THE DETERMINATION OF KINETIC PARAMETERS IN HEAT PROCESSING OF BABY FOOD

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ABSTRACT

Two methods of heat processing kinetic parameter determination by steady-state and unsteady-state heating procedures were studied. The unsteady-state procedure was used for colour and viscosity where large amounts of samples were required for measurement, and both were used in considering the destruction of ascorbic acid and riboflavin in a baby food.

To obtain accurate determination of the kinetic parameters, standard k and Ea, experimental methods had to be developed to measure the quality factors within narrow limits of accuracy.

Determination of the kinetic parameters by unsteady-state procedure involved the development of a computer method for the can temperature distribution calculation, the quality retention calculation, and finally determination of the empirical relationships of the standard parameters,k and Ea,to the residuals (differences between experimental and predicted concentrations). Temperature distribution in a can was predicted by a modified computer program based on an analytical solution to obtain a form fitting of the experimental heat penetration curve. From this, the quality retention was calculated by numerical integration. The standard k and Ea were roughly estimated from the literature either on the studied quality or on a similar quality. Then the ranges of standard k and Ea were assigned in an orthogonal composite design and used to calculate the retained quality which then was compared with the experimental result to obtain the absolute residual at each standard k and Ea. The average residual at each processing temperature was used in multiple linear regression to determine the relationships between the standard k and Ea, and the residual. By optimising the empirical equation the best values for the standard k and Ea were determined.

The standard k and Ea for ascorbic acid and riboflavin were also determined by the steady-state procedure. In this, small tubes of the baby food were heated in a constant temperature oil bath. Nearly identical results obtained for ascorbic acid by both methods indicated that the method used was feasible and the degradation of ascorbic acid was best described by a first order reaction. For riboflavin, different results were found from the two methods but these could be explained as the results of the low destruction rate of riboflavin on heating, the analytical error and the change in physical conditions from cans to tubes. So, use of the steady-state kinetic parameters for quality retention calculation in unsteady-state was confirmed experimentally.

For colour and viscosity changes in processing, the method of kinetic parameter determination in unsteady-state heating procedure was used assuming first order kinetics.

It was concluded in this food system for the temperature ranges of 60-139°C, the kinetic reaction rate at 129°C and the activation energy were $0.42\text{-}0.44 \times 10^{-4}$ s^{-1} and 77-85 kJ $mole^{-1}$, $0.11\text{-}0.25 \times 10^{-4}$ s^{-1} and 84-105 kJ $mole^{-1}$, 1.20×10^{-4} s^{-1} and 122 kJ $mole^{-1}$ and 1.65×10^{-4} s^{-1} and 151 kJ $mole^{-1}$ for ascorbic acid, riboflavin, colour and viscosity respectively.

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CONTENTS

APPENDICES

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION

Although the heating process has been known for a long time to affect both the nutritional and the sensory qualities of food products, there is a lack of quantitative data on the destruction of nutrients and on the changes in eating qualities by the heating process (Lund, 1975a,b; Lund, 1977). Thiamine is the only vitamin which is at all well documented (Farrer, 1955; Feliciotti and Esselen, 1957). There is some data available for other vitamins (Chittaporn, 1977) but they were determined under restricted conditions. Reliable kinetic information on other quality changes occurring in heat processing is practically non-existent.

At the present time, the nutrient value of a food after heat processing can only be determined empirically. Establishing the kinetics of changes in vitamins and food qualities during processing is necessary to provide general relationships which can be used for predictions of nutritional losses and food quality changes.

Ascorbic acid, riboflavin, colour and viscosity were the qualities selected for this study, the heat process used was can retorting (sterilisation) and the food was homogenised, baby food made from strained beef and mixed vegetables. Ascorbic acid and riboflavin were chosen as they are important constituents,there was no reliable information on the kinetic parameters and the analytical methods were simpler than the other vitamin assays. Can sterilisation was used because this data would be useful for the design of canning processes and because large samples were required for colour and viscosity measurements. Homogenised baby food was used because the heat transfer into the can was only by conduction, the food throughout the can was homogeneous and it was a mixed food system of commercial significance.

Being heated in a can, the food was subjected to a variation of temperature with time and position in the can. It was necessary for the quality retention calculation to determine the temperature distribution in the can, and this was obtained from a computer program based on unsteady-state heat transfer theory.

A method to determine the kinetic parameters was developed working from the processing time and temperature, and from the initial and final qualities, which were measured. This involved a computer program constructed for temperature distribution and quality retention prediction.

The kinetic parameters for ascorbic acid and riboflavin were also determined by a steady-state procedure where food was heated in a small tube in which instantaneous heating and cooling could be assumed. These kinetic parameters were compared with the ones obtained from the unsteady-state procedure to test the feasibility and accuracy of the computer model for the can.

2. LITERATURE REVIEW

2.1 INTRODUCTION

Canning, as a method of food preservation, has its origin in the work of Nicholas Appert (1750-1841) who was the first to use heat as a means of preserving food in hermetically sealed containers. Initially boiling water baths were used as heating medium but, sometime before 1830, the autoclave was introduced as a means of cooking canned foods under pressure. Further developments in processing equipment came with the introduction of agitating cookers and continuous sterilisers which helped to reduce processing time. The first spiral continuous cooker was patented in 1899. In recent years, there have been the introduction of hydrostatic pressure cookers (1936), high speed spinning cookers (1952), flame sterilisation (1957), high velocity air sterilisation (1974), and aseptic canning (1938). The aim of all these changes was to shorten the processing time and so reduce the quality changes during the heat processing. The value of high temperature short-time sterilisation lies in exploiting the principle that higher temperatures have less effect on quality in proportion to the lethal effects than lower temperatures. However, it has been found that the high temperature short time processes are not always beneficial in retaining the quality of canned food (Teixeira et al, 1969; Lund, 1977).

Although the canning process was introduced in 1800 and there have been many developments, very little is known on the optimisation of thermal processing for maximum quality retention. There is a lack of kinetic parameters showing the rate of quality destruction and the effect of temperature on the rate (Lund, 1977).

This chapter studies the quantitative estimation methods of the changes in food and reviews the literature on the kinetics of food quality changes during heat processing.

2.2 KINETIC THEORY OF THE CHANGES IN FOOD DURING HEAT PROCESSING

There are several types of changes occurring in heat processing - destruction of micro-organisms, enzymes, nutrients and changes in quality factors such as flavour, colour, texture. With micro-organisms and enzymes, the objective of the heat processing generally is inactivation, whereas with nutrients and other quality attributes, the objective is maximum retention. There are many factors affecting the extent of these changes. Lund (1975a) reviewed the factors affecting the thermal resistance of micro-organisms. Whitaker (1972) discussed the dependence of enzyme stability on many factors. Harris. and von Loesecke (1960) reviewed the effect of heat processing on nutrients. Other chemical changes - browning reaction, hydrolysis, oxidation-reduction reactions also occur and these may change food qualities e.g. colour and flavour changed by the browning reaction (Tannenbaum, 1976b). To follow the effect of heat on the food components including micro-organisms, two types of information are needed; (1) the kinetic reaction rate of destruction and (2) the dependence of the rate constant on temperature.

