB**	8	0	100.00	0	100.0
		24	93.38	36	94.20
		48	90.01	72	91.13
		72	81.61	108	87.78
		96	76.16	144	80.39
		120	70.25	180	70.73
		144	61.72	216	65.80
		168	58.36	252	57.95
		192	52.98	288	50.54
		216	48.83	324	44.99
		240	46.06	360	38.27
4.05 NB*	4	0	100.0	0	100.0
		24	85.04	36	89.59

		48	77.55	72	81.28
		72	72.17	108	77.23
		96	68.74	144	71.11
		120	61.43	180	65.98
		144	53.35	216	60.22
		168	50.71	252	52.8
		192	44.85	288	47.87
		216	40.80	324	40.05
		240	36.08	360	34.55
4.05 WB**	4	0	100.0	0	100.0
		24	86.82	36	91.89
		48	79.17	72	88.45
		72	74.41	108	80.55
		96	69.85	144	73.79
		120	63.91	180	69.81
		144	55.40	216	63.50
		168	52.08	252	55.58
		192	47.13	288	50.21
		216	43.09	324	44.66
		240	38.01	360	38.46
5.60 WB**	4	0	100.0	0	100.0
		24	82.38	36	84.85
		48	71.15	72	80.51
		72	68.22	108	78.62
		96	62.70	144	71.64
		120	56.57	180	63.48
		144	50.41	216	58.15
		168	47.89	252	50.49
		192	43.44	288	45.43
		216	40.08	324	41.90
		240	36.82	360	35.73

NB* = sample without buffer WB** = sample with buffer

Appendix [4]

Detailed heat penetration parameters for the celite food model.

Temperature (°C)	Constant Heating Time (min)	Average[1] (f_h) (min)	Average[1] (f_c) (min)	j_h[1]	j_c[1]
110.0	78.0	30.30	38.33	2.10	2.49
115.6	52.5	28.63	36.35	2.12	2.58
121.1	40.0	27.06	35.32	2.18	2.63
126.7	35.0	25.47	34.73	2.35	2.69
110.0	126.0	30.18	38.98	2.13	2.58
115.6	68.0	28.01	36.15	2.15	2.65
121.1	50.0	26.32	35.01	2.20	2.77
126.7	40.0	25.81	34.89	2.29	2.72
121.1	75.0	26.83	34.11	2.18	2.73
126.7	60.0	25.04	33.67	2.31	2.75
121.1	25.0	26.79	34.57	2.23	2.62
126.7	20.0	26.73	33.58	2.34	2.67
121.1	120.0	27.07	34.29	2.17	2.68
126.7	100.0	25.01	33.95	2.24	2.63
126.7	120.0	25.78	34.13	2.26	2.66
126.7	80.0	24.87	33.78	2.27	2.63
	Average	26.86	35.12	2.2196	2.6550
	SD	1.56	1.55	0.0759	0.0688
	CoV	5.94	4.43	3.42	2.59

1 = based on 16 observations; SD = Standard deviation; CoV = Coefficient of Variation (%)

Appendix [5]

Statistical variations in ascorbic acid retention (AA/DDW and AA/MIX) analysis by HPLC method.

Retort Temperature C	Total Heating Time (min)	Mean Retention (%) AA/DDW	SD	CoV	Mean Retention (%) AA/MIX	SD	CoV
110	84.0	87.99	1.25	1.4206	79.69	1.16	1.4556
	132.0	83.12	0.98	1.1790	73.65	1.35	1.8330
115.6	58.5	90.47	0.96	1.0611	82.54	1.38	1.6719
	75.0	87.45	1.42	1.6238	76.35	1.31	1.7158
121.1	31.0	95.24	1.05	1.1025	85.05	1.41	1.6578
	47.5	90.82	1.31	1.4424	81.21	1.35	1.6624
	57.0	89.67	1.33	1.4832	75.88	1.43	1.8846
	81.5	83.57	1.16	1.3881	68.08	1.39	2.0417
	129.0	74.43	1.18	1.5854	55.36	1.52	2.7457
126.7	29.5	92.85	0.91	0.9801	87.96	1.28	1.4552
	45.0	82.99	0.97	1.1688	79.36	2.35	2.9612
	49.0	78.72	1.39	1.7658	67.66	1.31	1.9362
	69.5	73.25	1.46	1.9932	63.09	0.93	1.4741
	89.5	64.79	1.37	2.1145	58.91	1.44	2.4444
	109.5	53.59	2.29	4.2732	38.56	1.34	3.4751
	129.5	29.21	1.37	4.6902	32.40	1.42	4.3827

SD = Standard deviation CoV = Coefficient of Variation (%).

Appendix [6]

Statistical variations in thiamine retention (B1/DDW and B1/MIX) analysis by HPLC method.