2.2.1 Theory of Kinetic Reaction Rate

According to the law of mass action, the velocity of reaction at a given temperature is proportional to the product of concentrations of the reacting substances. The rate of the disappearance of reactant, A, can be

$$\frac{dc_A}{dt} = -kc_A^a \, c_B^b \ldots c_N^n \qquad (2.1)$$

where dc_A/dt is the rate of disappearance of reactant, A

$c_A, c_B \ldots c_N$ are the concentrations of reactant A, B,...N

k is the reaction rate constant

t is time.

The order of the reaction is defined as the sum of the powers to which the concentration of all reactants are raised, this can be a fractional value or an interger.

Considering the destruction of nutrients or a specified food quality, the concentrations of water, oxygen, acid, alkali and reducing sugar are often important, as are the concentrations of metal catalysts and enzymes. However, the most important factor is the concentration of the reacting substance c_A. The destruction of nutrient or quality, A, at a given temperature is

$$\frac{dc_A}{dt} = -kc_A^n \qquad (2.2)$$

where c_A is the concentration of the nutrient or quality, A
n is the order of the reaction.

This equation can be separated and on integration gives:

$$\ln\frac{c_A}{c_{A_0}} = -kt \quad \text{where } n = 1 \qquad (2.3)$$

$$\text{and } c_A^{1-n} - c_{A_0}^{1-n} = (n-1)kt \text{ where } n \neq 1 \qquad (2.4)$$

where c_{A_0} is the concentration of A at zero time
c_A is the concentration of A at time t.

The order, n, cannot be found explicitly from the above equations so a trial-and-error solution must be used. This is not difficult as different values of n can be used in the equation to find the order, n, which most closely explains the experimental results.

If the reaction of nutrient or quality A destruction is a first order reaction, it will be described by equation (2.3). The plot of the logarithms of the reaction against time yields a straight line with slope "-k". So the reaction rate constant at a given temperature can be determined.

In a second order reaction, the destruction of A can be described as:

$$\frac{1}{c_A} - \frac{1}{c_{A_0}} = kt \qquad (2.5)$$

That is, the plot of $1/c_A$ against time will give a straight line with the slope k and the intercept $1/c_{A_0}$.

For zero reaction rate, the change in concentration of the reactant A is not dependent on the concentration, a plot of concentration versus time will yield a straight line of slope "-k" as $c_A - c_{A_0} = kt$. However, usually reactions are of zero order only at high concentrations of reactant. When the concentration is lowered the reaction rate becomes concentration dependent, that is the order of reaction rises from zero (Garrett, 1956). The order of ascorbic acid destruction was found to follow a zero order at high initial concentration and then the order changed to first order where concentration of ascorbic acid was lower.

For micro-organisms, the thermal destruction generally follows first order kinetics, the time required for the survivor curve to transverse one log cycle corresponds to a 90% reduction in the number of survivors (Lund, 1975a). The "decimal reduction time" or D value, which is the time required to reduce the population by 90%, can also be used to characterize the reaction rate constant of micro-organism destruction. The relationships between k and D can be expressed as:

$$D = \frac{2.303}{k} \qquad (2.6)$$

2.2.2 Temperature Dependence of the Reaction Rate

The effect of temperature on the reaction rate has long been known and the temperature - dependent term of a rate equation can be written in many forms according to various theories. The first quantitative formulation of the dependence of reaction rates on temperature was given by Arrhenius (1889) and this is still extensively used as:

$$k = Ae^{-Ea/RT} \qquad (2.7)$$

where A is the frequency factor
Ea is the activation energy
R is the gas constant
T is an absolute temperature.

This equation is found to fit many of the available experimental kinetic data (Aiba et al, 1965). Taking logarithms of the above equation gives:

$$\ln k = \ln A - \frac{Ea}{RT} \qquad (2.8)$$

The plot of ln k against 1/T yields a straight line with slope equal to -Ea/R. The influence of temperature on k is then expressed in terms of Ea, activation energy.

For micro-organisms, the thermal death time (TDT) method for describing the temperature dependence of the destruction rate was introduced by Bigelow (1921). The slope of the plot of log (TDT) against temperature, -1/z, is used to characterize the dependence of the reaction rate constant on temperature. In 1957, Ball and Olson pointed out that the use of "z" is equivalent to the use of the Q_{10} concept which is the rate quotient for a temperature interval of 10^oC. Since the use of thermal death time was adapted to the decimal reduction time (Stumbo, 1948a), the log D against linear temperature, has remained as a basis for process calculation and is still used to explain the effect of temperature on the destruction rate in term of "z".

Over wide temperature ranges, Gillespy (1948) as well as Pflug and Esselen (1953) reported that the plot of log D against the reciprocal of absolute temperature was more nearly linear. This is the form of the relationship predicted by the Arrhenius equation. Gillespy (1948) also pointed out that over small ranges of temperature, the linear plot gave a good approximation to the Arrhenius plot. He also gave the relationship between Ea and z as:

at a given temperature, T

$$z = \frac{2.303\ T^2R}{Ea} \tag{2.9}$$

over a range of temperature, T_1 to T_2 .

$$z = \frac{2.303\ T_1T_2R}{Ea} \tag{2.10}$$

Aiba et al (1965) discussed the types of relationships between reaction rate and temperature, and included Erying's theory of absolute reaction rate with the Q_{10} (or z) approach and the Arrhenius equation. According to Eyring:

$$k_T = gTe^{-\Delta H^*/RT}e^{\Delta S^*/R} \tag{2.11}$$

where ΔH^* is the heat of reaction of activation
ΔS^* is the entropy change of activation
g is a factor including Planck's and Boltzmann's constants
T is absolute temperature.

The Arrhenius and Eyring theories were found to be not significantly different. When used to extrapolate data, the Q_{10} (or z) basis of calculation gave values of D significantly less than the other theories. The Arrhenius equation also seemed to be applicable over a broader temperature range. Aiba et al stated that where an activation energy was less than 126 kJ mole^{-1}, the Arrhenius equation more accurately described the temperature dependence over a wide temperature range than the more commonly used TDT equation. But where an activation energy was higher than 126 kJ mole^{-1} both equations were comparable. Another advantage of the Arrhenius equation over the TDT equation was that it could be extrapolated safely while the "z" equation is known to become non-linear at high temperatures (Hayakawa, 1978).

The TDT equation was found to be easier to apply in industry because of its simplicity (Hayawaka, 1978); the Arrhenius equation was a more complicated computation. He also stated that the Ea value is more strongly influenced by errors in k values than the slope of z.

There have been a number of other variations of the rate of reaction versus temperature equations. Moore (1957) discussed some of these equations and stated that it was worthwhile making a correction of activation energy by $E = Ea + \frac{1}{2}RT$. Fennema (1975) described the temperature dependence of the destruction rate, $\dot{k}$, by an exponential function for enzymes and micro-organisms:

$$k_i = k_{i,o} \exp (a_i T) \qquad (2.12)$$

where $k_{i,o}$ is a value of k_i when the absolute temperature, T, is zero

T is absolute temperature

a_i is a constant.

For a range of temperature, equation (2.12) was used for process calculation (Thijssen et al, 1978).

$$k_i = k_{i,Tr} \exp (a_i(Ti - Tr)) \qquad (2.13)$$

where $k_{i,Tr}$ is a value of k_i at reference temperature, Tr.

These equations, (2.11) and (2.12), are just another way of expressing the Q_{10} concept.

2.2.3 Effect of Other Variables on the Reaction Rate

Besides depending on the temperature, the rates of the reaction are also affected by other variables, namely, pH, water activity, concentration of oxygen and concentration of minor components such as trace metals and enzymes (Labuza, 1972; Wanninger, 1972). Wanninger (1972) postulated a mathematical model for the effect of moisture content on the rate of reaction. Lee et al (1977) used the least squares technique in establishing an equation showing the effect of pH and moisture content on the kinetic reaction rate of ascorbic acid in tomato juice.

2.3 QUANTITATIVE ESTIMATION OF THE CHANGES IN FOOD DURING HEAT PROCESSING

The changes in food during heat processing can be expressed quantitatively by kinetic parameters. To determine these parameters, the initial concentration of reactant e.g. nutrients, quality factors, the concentration of reactant after certain heating time, and the temperature of heating either by measurement or calculation must be known.

2.3.1 Analysis of Concentration

As the accuracy of the kinetic parameters determined depends on the accuracy of the concentration measurement, reliable analytical techniques for the system under study must be used. Any assumptions made should be verified experimentally (Hill and Grieger-Block, 1980). Benson (1960) has presented a useful table which summarizes the errors in calculated rate constants caused by analytical errors for orders of reaction from zero to four. Inspection of the table illustrates the dilemma the kineticist faces in planning experiments (Hill and Grieger-Block, 1980).

2.3.2 Determination of Temperature Distribution

To determine the kinetic model for destruction of food components during heat processing, two procedures can be used: a steady-state procedure where thermal death time cans or tubes are commonly used and an unsteady-state procedure where food is heated in any container (Lenz and Lund, 1980). Theoretically, the heating and cooling to and from the desired temperature should be instantaneous so that no significant destruction occurs during the coming-up and coming-down periods but this is practically impossible. The problem of thermal lag in the steady-state has been tackled in different ways. In unsteady-state procedure, the temperature of food in a container (usually a can) changes with time and position. The temperature distribution in the container at any given process time must be determined as the calculation of the kinetic parameters is based on an average retention concentration. To determine the temperature distribution, two methods can be used - experimental measurement and theoretical prediction.

2.3.2.1 Determination of Thermal Lag in Steady-State Heating

Firstly, the thermal lag periods can be ignored if they are small and considered insignificant to the processing effect or they can be reduced by methods such as reducing the sample size (Lyster, 1970; Mulley et al, 1975), preheating the heating medium (Paulus et al, 1978; Saguy et al, 1978a), and/or using relatively long heating periods (Eagerman and Rouse, 1976; Navankasattusas, 1978) where the thermal lag period effect can be considered negligible..

Procedures for correcting thermal lag have been proposed and fell into three general categories - graphical method, numerical method and experimental manipulation. Farkas and Goldblith (1962) studying the kinetics of lipoxidase inactivation using thin walled, melting point, capillary tubes, estimated the thermal lag by extrapolating the first order reaction rate of destruction curve. Saper and Nickerson (1962) and Gupte et al (1964) also used a graphical method.

By the numerical method, the thermal lag was determined by two different methods. Firstly, a "z" value or a rate of reaction was assumed and used for calculating an equivalent time at a specified temperature (Sognefest and Benjamin, 1944; Tan and Francis, 1962). Secondly, iterative procedures were used (Resende et al, 1969; Hayakawa et al, 1977). This method was based on the assumption that the rate of reaction was first order. A "z" value was assumed, equivalent heating times calculated and graphed with the measured quality to determine a new "z" value. If there was a significant difference between the calculated and the assumed "z" value, calculation were repeated using the determined "z" value.

In the experimental manipulation method, the coming-up time is determined and then actual timing started from this period. The method was used by Feliciotti and Esselen (1957), Hamm and Lund (1978).

2.3.2.2 Experimental Heat Penetration Measurement

The measurement of heat penetration in a can was first done by Prescott and Underwood (1897) using a maximum recording thermometer. Because the metal mounting tube of the thermometer, or the stem of the thermometer itself, if no mounting tube was used, could conduct heat to the bulb and thus distort the temperature record, this method was criticised by Bigelow et al (1920). The use of a chemical thermometer first described by Bitting (1912) was also criticised by Bigelow et al (1920) for the same reason. However a mercury in steel recording thermometer described by Bigelow et al (1920) also had the same heat conduction errors.

The use of thermocouples in cans was first described by Bitting and Bitting (1917). The thermocouple probe in glass was described and used extensively by Thompson (1919) and Bigelow et al (1920). In 1927, Ford and Osborne stated that a thin wall copper tube used as part of the probe could probably be subjected to greater conduction errors in conduction heated food than the glass thermometer. Various improvements of a mechanical nature have been made on heat penetration thermocouple probes (Benjamin, 1938; Ecklund, 1949). Conduction errors had been shown to be negligible except for small cans of conduction heated product; the correlation factor for this error has been proposed also by Ball (1923) and Ecklund (1949, 1956). In 1965, Board introduced the method of mounting thermocouples in cans without the use of support. The two wires pass through diametrically opposed holes in the can walls or through holes in the can ends and are sealed with a heat resistant epoxy resin adhesive. This method is probably the least susceptible to conduction errors.

As the can must be fitted with thermocouples before filling by this method , Board and Stekly (1978) designed a simple new thermocouple assembly which allowed the hot junction to be placed at the desired measuring point after the can was filled and closed.

Sensitive galvanometers have been used to indicate the potential produced by the thermocouple junction (Thompson, 1919). Potentiometric devices (zero current at balance) had become to be preferred later on as the voltage indicated was independent of the resistance of the lead wires (Ecklund, 1949). Automatic or manual cold junction compensation have both been used, as well as ice-flask reference junctions. Various types of recording potentiometer have been introduced and used (Clifcorn et al, 1950; Hoare and Warrington, 1963).