Retort Temperature C	Total Heating Time (min)	Mean Retention (%) B1/DDW	SD	CoV	Mean Retention (%) B1/MIX	SD	CoV
110.0	84.0	26.48	1.11	4.1918	25.15	1.08	4.2942
	132.0	22.02	1.03	4.6776	18.87	1.19	6.3063
115.6	58.5	24.81	1.02	4.1112	23.37	1.32	5.6483
	75.0	23.86	1.21	5.0712	22.68	1.42	6.2610
121.1	31.0	22.46	1.12	4.9866	21.49	1.12	5.2117
	47.5	21.89	1.21	5.5276	19.73	1.27	6.4369
	57.0	20.35	1.29	6.3391	18.59	1.16	6.2399
	81.5	18.98	1.21	6.3751	17.85	1.42	7.9552
	129.0	--- No B1 sample			No B1 sample		
126.7	29.5	22.46	1.04	4.6305	21.83	1.17	5.3596
	45.0	21.47	1.14	5.3097	20.24	1.23	6.0771
	49.0	18.77	1.17	6.2334	17.86	1.17	6.5510
	69.5	15.60	1.01	6.4744	14.39	1.14	7.9222
	89.5	--- No B1 sample			No B1 sample		
	109.5	--- No B1 sample			No B1 sample		
	129.5	--- No B1 sample			No B1 sample		

SD = Standard deviation CoV = Coefficient of Variation (%)

Appendix [7]

Retention (%) of ascorbic acid (AA) and thiamine (B1) in test samples of wetted celite in the two systems (double distilled water, DDW, and mixture, MIX) following thermal processing.

Temperature C	Total Heating Time (min)	Retention (%)			
		AA/DDW	AA/MIX	B1/DDW	B1/MIX
110.0	84	87.99	79.69	26.48	25.15
115.6	58.5	90.47	82.54	24.81	23.37
121.1	47.5	90.82	81.21	21.89	19.73
126.7	45.0	82.99	79.36	21.47	20.24
110.0	132.0	83.12	73.65	22.02	18.87
115.6	75.0	87.45	76.35	23.86	22.68
121.1	57.0	89.67	75.88	20.35	18.59
126.7	49.0	78.72	67.66	18.77	17.86
121.1	81.5	83.57	68.08	18.98	17.85
126.7	69.5	73.25	63.09	15.60	14.39
121.1	31.0	95.24	85.05	22.46	21.49
126.7	29.5	92.85	87.96	22.46	21.83
121.1	129.0	74.43	55.36	- No B1 Sample -	
126.7	89.5	64.79	58.91	- No B1 Sample -	
126.7	109.5	53.59	38.56	- No B1 Sample -	
126.7	129.5	29.21	32.40	- No B1 Sample -	

Appendix [8]

Retention (%) of ascorbic acid in the two systems (AA/DDW and AA/MIX) as a function of the accumulated centrepoint lethality (based on z = 10 C), following thermal processing in cans filled with celite.

Temperature C	Total Heating Time (min)	Lethality (Improved General)	Experimental Retention (%) AA/DDW	Experimental Retention (%) AA/MIX
110.0	84.0	4.08	87.99	79.69
115.6	58.5	5.27	90.47	82.54
121.1	47.5	13.39	90.82	81.21
126.7	45.0	27.31	82.99	79.36
110.0	132.0	8.30	83.12	73.65
115.6	75.0	12.41	87.45	76.35
121.1	57.0	27.93	89.67	75.88
126.7	49.0	51.86	78.72	67.66
121.1	81.5	50.74	83.57	68.08
126.7	69.5	111.54	73.25	63.09
121.1	31.0	1.99	95.24	85.05
126.7	29.5	1.59	92.85	87.96
121.1	129.0	104.16	74.43	55.36
126.7	89.5	170.93	64.79	58.91
126.7	109.5	236.92	53.59	38.56
126.7	129.5	302.9	29.21	32.40

Appendix [9]

Color formation (100 - Y%) in test samples of wetted celite in the two systems (double distilled water, DDW, and mixture, MIX) following thermal processing.

Temperature C	Total Heating Time (min)	Color Formation			
		Y%/DDW	(100-Y%)	Y%/MIX	(100-Y%)/MIX
110.0	84.0	89.58	10.42	94.79	5.21
115.6	58.5	90.74	9.26	95.27	4.73
121.1	47.5	82.92	17.08	90.32	9.68
126.7	45.0	84.65	15.35	86.77	13.23
110.0	132.0	85.67	14.33	91.53	8.47
115.6	75.0	86.32	13.68	92.39	7.61
121.1	57.0	81.51	18.49	87.09	12.91
126.7	49.0	73.37	26.63	78.96	21.04
121.1	81.5	70.78	29.22	79.98	20.02
126.7	69.5	65.97	34.03	71.84	28.16
121.1	31.0	84.36	15.64	93.19	6.81
126.7	29.5	85.80	14.20	93.46	6.54
121.1	129.0	56.80	43.20	59.12	40.88
126.7	89.5	46.18	53.82	54.10	45.90
126.7	109.5	35.93	64.07	47.96	52.04
126.7	129.5	31.28	68.72	36.14	63.86

Appendix [10]

Retention (%) of color in the two systems (Y%/DDW and Y%/MIX) as a function of the accumulated centrepoint lethality (based on z =10 C), following thermal processing in cans filled with celite.

Temperature C	Total Heating Time (min)	Lethality (Improved General)	Experimental Retention (%) Y%/DDW	Experimental Retention (%) Y%/MIX
110.0	84.0	4.08	89.58	94.79
115.6	58.5	5.27	90.74	95.27
121.1	47.5	13.39	82.92	90.32
126.7	45.0	27.31	84.65	86.77
110.0	132.0	8.30	85.67	91.53
115.6	75.0	12.41	86.32	92.39
121.1	57.0	27.93	81.51	87.09
126.7	49.0	51.86	73.37	78.96
121.1	81.5	50.74	70.78	79.98
126.7	69.5	111.54	65.97	71.84
121.1	31.0	1.99	84.36	93.19
126.7	29.5	1.59	85.80	93.46
121.1	129.0	104.16	56.80	59.12
126.7	89.5	170.93	46.18	54.10
126.7	109.5	236.92	35.93	47.96
126.7	129.5	302.9	31.28	36.14

Appendix [11]

Predicted centrepoint temperature values obtained by Teixeira's, Finnegan's, and Ball's Models with actual temperature-time values throughout the can (size 211 x 400) filled with celite.