There are other errors in using thermocouples caused by the breakdown of insulation at a point distant from the junction or/and the breakdown of insulation or earthing of thermocouple leads outside the can. These breakdowns could cause dropping in potential difference by the current flowing between the points of contact of the wire and electrotytes which could be food products, cooling water etc. These effects have been discussed by Middlehurst et al (1964) who demonstrated that very high emf (up to 4mV) could be generated in unfavorable condition.

Even though the methods of measurement have been developed from the use of thermometers to thermocouples where more points in the can can be followed by continuous recording potentiometric devices, there is a limitation on the number of points that can be followed and on the time interval of recorded temperature. Therefore, a theoretical determination is needed for calculating temperature distribution in the can.

2.3.2.3 Theoretical Determination

A number of attempts to use basic heat transfer theory in the calculation of heat penetration have been made (Olson and Schultz, 1942; Hicks, 1951; Gillespy, 1953; Ball and Olson, 1957; Board et al, 1960; Charm, 1961; Stumbo, 1964). Various forms of the heat conduction equations (Thompson, 1919; Carslaw and Jaeger, 1959) were used for determining the temperature of food during heating and cooling. Thompson (1919) gave the fundamental equation describing heat penetration in uniform conduction heating finite cylinders and used these formulae to calculate values of thermal diffusivity from various experimental heating curves. For practical purposes, simplifications were made in the equation by neglecting terms which were important only at the beginning of heating. The prediction of the cooling curve was not as satisfactory as prediction of the heating curve. Hicks (1951) proposed the method of prediction of heating and cooling curves based on the heat transfer equations (Carslaw and Jaeger, 1959) using only the first term in the series for the heating phase and a number of terms in series for cooling phase. Gillespy (1953) had also outlined a method of calculation for centre temperature in conduction heating can based on the fundamental heat conduction equation of Carslaw and Jaeger and Duhamel's theorem. Complex heating and cooling cycles could be calculated.

As the technology of the computer has been improved and become more advanced, computer programs have been written and used for calculating the temperature distribution in the cans during conduction heating based on the heat transfer equations (Carslaw and Jaeger, 1959) by many workers (Hawakawa and Ball, 1969; Flambert and Deltour, 1972b; Lenz and Lund, 1977a). The finite difference method has been also used for solving the heat transfer equations using the computer program by Teixeira et al (1969) and Flambert and Deltour (1972b). The later technique could also be applied where the thermal properties of the foods were changed with temperature.

2.3.3 Calculation of Kinetic Parameters

In a steady-state procedure, the raw data of concentration of the desired factor versus heating conditions (temperature and time) can be analysed by various methods reviewed by Hill and Grieger-Block (1980). The data at each temperature are compared to a model of the kinetics (zero-, first-, or second-order model); a rate constant can be calculated for that heating temperature when the data sufficiently match the model (Lenz and Lund, 1980). Then the temperature dependence of the rate can be determined.

In an unsteady-state procedure, the calculation of kinetics is based on mass average prediction. This method firstly developed for estimating mass average sterilizing values. Gillespy (1951) used only the first term in the series of analytical formulae for heat conduction in a cylinder in estimating the temperature distribution and developing parametric tables for determining mass average sterilizing values. Stumbo (1953) developed a mathematical procedure to evaluate the capacity of a heat process to reduce the number of bacteria in a container of food by considering the heat treatments received by all points throughout the container rather than that received at any one point. Ball and Olson (1957) developed a similar method based on Stumbo's original work, which they applied to the evaluation of thiamine retentions in conduction-heated foods. Hicks (1951) used the fundamental heat conduction equation, exponential integral functions and graphical integrations to evaluate survival probabilities for the whole container. He introduced the very useful concept of an equivalent volume, which, when multiplied by the residual number of spores per unit volume, at the centre point would give the total number of viable spores to be expected in the container. In 1952, he had also reviewed the similarity and the implication of the methods of Stumbo (1948a, 1949a), Gillespy (1951) and Hicks (1951).

Hayakawa and Timbers (1967) observed that Stumbo's formula did not give reliable answers when it was applied to the z and D values of organoleptic or nutritional factors which are considerably greater than those of micro-organisms. In 1971, Jen et al removed this limitation by deriving another formula which also does not require complicated calculations for evaluating mass average sterilizing values. This formula is based on and similar to Stumbo (1953). Hayakawa (1969) used dimensional analysis and found that six dimensionless groups, which are not included in both Stumbo and Jen's formula, are required for the unique mathematical estimation of a mass average sterilizing values. The reliability of the formula derived by Jen et al should be investigated in the future, stated Hayakawa (1977). He also derived new tables of dimensionless groups for calculating the lethality or quality retention of processed foods. In 1977, Downes and Hayakawa developed the table based on a new parameter, Ks, developed by Hayakawa using the combination of the major theoretical advances of Stumbo (1973), Jen et al

(1971) and Hayakawa (1970) for mass average sterilizing value calculation.

Recent advances in computer technology have also led to computerization of thermal process calculations. Manson and Zahradnik's (1967) program was based on Stumbo's method. Hayakawa and Timbers (1967) calculated the mass average sterilizing value of a thermal process based on a first term approximation of the Fourier-Bessel series for heat conduction in a finite cylinder. Hayakawa (1969) applied his method to the evaluation of thiamine retention. Teixeira et al (1969) developed a numerical solution of a finite difference approximation applied to both lethality and thiamine retention calculation. Flambert and Deltour (1972a) used the same method as Teixeira (1967) with 10 increments on the radius and on the half height and 0.125 minute time increments with the first order reaction rate as D and z and calculated the mean temperature and the mean residual concentration of the entire process. Manson et al (1970) used the same method as Teixeira applied to a rectangular can of solid food. Sasseen's program (1969) is for estimating sterilizing values by Ball's method (1923). Lenz and Lund (1977) proposed a Lethality - Fourier number method for process evaluation, which is also used for predicting the quality retention, based on the theoretical heat transfer equation of the analytical method in combination with the kinetic reaction rate constants, k and Ea. This method was shown to be as accurate as other available methods for predicting the mass average retention of thermally vulnerable components in conduction heating of a food. Thijssen et al (1978) proposed a short-cut method for the calculation of sterilisation conditions yielding optimum quality retention for conduction-type heating based on the use of the computer in analyzing the temperature distribution in the can and the overall quality retention.