Retort operating temperature = 121.1 C and Process time = 77.73 min

Experimental Data		Teixeira's Model		Finnegan's Model		Ball's Model	
Time (min)	Temperature (C)	Time (min)	Temperature (C)	Time (min)	Temperature (C)	Time (min)	Temperature (C)
0.0	14.85	0.00	15.00	0.00	15.00	0.00	15.00
0.5	15.01	0.50	15.00	1.43	15.35	1.43	15.31
1.0	15.29	1.00	15.00	2.86	16.40	2.86	16.23
1.5	15.32	1.50	15.00	4.29	18.17	4.29	17.78
2.0	15.39	2.00	15.01	5.72	20.68	5.72	19.99
2.5	15.43	2.50	15.09	7.15	23.97	7.15	22.87
3.0	15.48	3.00	15.32	8.58	28.11	8.58	26.48
3.5	15.50	3.50	15.80	10.01	33.18	10.01	30.88
4.0	15.50	4.00	16.59	11.43	39.28	11.43	36.14
4.5	15.67	4.50	17.71	12.86	46.59	12.86	42.39
5.0	15.68	5.00	19.15	14.29	55.11	14.29	49.78
5.5	15.83	5.50	20.88	15.72	63.02	15.72	57.78
6.0	16.01	6.00	22.86	17.15	69.98	17.15	64.93
6.5	16.21	6.50	25.05	18.58	76.12	18.58	71.28
7.0	16.54	7.00	27.41	20.01	81.52	20.01	76.91
7.5	17.13	7.50	29.90	21.44	86.28	21.44	81.91
8.0	18.07	8.00	32.48	22.87	90.47	22.87	86.35
8.5	19.48	8.50	35.12	24.30	94.16	24.30	90.29
9.0	21.52	9.00	37.80	25.73	97.41	25.73	93.79
9.5	24.72	9.50	40.50	27.16	100.27	27.16	96.89
10.0	31.43	10.00	43.20	28.59	102.79	28.59	99.65
10.5	40.57	10.50	45.88	30.02	105.01	30.02	102.09
11.0	51.11	11.00	48.53	31.44	106.96	31.44	104.26
11.5	58.89	11.50	51.14	32.87	108.68	32.87	106.19
12.0	63.47	12.00	53.70	34.30	110.20	34.30	107.89
12.5	66.94	12.50	56.21	35.73	111.54	35.73	109.41
13.0	69.84	13.00	58.66	37.16	112.71	37.16	110.76
13.5	72.50	13.50	61.05	38.59	113.75	38.59	111.95
14.0	75.00	14.00	63.38	40.02	114.66	40.02	113.01
14.5	77.30	14.50	65.63	41.45	115.46	41.45	113.96
15.0	79.30	15.00	67.82	42.88	116.17	42.88	114.79
15.5	81.30	15.50	69.94	44.31	116.79	44.31	115.53
16.0	83.10	16.00	71.99	45.74	117.34	45.74	116.19
16.5	84.90	16.50	73.97	47.17	117.82	47.17	116.78
17.0	86.60	17.00	75.89	48.60	118.25	48.60	117.30
17.5	88.10	17.50	77.73	50.03	118.62	50.03	117.76

18.0	89.40	18.00	79.51	51.45	118.95	51.45	118.16
18.5	90.70	18.50	81.23	52.88	119.25	52.88	118.53
19.0	91.90	19.00	82.88	54.31	119.50	54.31	118.85
19.5	93.10	19.50	84.47	55.74	119.73	55.74	119.13
20.0	94.20	20.00	86.00	57.17	119.93	57.17	119.39
20.5	95.30	20.50	87.47	58.60	120.10	58.60	119.61
21.0	96.40	21.00	88.88	60.03	120.25	60.03	119.81
21.5	97.40	21.50	90.24	61.46	120.39	61.46	119.99
22.0	98.40	22.00	91.55	62.89	120.51	62.89	120.15
22.5	99.40	22.50	92.80	64.32	120.61	64.32	120.29
23.0	100.30	23.00	94.01	65.75	120.71	65.75	120.41
23.5	101.10	23.50	95.16	67.18	120.79	67.18	120.52
24.0	102.00	24.00	96.27	68.61	120.86	68.61	120.62
24.5	102.70	24.50	97.33	70.04	120.92	70.04	120.71
25.0	103.50	25.00	98.35	71.46	120.98	71.46	120.78
25.5	104.20	25.50	99.33	72.89	121.03	72.89	120.85
26.0	104.80	26.00	100.27	74.32	121.07	74.32	120.91
26.5	105.50	26.50	101.17	75.75	121.11	75.75	120.97
27.0	106.10	27.00	102.03	77.18	121.14	77.18	121.01
27.5	106.70	27.50	102.86	78.61	121.17	78.61	121.06
28.0	107.30	28.00	103.65	80.04	121.20	80.04	121.09
28.5	107.80	28.50	104.41	81.47	121.22	81.47	120.92
29.0	108.40	29.00	105.14	82.90	121.07	82.90	120.50
29.5	108.90	29.50	105.83	84.33	120.61	84.33	119.81
30.0	109.40	30.00	106.50	85.76	119.84	85.76	118.86
30.5	109.90	30.50	107.14	87.19	118.74	87.19	117.62
31.0	110.30	31.00	107.75	88.62	117.30	88.62	116.10
31.5	110.70	31.50	108.34	90.05	115.52	90.05	114.27
32.0	111.20	32.00	108.90	91.47	113.35	91.47	112.11
32.5	111.80	32.50	109.44	92.90	110.79	92.90	109.61
33.0	112.30	33.00	109.95	94.33	107.78	94.33	106.72
33.5	112.80	33.50	110.45	95.76	104.29	95.76	103.41
34.0	113.20	34.00	110.92	97.19	100.23	97.19	99.61
34.5	113.50	34.50	111.37	98.62	95.50	98.62	95.25
35.0	113.90	35.00	111.80	100.05	89.97	100.05	90.21
35.5	114.10	35.50	112.22	101.48	83.39	101.48	84.30
36.0	114.40	36.00	112.61	102.91	76.42	102.91	77.86
36.5	114.70	36.50	112.99	104.34	70.12	104.34	71.94
37.0	114.90	37.00	113.35	105.77	64.41	105.77	66.54
37.5	115.20	37.50	113.70	107.20	59.25	107.20	61.61
38.0	115.50	38.00	114.03	108.63	54.57	108.63	57.11
38.5	115.70	38.50	114.35	110.06	50.34	110.06	53.00
39.0	116.00	39.00	114.66	111.48	46.51	111.48	49.25
39.5	116.20	39.50	114.95	112.91	43.05	112.91	45.83
40.0	116.40	40.00	115.23	114.34	39.91	114.34	42.71
40.5	116.70	40.50	115.49	115.77	37.07	115.77	39.85
41.0	116.90	41.00	115.75	117.20	34.50	117.20	37.25
41.5	117.10	41.50	115.99	118.63	32.18	118.63	34.88
42.0	117.30	42.00	116.23	120.06	30.07	120.06	32.71
42.5	117.50	42.50	116.45	121.49	28.17	121.49	30.73

43.0	117.60	43.00	116.67	122.92	26.44	122.92	28.92
43.5	117.80	43.50	116.87	124.35	24.88	124.35	27.27
44.0	118.00	44.00	117.07	125.78	23.47	125.78	25.76
44.5	118.10	44.50	117.25	127.21	22.19	127.21	24.39
45.0	118.30	45.00	117.43	128.64	21.03	128.64	23.14
45.5	118.40	45.50	117.61	130.07	19.99	130.07	21.99
46.0	118.60	46.00	117.77	131.49	19.04	131.49	20.94
46.5	118.70	46.50	117.93	132.92	18.18	132.92	19.99
47.0	118.80	47.00	118.08	134.35	17.40	134.35	19.12
47.5	119.00	47.50	118.22	135.78	16.70	135.78	18.32
48.0	119.10	48.00	118.36	137.21	16.06	137.21	17.60
48.5	119.20	48.50	118.49	138.64	15.49	138.64	16.94
49.0	119.30	49.00	118.62	140.07	14.97	140.07	16.33
49.5	119.40	49.50	118.74	141.50	14.50	141.50	15.78
50.0	119.50	50.00	118.85				
50.5	119.60	50.50	118.96				
51.0	119.70	51.00	119.07				
51.5	119.70	51.50	119.17				
52.0	119.80	52.00	119.26				
52.5	119.90	52.50	119.36				
53.0	120.00	53.00	119.44				
53.5	120.00	53.50	119.53				
54.0	120.10	54.00	119.61				
54.5	120.20	54.50	119.69				
55.0	120.20	55.00	119.76				
55.5	120.30	55.50	119.83				
56.0	120.30	56.00	119.90				
56.5	120.40	56.50	119.96				
57.0	120.40	57.00	120.03				
57.5	120.50	57.50	120.09				
58.0	120.50	58.00	120.14				
58.5	120.60	58.50	120.20				
59.0	120.60	59.00	120.25				
59.5	120.70	59.50	120.30				
60.0	120.70	60.00	120.35				
60.5	120.80	60.50	120.39				
61.0	120.80	61.00	120.43				
61.5	120.80	61.50	120.48				
62.0	120.90	62.00	120.52				
62.5	120.90	62.50	120.55				
63.0	120.90	63.00	120.59				
63.5	120.90	63.50	120.62				
64.0	121.00	64.00	120.66				
64.5	121.00	64.50	120.69				
65.0	121.00	65.00	120.72				
65.5	121.00	65.50	120.75				
66.0	121.00	66.00	120.78				
66.5	121.10	66.50	120.80				
67.0	121.10	67.00	120.83				
67.5	121.10	67.50	120.85				

68.0	121.10	68.00	120.88
68.5	121.10	68.50	120.90
69.0	121.10	69.00	120.92
69.5	121.20	69.50	120.94
70.0	121.20	70.00	120.96
70.5	121.20	70.50	120.98
71.0	121.20	71.00	121.00
71.5	121.20	71.50	121.01
72.0	121.20	72.00	121.03
72.5	121.20	72.50	121.05
73.0	121.20	73.00	121.06
73.5	121.20	73.50	121.07
74.0	121.20	74.00	121.09
74.5	121.30	74.50	121.10
75.0	121.30	75.00	121.11
75.5	121.30	75.50	121.13
76.0	121.30	76.00	121.14
76.5	121.30	76.50	121.15
77.0	121.30	77.00	121.16
77.5	121.30	77.50	121.17
78.0	121.30	78.00	121.18
78.5	121.30	78.50	121.19
79.0	121.30	79.00	121.20
79.5	121.30	79.50	121.20
80.0	121.30	80.00	121.21
80.5	121.30	80.50	121.22
81.0	121.30	81.00	121.23
81.5	121.30	81.50	121.23
82.0	121.30	82.00	121.24
82.5	121.30	82.50	121.25
83.0	121.30	83.00	121.25
83.5	121.40	83.50	121.25
84.0	121.40	84.00	121.21
84.5	121.40	84.50	121.02
85.0	121.40	85.00	120.59
85.5	121.40	85.50	119.86
86.0	121.40	86.00	118.78
86.5	121.40	86.50	117.36
87.0	121.40	87.00	115.62
87.5	121.30	87.50	113.61
88.0	120.70	88.00	111.37
88.5	119.90	88.50	108.95
89.0	119.10	89.00	106.38
89.5	114.60	89.50	103.70
90.0	103.60	90.00	100.95
90.5	98.40	90.50	98.15
91.0	93.50	91.00	95.33
91.5	88.60	91.50	92.51
92.0	85.40	92.00	89.70
92.5	83.20	92.50	86.92