2.4 CHANGES OF FOOD DURING HEAT PROCESSING

There are a number of studies on the change of nutrients during heat processing reviewed in Bender (1966), Cain (1967), Schroeder (1971), Harris and Karmas (1973), Priestley (1979). Unfortunately, the majority of the data is the result of end point analysis, that is, the measurement of concentration at the beginning and at the conclusion of a given process or storage period. These data were generally not subjected to kinetic analysis. However, Lund (1975) and Chittaporn (1977) have reviewed the kinetic parameters for various nutrients by either collection or calculation of the existing data. Lund (1975) had also included some kinetic parameters for enzymatic inactivation, chlorophyll destruction, browning reaction, colour, texture and flavour. Inspection of Lund's table shows that only one determination of "k" and "Ea" was found for both ascorbic acid and riboflavin. Thiamine was the only vitamin that seemed to be well characterized. Although there were a number of "k" and "Ea" reported for chlorophyll destruction and browning reaction, only one "k" and "Ea" was reported for colour. However, there are a number of studies on the kinetics of the nutritional and quality changes of food during processing after 1975 - Hamn and Lund (1978) on pantothenic acid, Navankasattusas (1978) on vitamin B6, Saguy et al (1978a) on betanin and betalamic acid, Chen and Cooper (1979) and Paine-Wilson and Chen (1979) on folacin, Slater et al (1979) on vitamin A and Widicus et al (1980) on α - tocopherol. There were, also, a number of studies on ascorbic acid, but most of them were on dehydrated foods. The kinetic reaction rate and the activation energy were found to be in a wide range (section 2.3.1). For riboflavin, the kinetic studies were mostly on the photodegradation. Only one study, of Ohlsson (1980), was found for the changes in sensory quality on heating.

Therefore, because of the lack of kinetic data, ascorbic acid and riboflavin were chosen in this study. Colour and viscosity were the two sensory qualities chosen as flavour analysis involved subjective measurement which was difficult to measure accurately. The details of the kinetic studies on these chosen qualities were reviewed.

2.4.1 Ascorbic Acid

Ascorbic acid is known as one of the most heat labile vitamins as reviewed up to 1960 by Harris and Von Loesecke and thereafter by Lang in 1970 and de Ritter in 1976. The destruction of ascorbic acid in food can follow either an aerobic oxidation reaction or an anaerobic pathway (Tannenbaum, 1976a). Both of these reactions have common intermediates and are hardly distinguishable. The specific pathways and the degradation rate are determined by factors such as oxidation-reduction potential of the system, temperature, oxygen, pH, moisture content, trace metals especially copper and iron, enzymes, sugar concentration and amino acid. (Joslyn, 1949a,b; Kurata and Sakurai, 1967a,b,c; Bauernfeind and Pinkert, 1970; Huelin et al, 1971). Iron was found to be effective to a lesser extent than copper (Bauernfeind and Pinkert, 1970). Khan and Martell (1967) found that in the pH range of 2-5, the destruction of ascorbic acid increased with increasing pH and the decomposition rate was strongly accelerated by temperature. The rate of ascorbic acid destruction was found to reach a maximum at the pH near to pKa (Lee et al, 1977). It was also found that alcohol and sugar might be either pro- or anti-oxidant depending on their concentration and on the presence of natural substances in food such as anthocyanin or other phenolic compound. Huelin (1953) studying the anaerobic decomposition of ascorbic acid found that the destruction rate was accelerated by both sucrose and fructose.

Moisture content and water activity are important factors especially in dried products and they were extensively studied (Gooding, 1962; Karel and Nickerson, 1964; Jensen, 1967; Vojnovich and Pfeifer, 1970; Lee and Labuza, 1975; Kirk et al, 1977; Reimer and Karel, 1977; Dennison and Kirk, 1978; Laing et al, 1978; and Papanicolaou and Sauvageot, 1979). The destruction rate was found to increase with increase in total moisture content and water activity. This was explained as the result of dilution of the aqueous phase causing a decrease in viscosity which led to increase in mobility (Lee and Labuza, 1975). The activation energy was found to increase with moisture content (Jensen, 1967; Vojnovich and Pfeifer, 1970), but Lee and Labuza (1975) found that there was no effect of water activity on the activation energy. The reason for this variation was stated to be unknown by Kirk et al (1977).

Oxygen or air, as shown by Clifcorn (1948), Mapson (1956), Bender (1958a) and Chichester (1973), did effect the destruction rate of ascorbic acid in canned foods. The effect of oxygen on the rate of ascorbic acid destruction in liquid foods was also reported (Joslyn and Miller, 1949a,b; Bayes, 1950; Khan and Martell, 1967; Ford et al, 1969). In a dehydrated food system, Kirk et al (1977) found that the rate of ascorbic acid destruction was dramatically increased with the presence of oxygen, as did Dennison and Kirk (1978).

The anaerobic mechanism of ascorbic acid destruction in a canned food was reported by Huelin (1953) and Huelin et al (1967). In 1978, Reimer and Karel found that ascorbic acid destruction in dehydrated tomato juice was largely an anaerobic reaction. Papanicolaou and Sauvageot (1979) also found that vitamin C destruction differed just a little between samples of freeze-dried orange juice stored under vacuum, nitrogen or air. Therefore, it is likely that both aerobic and anaerobic mechanisms could be involved depending on other factors such as pH and compositional factors.

In heat processing, especially, in the canning process, the retention of ascorbic acid has been studied by many workers on various food products (Guerrant et al, 1947; Lamb et al, 1947; Wagner et al, 1947; Cameron et al, 1949; Watt and Merrill, 1963; Marchesini et al, 1975; Lee et al,1976). The percentage of ascorbic acid retention varied with types of products as the processing conditions were different, the retention was found to vary from 26-90%. Unfortunately the kinetic parameters cannot be determined as the data available were inadequate. The orders reported in the literature of the destruction reaction of ascorbic acid were conflicting. It was reported as either zero, first or pseudo-first order reaction (Barron et al, 1936; Peterson and Walton, 1943; Weissberger and Thomas, 1943). Aerobic destruction of ascorbic acid was confirmed to follow first order kinetics (Freed et al, 1949; Joslyn and Miller, 1949a). Anaerobic destruction of ascorbic acid was also found to follow first order reaction kinetics (Huelin, 1953). In heating processes, the destruction of ascorbic acid was found to be described by first order kinetics (Paulus et al, 1978; Saguy et al, 1978b; Lathrop and Leung, 1980). The first order kinetics was also found on the storage of food products - Vojnovich and Pfeifer (1970) in wheat flour, corn soya milk, infant cereal; Lee et al (1977), Nagy and Smoot (1977) and Davidek et al (1974) in fruit juices; Lee and Labuza (1975), Kirk et al (1977), Reimer and Karel (1977) and Dennison and Kirk (1978) in intermediate moisture food. The data presented by Sistrunk and Cash (1970), Clydesdale et al (1971) and Abrams (1975) on the effect of heat on the ascorbic acid of food were analysed by this author and it was found that most of them could be treated as a first order reaction.

On the other hand, Garrett (1956) studying the stability of ascorbic acid in a pharmaceutical preparation concluded that ascorbic acid has an initial pseudo-zero order reaction which subsequently become pseudo-first order reaction. The deviation from first order rate of reaction of ascorbic acid was also found by Joslyn and Miller (1949a). Singh et al (1976) found that under limited supply of oxygen, the degradation of ascorbic acid in infant formulae could be described as a second order reaction whereas Laing et al (1978) concluded that the degradation rate of ascorbic acid in intermediate moisture food followed a zero order reaction.