93.0	81.50	93.00	84.18
93.5	80.00	93.50	81.48
94.0	78.60	94.00	78.84
94.5	77.10	94.50	76.26
95.0	75.60	95.00	73.75
95.5	74.10	95.50	71.30
96.0	72.50	96.00	68.92
96.5	71.00	96.50	66.61
97.0	69.56	97.00	64.38
97.5	68.11	97.50	62.21
98.0	66.63	98.00	60.12
98.5	65.15	98.50	58.10
99.0	63.67	99.00	56.15
99.5	62.18	99.50	54.27
100.0	60.71	100.00	52.46
100.5	59.23	100.50	50.72
101.0	57.77	101.00	49.04
101.5	56.31	101.50	47.42
102.0	54.87	102.00	45.87
102.5	53.45	102.50	44.37
103.0	52.04	103.00	42.94
103.5	50.65	103.50	41.56
104.0	49.30	104.00	40.23
104.5	47.97	104.50	38.96
105.0	46.66	105.00	37.74
105.5	45.38	105.50	36.57
106.0	44.13	106.00	35.44
106.5	42.92	106.50	34.36
107.0	41.74	107.00	33.33
107.5	40.57	107.50	32.34
108.0	39.44	108.00	31.39
108.5	38.35	108.50	30.47
109.0	37.29	109.00	29.60
109.5	36.26	109.50	28.76
110.0	35.25	110.00	27.96
110.5	34.27	110.50	27.19
111.0	33.32	111.00	26.45
111.5	32.40	111.50	25.75
112.0	31.51	112.00	25.07
112.5	30.65	112.50	24.42
113.0	29.81	113.00	23.80
113.5	28.99	113.50	23.21
114.0	28.20	114.00	22.64
114.5	27.43	114.50	22.10
115.0	26.69	115.00	21.58
115.5	25.97	115.50	21.08
116.0	25.27	116.00	20.60
116.5	24.59	116.50	20.14
117.0	23.94	117.00	19.70
117.5	23.30	117.50	19.28

118.0	22.68	118.00	18.88
118.5	22.08	118.50	18.50
119.0	21.51	119.00	18.13
119.5	20.94	119.50	17.78
120.0	20.40	120.00	17.44
120.5	19.88	120.50	17.12
121.0	19.37	121.00	16.81
121.5	18.87	121.50	16.52
122.0	18.39	122.00	16.24
122.5	17.93	122.50	15.97
123.0	17.48	123.00	15.71
123.5	17.04	123.50	15.46
124.0	16.62	124.00	15.22
124.5	16.21	124.50	15.00
125.0	15.81	125.00	14.78
125.5	15.43	125.50	14.57
126.0	15.05		
126.5	14.69		
127.0	14.34		
127.5	14.00		
128.0	13.67		
128.5	13.35		
129.0	13.04		
129.5	12.74		
130.0	12.44		
130.5	12.16		
131.0	11.89		
131.5	11.62		
132.0	11.36		
132.5	11.11		
133.0	10.88		
133.5	10.64		
134.0	10.41		
134.5	10.19		
135.0	9.98		
135.5	9.77		
136.0	9.57		
136.5	9.37		
137.0	9.18		
137.5	9.00		
138.0	8.82		
138.5	8.64		
139.0	8.48		
139.5	8.32		
140.0	8.16		
140.5	8.00		
141.0	7.86		
141.5	7.71		
142.0	7.57		
142.5	7.44		

143.0	7.30
143.5	7.17
144.0	7.05
144.5	6.93
145.0	6.82
145.5	6.70
146.0	6.59
146.5	6.48
147.0	6.38
147.5	6.28
148.0	6.18
148.5	6.08
149.0	5.99
149.5	5.90
150.0	5.82
150.5	5.73
151.0	5.65
151.5	5.57
152.0	5.49
152.5	5.42
153.0	5.34
153.5	5.27
154.0	5.20
154.5	5.13
155.0	5.07
155.5	5.00
156.0	4.94
156.5	4.87
157.0	4.81
157.5	4.75
158.0	4.70
158.5	4.64
159.0	4.59
159.5	4.53
160.0	4.49
160.5	4.43
170.00	4.38
170.50	4.34
171.00	4.29
171.50	4.25
172.00	4.21
172.50	4.17
173.00	4.13
173.50	4.09

Appendix [12]

Verification of quality factors (ascorbic acid, thiamine, and color formation) by Teixeira's model with predicticns based on the experimental kinetic parameters.

Sample Description	Method	Retort Temperature (C)	Total process Time(min)	Teixeira Retention(%)	Experimental Retention (%)
AA/DDW	Ampoule (4 mL)	110.10	84.0	83.38	87.99
		115.29	58.5	85.86	90.47
		121.38	47.5	85.24	90.82
		126.30	45.0	82.46	82.99
		110.14	132.0	73.32	83.12
		116.20	75.0	80.02	87.45
		121.81	57.0	80.88	89.67
		126.96	49.0	79.69	78.72
		121.39	81.5	71.76	83.57
		126.30	69.5	70.03	73.25
		123.09	31.0	91.32	95.24
		127.24	29.5	90.11	92.85
		121.42	129.0	56.11	74.43
		126.30	109.5	53.28	53.59
		126.30	129.5	46.47	29.21
		126.30	89.5	61.10	64.79
	Capillary	110.10	84.0	78.57	87.99
		115.29	58.5	82.31	90.47
		121.38	47.5	82.42	90.82
		126.30	45.0	80.08	82.99
		110.14	132.0	66.64	83.12
		116.20	75.0	75.76	87.45
		121.81	57.0	77.72	89.67
		126.96	49.0	77.28	78.72
		121.39	81.5	67.82	83.57
		126.30	69.5	67.19	73.25
		123.09	31.0	89.35	95.24
		127.24	29.5	88.33	92.85
		121.42	129.0	51.40	74.43
		126.30	109.5	50.18	53.59
		126.30	129.5	43.35	29.21
		126.30	89.5	58.07	64.79

AA/MIX	Ampoule	110.10	84.0	38.73	79.69
	(4 mL)	115.29	58.5	48.18	82.54
		121.38	47.5	52.35	81.21
		126.30	45.0	52.49	79.36
		110.14	132.0	24.18	73.65
		116.20	75.0	40.31	76.35
		121.81	57.0	46.97	75.88
		126.96	49.0	49.91	67.66
		121.39	81.5	35.92	68.08
		126.30	69.5	39.44	63.09
		123.09	31.0	62.48	85.05
		127.24	29.5	62.71	87.96
		121.42	129.0	21.22	55.36
		126.30	109.5	24.73	38.56
		126.30	129.5	19.58	32.40
		126.30	89.5	31.23	58.91
	Capillary	110.10	84.0	44.28	79.69
		115.29	58.5	53.68	82.54
		121.38	47.5	57.51	81.21
		126.30	45.0	57.25	79.36
		110.14	132.0	28.63	73.65
		116.20	75.0	45.23	76.35
		121.81	57.0	51.74	75.88
		126.96	49.0	54.41	67.66
		121.39	81.5	39.91	68.08
		126.30	69.5	43.14	63.09
		123.09	31.0	68.08	85.05
		127.24	29.5	68.09	87.96
		121.42	129.0	23.92	55.36
		126.30	109.5	27.14	38.56
		126.30	129.5	21.53	32.40
		126.30	89.5	34.22	58.91

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B1/DDW	Ampoule	110.10	84.0	86.63	26.48
	(4 mL)	115.29	58.5	87.42	24.81
		121.38	47.5	85.04	21.89
		126.30	45.0	80.09	21.47
		110.14	132.0	77.71	22.02
		116.20	75.0	81.25	23.86
		121.81	57.0	79.91	20.35
		126.96	49.0	76.31	18.77
		121.39	81.5	69.72	18.98
		126.30	69.5	64.56	15.60
		123.09	31.0	91.50	22.46
		127.24	29.5	89.32	22.46
		121.42	129.0	52.33	ns

		126.30	109.5	44.81	ns
		126.30	129.5	37.31	ns
		126.30	89.5	53.81	ns
	Capillary	110.10	84.0	82.79	26.48
		115.29	58.5	84.48	24.81
		121.38	47.5	82.57	21.89
		126.30	45.0	77.96	21.47
		110.14	132.0	72.01	22.02
		116.20	75.0	77.49	23.86
		121.81	57.0	77.03	20.35
		126.96	49.0	74.15	18.77
		121.39	81.5	65.99	18.98
		126.30	69.5	61.94	15.60
		123.09	31.0	89.92	22.46
		127.24	29.5	87.88	22.46
		121.42	129.0	47.81	ns
		126.30	109.5	42.03	ns
		126.30	129.5	34.61	ns
		126.30	89.5	51.05	ns
B1/MIX	Ampoule	110.10	84.0	77.63	25.15
	(4 mL)	115.29	58.5	81.21	23.37
		121.38	47.5	80.92	19.73
		126.30	45.0	77.99	20.24
		110.14	132.0	65.09	18.87
		116.20	75.0	74.05	22.68
		121.81	57.0	75.67	18.59
		126.96	49.0	74.74	17.86
		121.39	81.5	64.86	17.85
		126.30	69.5	63.55	14.39
		123.09	31.0	88.54	21.49
		127.24	29.5	87.23	21.83
		121.42	129.0	47.32	ns
		126.30	109.5	45.21	ns
		126.30	129.5	38.12	ns
		126.30	89.5	53.62	ns
	Capillary	110.10	84.0	77.17	25.15
		115.29	58.5	80.72	23.37
		121.38	47.5	80.27	19.73
		126.30	45.0	77.07	20.24
		110.14	132.0	64.37	18.87
		116.20	75.0	73.31	22.68

		121.81	57.0	74.81	18.59
		126.96	49.0	73.71	17.86
		121.39	81.5	63.65	17.85
		126.30	69.5	62.10	14.39
		123.09	31.0	88.18	21.49
		127.24	29.5	86.75	21.83
		121.42	129.0	45.72	ns
		126.30	109.5	43.31	ns
		126.30	129.5	36.16	ns
		126.30	89.5	51.88	ns