Lin and Agalloco (1979) reviewed the effect of temperature, pH and oxygen on the destruction kinetics of ascorbic acid and stated that the order of reaction depended on both oxygen and initial concentration.

The reaction rate and the activation energy of ascorbic acid destruction, either collected or calculated from the literature, are shown in Table 2.1. Assuming that the destruction rate of ascorbic acid in various foods was a first order reaction, Chittaporn (1977) had predicted the reaction rate and the activation energy using all data available before 1977 and found that the reaction rate was 2.33×10^{-4} s^{-1} at $129^{\circ}C$ and the activation energy was 88.2 kJ $mole^{-1}$. Subsequent to 1977, more recent results have continued to show a wide variation, from 14 to 172 kJ $mole^{-1}$.

TABLE 2.1 Reaction Rate Constants and Activation Energies for Ascorbic Acid

Reference	Product	Conditions	Reaction Rate $k \times 10^{4} s^{-1}$	Activation Energy kJ mole^{-1} (kcal mole^{-1})
Brenner et al, 1948	Canned food	High temperature storage 21-37.8°C, pH 4.35	0.00018, 37.8°C	108(25.7)*
Lamb et al, 1951	Canned tomato juice and tomato paste	Storage, 21-37.8°C	0.00022, 37.8°C	81(19.3)*
Huelin, 1953	Ascorbic acid in citrate-phosphate buffer solution	temperature 30-100°C, pH 2.2 pH 6.0	 0.00383, 100°C 0.03167, 100°C	 78(18.6)* 96(22.9)*
Garrett, 1956	Liquid - multivitamin	from first order plot from pseudo-zero order plot	0.00289, 70°C -	97(23.1) 96(22.8)
Jensen, 1967	Seaweed	Moisture 11.1 gH_2O/100 g solid Moisture 17.6 gH_2O/100 g solid Moisture 33.3 gH_2O/100 g solid	- - -	32(7.7) 55(13.1) 127(30.3)
Vojnovich and Pfeifer, 1970	Flour	temperature 26-45°C, water activity 0.65 water activity 0.55 water activity 0.25	 0.00228, 45°C 0.00022, 45°C 0.00005, 45°C	 94(22.3) 67(16.0) 46(11.0)
Blaug and Hajratwala, 1972	Ascorbic acid in buffer solution (aerobic oxidation)	temperature 60-85°C, pH 5.6	0.01500, 85°C	76(18.0)
Labuza, 1972	General review	-	-	37-189(8.8-45.0)
Davidek et al, 1974	Orange drink	L-dehydroascorbic acid, 4-30°C	0.06700, 30°C	59(14.1)
Abrams, 1975	Frozen Brussel sprouts	cooking temperature range	0.42778-0.47083, 100°C	-
Lee and Labuza, 1975	Intermediate moisture model food	temperature 23-45°C, water activity 0.23-0.84	-	70-95(16.7-22.6)
Flaumenbaum et al, 1977	Citrus, strawberry, tomato juice and paprika puree	-	0.20000-0.88000	-
Kirk et al, 1977	Fortified dehydrated model system Multivitamin model system	temperature 10-37°C, water activity 0.1-0.65 temperature 10-37°C, water activity 0.1-0.65	0.00114-0.01822, 37°C 0.00114-0.00981, 37°C	34-81(8.0-19.2) 48-84(11.5-20.0)
Lee et al, 1977	Canned tomato juice	temperature 0-37.8°C, pH 4.06 pH 6.90	 0.00028, 37.8°C 0.00025, 37.8°C	 14(3.3) 29(6.9)
Nagy and Smoot, 1977	Canned single strength orange juice	temperature 21.1-48.9°C temperature 4.4-21.1°C	- -	112(26.7) 53(12.7)
Dennison and Kirk, 1978	Dehydrated model food system	temperature range 10-37°C, water activity 0.10 water activity 0.40 water activity 0.65	 0.00206, 37°C 0.00839, 37°C 0.01397, 37°C	 45(10.7) 67(16.0) 77(18.3)
Laing et al, 1978	Intermediate moisture food system	temperature 61-105°C, water activity 0.69 water activity 0.80 water activity 0.90	 - - -	 59(14.0)* 71(17.0)* 67(16.0)*
Paulus et al, 1978	Spinach puree	temperature 105-130°C	0.07681, 130°C	30(7.2)
Reimer and Karel, 1978	Dehydrated tomato juice	water activity 0.00 water activity 0.75	0.00056, 37°C 0.00006, 37°C	103(24.6) 68(16.2)
Saguy et al, 1978	Grapefruit juice	temperature 60-96°C	0.21267-0.50367, 61°C	21-48(5.0-11.3)
Lathrop and Leung, 1980	Peas in brine in TDT cans	temperature 110-132°C	0.08333, 110°C	172(41.0)

* Calculated from the data presented in the reference

** Zero-order reaction was predicted.

2.4.2 Riboflavin

Riboflavin is comparatively stable to heat but unstable to light, especially in the visible spectrum (< 500 nm). The sensitivity to light increases with temperature and pH (Harris and von Loesecke, 1960). It is stable to oxygen and acid but unstable to alkaline conditions (Bender, 1966).

Leaching is the main cause of riboflavin loss during food processing since it is a water soluble vitamin. Retention of 60% to 100% was found after blanching (Hein and Hutchings, 1971; Barratt, 1973). The effect of cooking on riboflavin retention of various kinds of meats were studied, 56-98% retention was found by Griswold et al (1947, 1949), 74% retention was found by McIntire et al (1944), 55-75% retention was found by Noble (1970), whereas almost 100% retention was found by Engler and Bowers (1976). Ang et al (1975) reported that less than 10% loss of riboflavin was found after three hours holding at 82°C. Cain (1967) stated that dehydrated beef and sweet potatoes retained all their riboflavin content. For milk, heat treatment was found to have little effect on riboflavin (Ford et al, 1969; Rolls and Porter, 1973). However, loss can be significant if milk is exposed to sunlight (Singh et al, 1975; Sattar et al, 1977). The temperature was also found to have an effect on riboflavin destruction rate.

In canning, different conclusions have been drawn. Hellendorn et al (1971) showed that in canned meat and vegetable dishes, sterilisation and storage at 22°C for five days produced no significant losses in riboflavin. While Watt and Merrill (1963) reported that the losses of riboflavin in canned vegetables could be as high as 70% (including loss in preprocessing); except tomatoes and tomato juice that seemed to show better riboflavin retention which may be due to their higher acidity or higher ascorbic acid or less leaching during their processing. The loss of 0-30% during canning was also reported by Guerrant et al (1946); Lamb et al (1947); Wagner et al (1947); Cain (1967). Burger and Walters (1973) reported 6% loss for canned chopped beef, 12% loss for canned corned beef and 29% loss for pork bacon.