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Y%/DDW	Ampoule	110.10	84.0	97.38	89.58
	(4 mL)	115.29	58.5	97.64	90.74
		121.38	47.5	97.31	82.92
		126.30	45.0	96.48	84.65
		110.14	132.0	95.49	85.67
		116.20	75.0	96.45	86.32
		121.81	57.0	96.34	81.51
		126.96	49.0	95.79	73.37
		121.39	81.5	94.25	70.78
		126.30	69.5	93.36	65.97
		123.09	31.0	98.49	84.36
		127.24	29.5	98.15	85.80
		121.42	129.0	90.02	56.80
		126.30	109.5	88.32	35.93
		126.30	129.5	85.90	31.28
		126.30	89.5	90.81	46.18
Y%/MIX	Ampoule	110.10	84.0	96.11	94.79
	(4 mL)	115.29	58.5	96.70	95.27
		121.38	47.5	96.51	90.32
		126.30	45.0	95.75	86.77
		110.14	132.0	93.44	91.53
		116.20	75.0	95.19	92.39
		121.81	57.0	95.37	87.09
		126.96	49.0	95.01	78.96
		121.39	81.5	92.85	79.98
		126.30	69.5	92.27	71.84
		123.09	31.0	98.00	93.19
		127.24	29.5	97.69	93.46
		121.42	129.0	87.86	59.12
		126.30	109.5	86.74	47.96
		126.30	129.5	84.09	36.86
		126.30	89.5	89.47	52.86

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ns = no thiamine samples.

Kinetic parameters:

AA/DDW	Ampoule (4 mL)	Do = 455.0 min ; z = 39.4 C.
	Capillary	Do = 402.0 min ; z = 48.8 C.
AA/MIX	Ampoule (4 mL)	Do = 208.7 min ; z = 212.8 C.
	Capillary	Do = 215.0 min ; z = 151.8 C.
B1/DDW	Ampoule (4 mL)	Do = 394.3 min ; z = 26.44 C.
	Capillary	Do = 349.5 min ; z = 30.60 C.
B1/MIX	Ampoule (4 mL)	Do = 354.3 min ; z = 43.80 C.
	Capillary	Do = 337.8 min ; z = 42.40 C.
Y%/DDW	Ampoule (4 mL)	Do = 2455.4 min ; z = 30.20 C.
Y%/MIX	Ampoule (4 mL)	Do = 2029.4 min ; z = 38.10 C.

Appendix [13]

"(1) Optimization of Quality Factors."

Table 1A. Retention (%) of several quality factors as predicted by Teixeira model.

Temperature (C)	Process Time (min)	Quality Factors Teixeira Model (1)	(2)	(3)	(4)	(5)	(6)	Retention (%) (7)	(8)	(9)
110	121.5	78.86	64.14	57.71	69.56	58.63	42.34	0.65	3.32	94.36
112	95.8	79.51	67.23	62.27	72.50	62.23	47.10	1.42	6.00	95.01
114	77.9	79.83	69.61	65.83	74.75	65.04	50.98	2.54	9.18	95.49
116	65.8	79.60	71.05	68.27	76.16	66.82	53.62	3.78	12.27	95.79
118	57.7	78.62	71.50	69.59	76.70	67.47	54.89	4.80	14.72	95.91
120	51.7	77.17	71.40	70.30	76.77	67.53	55.41	5.65	16.72	95.94
122	47.1	75.28	70.89	70.59	76.49	67.14	55.39	6.33	18.38	95.89
124	43.5	72.91	69.99	70.49	75.87	66.33	54.87	6.80	19.53	95.78
126	40.5	70.19	68.83	70.16	75.05	65.25	54.08	7.15	20.49	95.62
128	38.0	67.08	67.42	69.61	74.00	63.92	53.00	7.38	21.20	95.41
130	35.9	63.43	65.60	68.72	72.62	62.17	51.49	7.41	21.55	95.13
132	34.2	59.53	63.62	67.69	71.07	60.27	49.85	7.37	21.77	94.80
134	32.7	55.39	61.40	66.48	69.30	58.14	48.01	7.26	21.81	94.41
136	31.4	51.03	58.87	65.00	67.24	55.72	45.91	7.01	21.61	93.94
138	30.2	47.09	56.50	63.63	65.25	53.47	44.05	6.90	21.55	93.45
140	29.2	43.03	53.76	61.93	62.90	50.88	41.85	6.62	21.20	92.85
142	28.2	39.56	51.20	60.31	60.63	48.48	39.90	6.44	20.96	92.23
143.3	27.6	37.63	49.65	59.30	59.21	47.03	38.76	6.36	20.84	91.80

Kinetics data for:

(1) =	D=202.0 min ; z = 16.7 C .	(Teixeira et al., 1969)
(2) =	D=188.0 min ; z = 25.0 C .	(Teixeira et al., 1969)
(3) =	D=202.0 min ; z = 33.3 C .	(Teixeira et al., 1969)
(4) = B1 in pea puree(nat.pH)	D=246.9 min ; z = 26.7 C .	(Mulley et al., 1974)
(5) = B1 in whole peas	D=164.0 min ; z = 26.1 C .	(Bendix et al., 1951)
(6) = Chlorophyll in pea puree	D=113.0 min ; z = 28.9 C .	(Lenz & Lund, 1974)
(7) = Color (-a/b) in peas	D= 25.0 min ; z = 39.4 C .	(Timbers, 1971)
(8) = Chlorop. b in spinach (nat pH)	D=48.3 min ; z = 58.9 C .	(Herrmann, 1970)
(9) = C in liquid multivitamin preparation	D=1612.8 min; z = 27.8 C .	(Garrett, 1956)

"(2) Comparisons between predicted quality Factors from Ball and Teixeira models."

Table 1B. Retention (%) of selected quality factors as predicted by Ball model.

Temperature (C)	Process Time (min)	Quality Factors Ball's Model					Retention (%)	
		AA/DDW	B1/DDW	Ref.vitamin A	Ref. Pigment	AA/Peas	Chlorophyll a	Maillard
110	121.5	76.61	81.21	84.13	27.34	96.11	0.01	75.42
112	95.8	80.21	83.74	86.09	34.67	96.41	0.04	78.46
114	77.9	83.02	85.80	87.74	41.13	96.70	0.14	81.02
116	65.8	85.01	87.29	88.93	46.16	96.94	0.33	82.96
118	57.7	86.33	88.26	89.71	49.77	97.09	0.57	84.26
120	51.7	87.38	89.07	90.36	52.72	97.22	0.88	85.32
122	47.1	87.94	89.42	90.60	54.54	97.35	1.25	86.23
124	43.5	88.80	90.17	91.27	56.86	97.48	1.65	86.99
126	40.5	89.41	90.70	91.73	58.59	97.62	2.12	87.74
128	38.0	89.63	90.81	91.78	59.47	97.78	2.65	88.46
130	35.9	90.69	91.96	92.90	62.01	97.92	3.22	89.11
132	34.2	91.14	92.41	93.31	63.25	98.03	3.73	89.60
134	32.7	91.50	92.76	93.63	64.27	98.14	4.29	90.08
136	31.4	91.82	93.07	93.92	65.16	98.24	4.84	90.51
138	30.2	92.15	93.41	94.25	66.07	98.36	5.50	90.99
140	29.2	92.40	93.66	94.48	66.77	98.43	6.04	91.33
142	28.2	92.72	94.00	94.80	67.61	98.55	6.82	91.80
143.3	27.6	92.91	94.21	95.00	68.13	98.63	7.34	92.10

Kinetics data for:

AA/DDW =	D is 455.0 min	z = 39.4 C .	(Ampoule Experimental data)
B1/DDW =	D is 394.3 min	z = 26.4 C .	(Ampoule Experimental data)
Vitamin A =	D is 401.0 min	z = 23.0 C .	(Wilkinson et al., 1982)
Pigment(Betanine) =	D is 139.3 min	z = 70.0 C .	(von Elbe et al., 1974)
Vitamin AA in peas =	D is 1003.0 min	z = 16.0 C .	(Lathrop & Leung, 1980)
Chlorophyll a in spinach =	D is 13.0 min	z = 40.1 C .	(Gupte et al., 1964)
Maillard Reaction in Apple Juice =	D is 271 min	z = 25.0 C .	(Herrmann, 1970 from Lund, 1975)

Table 1C. Retention (%) of selected quality factors as predicted by Teixeira model.

Temperature (C)	Process Time (min)	Quality Factors Teixeira Model					Retention (%)	
		AA/DDW	B1/DDW	Ref.vitamin A	Ref. Pigment	AA/Peas	Chlorophyll a	Maillard
110	121.5	75.60	79.84	82.78	27.34	95.63	0.01	73.47
112	95.8	78.86	81.88	84.26	34.39	95.73	0.03	75.91
114	77.9	81.33	83.42	85.35	40.56	95.76	0.09	77.75
116	65.8	83.02	84.38	85.95	45.36	95.66	0.21	78.85
118	57.7	83.99	84.72	86.01	48.69	95.37	0.34	79.18
120	51.7	84.60	84.74	85.78	51.19	94.95	0.49	79.09
122	47.1	84.94	84.51	85.30	53.08	94.40	0.64	78.66
124	43.5	85.07	84.05	84.58	54.46	93.68	0.77	77.93
126	40.5	85.06	83.43	83.68	55.54	92.80	0.89	76.98
128	38.0	84.94	82.64	82.59	56.34	91.72	0.99	75.81
130	35.9	84.63	81.59	81.20	56.79	90.35	1.04	74.30
132	34.2	84.25	80.40	79.63	57.10	88.71	1.09	72.62
134	32.7	83.76	79.03	77.83	57.22	86.74	1.10	70.70
136	31.4	83.13	77.40	75.72	57.12	84.33	1.09	68.48
138	30.2	82.54	75.79	73.60	57.13	81.68	1.11	66.32
140	29.2	81.76	73.84	71.09	56.86	78.48	1.08	63.78
142	28.2	81.01	71.90	68.57	56.67	75.03	1.07	61.31
143.3	27.6	80.53	70.64	66.94	56.56	72.71	1.06	59.76

Kinetics data for:

AA/DDW =	D is 455.0 min	z = 39.4 C .	(Ampoule Experimental data)
B1/DDW =	D is 394.3 min	z = 26.4 C .	(Ampoule Experimental data)
Vitamin A =	D is 401.0 min	z = 23.0 C .	(Wilkinson et al., 1982)
Pigment(Betanine) =	D is 139.3 min	z = 70.0 C .	(von Elbe et al., 1974)
Vitamin AA in peas =	D is 1003.0 min	z = 16.0 C .	(Lathrop & Leung, 1980)
Chlorophyll a in spinach =	D is 13.0 min	z = 40.1 C .	(Gupte et al., 1964)
Maillard Reaction in Apple Juice =	D is 271 min	z = 25.0 C .	(Herrmann, 1970 from Lund, 1975)