So it would appear that riboflavin losses do occur on processing, including canning. These losses, in the case of wet treatment, are probably due to a combination of leaching, light and thermal degradation.

Very little kinetic work had been done on riboflavin. Singh et al (1975) and Sattar et al (1977) had studied the light induced losses of riboflavin and concluded that the destruction reaction was definitely first order in nature. Allen and Parks (1979) also found that the photodegradation of riboflavin in milk exposed to fluorescent light (2690 lux) could be described by first order reaction. The data presented by Ang et al (1975) could not be fitted to a first order reaction by the present author. Gillespy (1962) assumed first order reaction and determined the activation energy for riboflavin destruction as 96.6 kJ mole^{-1} (23.0 kcal mole^{-1}). Chittaporn (1977) also assumed first order reaction and calculated the kinetic reaction rate from the data collected from the literature, (Table 2.2) and found that activation energy determined from the calculated "k" was 46.2 kJ mole^{-1} (11 kcal mole^{-1}). Singh et al (1975) found that the activation energy varied from 33.6-172.2 kJ mole^{-1} (8-41 kcal mole^{-1}) in their study of milk depending on the type of container as it affected the amount of light. From the latest data of Salunkhe et al (1978) and Kramer et al (1977), the first order reaction was assumed and the activation energy was found to range from 43.3-63.4 kJ mole^{-1} (10.3-15.1 kcal mole^{-1}) depending on the food studied in Salunkhe et al and from 6.7-23.5 kJ mole^{-1} (1.6-5.6 kcal mole^{-1}) for salisbury and beef patties with the TVP in Kramer et al.

The variation in the kinetic reaction rate and the activation energy reported may be due to the type of food, the initial concentration, the method of study and the conditions being studied. However, it is obvious that the data on the effect of heat are very limited.

TABLE 2.2 Reaction Rate Constants for Riboflavin

Reference	Type of Product	Moisture Content %	Temp. °C	$k \times 10^4$ s^{-1}
Singh et al, 1975	Milk	-	1.7	0.00216
Singh et al, 1975	Milk	-	4.4	0.00243
Guerrant et al, 1945	Canned tomato juice	-	5.6	0.00003
Guerrant et al, 1945	Canned green lima beans	-	5.6	0.00003
Guerrant et al, 1945	Canned whole kernel corn	-	5.6	0.00004
Singh et al, 1975	Storage of milk	-	10.0	0.00306
Guerrant et al, 1945	Canned tomato juice	-	29.4	0.00006
Guerrant et al, 1945	Canned green lima beans	-	29.4	0.00006
Guerrant et al, 1945	Canned whole kernel corn	-	29.4	0.00005
Guerrant et al, 1945	Canned tomato juice	-	43.3	0.00018
Guerrant et al, 1945	Canned green lima beans	-	43.3	0.00009
Guerrant et al, 1945	Canned whole kernel corn	-	43.3	0.00009
Greenwood et al, 1944	Canned luncheon pork	55.0	99.0	0.04761
Cook and Dundaram, 1963	Boiled artichokes	In water	100.0	0.02674
Greenwood et al, 1944	Canned luncheon pork	55.0	110.0	0.01411
Greenwood et al, 1944	Canned luncheon pork	55.0	118.5	0.00742
Greenwood et al, 1944	Canned luncheon pork	55.0	126.5	0.02150
Cook and Sundaram, 1963	Boiled artichokes	In water	121.0	2.38072
Kennedy and Ley, 1971	Fish in pressure cooker	-	121.0	39.30361

2.4.3 Colour

Since the model system used in the present study is a mixed, complicated natural food system consisting of various raw materials and ingredients, many reactions could be involved but only two main colour reactions, browning reaction and pigment/chlorophyll destruction, were studied and information was collected only on these colour changes.

2.4.3.1 Browning Reaction

Browning reaction, which occurs in food during processing caused the colour change to brown or brownish-black, can be classified into two categories, enzymatic and non-enzymatic reaction. The enzymatic browning reaction can occur in food by the action of catalytic enzymes, phenolase or polyphenolase. As this reaction involves enzymes which would be destroyed by heat, so during thermal processing where the temperature is rather high, only non-enzymatic browning reaction will play an important role in colour changes.

There are three main types of non-enzymatic browning reaction, the carbonyl-amino acid reaction which is generally known as "Maillard" reaction, the caramelization reaction which occurs at relatively high temperature with polyhydroxy-carbonyl compounds, and the oxidative reaction where ascorbic acid or polyphenols are converted to di- or polycarbonyl compounds. The details of mechanisms of these reactions were reviewed by many workers (Hodge, 1953; Reynolds, 1963; Lea,1965; Reynolds, 1965; Hurst, 1972; Adrain, 1974; McWeeny et al, 1974).

The intermediates, pigments and melanoids formed by the reactions are altered by a number of factors. Their composition will depend, not only on the sugar and amino compounds involved but also on (a) the sugar: amino compound ratio (Schnickels et al, 1976; Warmbier, 1976; Warmbier et al, 1976), (b) the water content, the higher the water content, the quicker the rate of browning (Stadtman et al, 1946; Legault et al, 1951; Pearson et al, 1962; Labuza and Warren, 1976), (c) the temperature of the reaction, (d) the pH of the reaction mixture and its buffer capacity (Pearson et al, 1962) where the maximum brown colour was found to be produced between pH 5.6 and 5.9 and (e) the presence of other compounds or ions such as ascorbic acid which was found to have an effect on the browning extent (Karel and Nickerson, 1964; Clegg and Morton, 1965; Clegg, 1966). In meat, Khayat (1978) found that reducing sugar content was an important factor in brown colour development during thermal processing.

Time and temperature were found to effect the rate of browning reaction (Pokorny et al, 1975; Warmbier et al, 1976). Warmbier et al (1976) studied and found that the rate of pigment formation followed a zero-order kinetic reaction rate after an initial short induction period while the rate of glucose utilization and loss of available lysine obeyed the first order reaction. Pokorny et al (1975) studied the non-enzymic browning of cauliflower and found that it followed the kinetics of a first order reaction at high temperatures and that of a zero order reaction at lower temperatures. Resnik and Chirife (1979) studied the effect of moisture content and temperature on some aspects of non-enzymic browning of dehydrated apples, moisture content ranged from nearly zero to 83%, and temperature ranged from 55-83^{o}C and concluded that the rate of increase of OD_{282} which is associated with the presence of 5-hydroxy-methyl-furfural followed zero reaction kinetics.

The kinetic parameters were collected and are shown in Table 2.3. The activation energies for the browning reaction found by various workers were in the same range, it was found to be more than 105 kJ mole^{-1} (25.0 kcal mole^{-1}). However, the variation in " k " was high as the methods of determination used by various workers were different. Therefore, the method of determination must be followed in order to used those " k " values with the activation energy.

TABLE 2.3 Reaction Rate Constants and Activation Energies for Non-Enzymatic Browning Reaction

Reference	Food Product	pH	Temperature range °C	Moisture Content $gH_2O/100$ g (dry basis)	Reaction Rate k x $10^4 s^{-1}$	Activation Energy kJ $mole^{-1}$ (kcal $mole^{-1}$)
Stadtman et al, 1946	Dried apricot	-	-	-	-	109 (26.0)
Legault et al, 1947	Unsulfited carrot	-	20-49	5.4	0.00139, 49°C	166 (39.4)
				6.2	0.00174, 49°C	163 (38.7)
				8.0	0.00255, 49°C	159 (37.9)
	Unsulfited Onion	-	20-49	3.5	0.00266, 49°C	177 (42.2)
	Unsulfited white potato	-	20-49	5.3	0.00020, 49°C	169 (40.3)
				7.6	0.00051, 49°C	161 (38.4)
				8.9	0.00086, 49°C	152 (36.2)
	Unsulfited sweet potato	-	20-49	7.4	0.00006, 49°C	134 (31.9)
Legault et al, 1951	Sulfited white potato	-	20-49	5.3	0.00011, 49°C	172 (41.0)
				7.6	0.00020, 49°C	151 (36.0)
				9.2	0.00026, 49°C	143 (34.0)
	Sulfited carrot	-	20-49	5.4	0.00011, 49°C	168 (40.0)
				6.2	0.00012, 49°C	151 (36.0)
				8.0	0.00013, 49°C	147 (35.0)
	Sulfited cabbage	-	20-49	2.1	-	176 (42.0)
				3.5	-	160 (38.0)
				7.1	-	147 (35.0)
Hendel et al, 1955	Dried potato	-	40-80	4.9	0.05139, 80°C	155 (37.0)
				9.4	0.07778, 80°C	134 (32.0)
				15.0	0.10000, 80°C	118 (28.0)
				33.0	0.05667, 80°C	105 (25.0)
				110.0	0.02778, 80°C	105 (25.0)
				370.0	0.01416, 80°C	109 (26.0)
Burton, 1963	Homogenized goat's milk	6.5-6.6	93.3-121.1	-	355.40000, 121.1°C	113 (27.0)
	Non-homogenized goat's milk	6.5-6.6	93.3-121.1	-	421.80000, 121.1°C	113 (27.0)
Hermann, 1970	Apple juice	-	37.8-130	-	1.42167, 121.1°C	113 (27.0)
Hermann, 1970	Apple juice	-	37.8-130	-	1.34667, 121.1°C	87 (20.7)
Mizrahi et al, 1970	Dehydrated cabbage	-	-	1.0	-	172 (41.0)
		-	-	18.0	-	109 (26.0)
Drilleau and Prioult, 1971	Apple juice	-	-			118-166 (28-39.6)*
Flink et al, 1974	Milk	-	-	-	2.77778, 100°C, 0%RH	197 (47.0)
					41.66700, 100°C, 11%RH	223 (53.0)
					111.11100, 100°C, 32%RH	139 (33.0)
Pokorny et al, 1975	Cauliflower	-	40-50	-	-	144 (34.2)
			50-80	-	-	105 (25.1)
Resnik and Chirife, 1979	Dehydrated apple	-	55-83	0.0	-	172 (41.0)*
				83.0	-	122 (29.0)*

*5-HMF formation

2.4.3.2 Pigment/Chlorophyll Destruction

In foods that contain chlorophylls, the change in colour from a bright green to an olive-green or olive-yellow colour on processing has been the concern of food processors since the introduction of thermal processing. The change is due to the conversion of chlorophylls to their respective pheophytins and further breakdown products such as pheophorbides and chlorins (Mackinney and Weast, 1940; Westcott et al, 1955; Gilpin et al, 1959; Gold and Weckel 1959 and Spencer, 1973). The percentage of change of chlorophylls to pheophytins has been studied by many workers. Kaur and Manjrekar (1975) found that canned sarson-ka-sag (prepared mustard green) lost about 50% of the chlorophyll during processing. In green peas, Aczel (1971, 1973) found that chlorophyll content was reduced by 10-16% during blanching and then all chlorophyll was converted to pheophytin during sterilisation. The degradation of chlorophyll was found to be dependent on time of processing (Sweeny and Martin, 1958 and Lee et al, 1974). Many workers found that the extent of degradation of chlorophyll depended on pH and heat source (Sweeney and Martin, 1961; Buckle and Edward, 1970; Lee et al, 1974). Lee et al (1974) also found that steam had more effect on chlorophyll than boiling water which had more effect than hot air and microwave.

The effect of time and temperature on the degradation of chlorophyll has been studied by many workers. Gold and Weckel (1959) studied the conversion during sterilisation of canned green peas and found that it was pseudo-first order reaction. Epstein (1959), also found that the loss of green colour of HTST processed peas was pseudo-first order. Mckinney and Weast (1940) stated in their work that the conversion of chlorophyll in aqueous acetone and acid solution was a first order reaction in respect to both acid and chlorophyll content. Sweeney and Martin (1958) found that it could be described by either a zero order or first order reaction in heated broccoli. However, Schanderl et al, (1962), Gupte et al, (1964) and Haisman and Clarke (1975) found that the conversion of chlorophyll occured only above a threshold temperature of 50-60°C and the conversion was most probably a first order reaction. In 1964, Gupte et al investigated and determined not only the kinetics of chlorophyll degradation in spinach puree but also the thermodynamic energies for this degradation based on a first order reaction. Hayakawa and Timbers (1977) studied the influence of various thermal treatments on the visual green colour of canned asparagus, green beans and peas and determined the kinetic reaction rate constant by assuming that the reaction was a first order. The kinetic reaction rate constant for chlorophyll was also studied by other workers such as Dietrich et al (1970) for green beans, Lenz and Lund (1974) for pea puree and spinach puree, Hermann (1970) for spinach. Tan and Francis (1962) who studied the effect of processing on the pigments and colour of spinach puree, provided a result adequate for calculating the kinetic reaction rate. The value of the kinetic parameters determined by various workers are summarized in Table 2.4. The kinetic reaction rate for chlorophyll a and b varied depending on the type of food, pH, temperature range. Lund (1975b) concluded that the variability of results obtained in different laboratories may be due to the heating technique and the analytical method. He suggested that the activation energy for chlorophyll a should be 42-105 kJ mole^{-1} (10-25 kcal mole^{-1}) and for chlorophyll b, Ea should be lower because it appears to be more stable.

2.4.3.3 Total Colour Change

There were some workers studying the total colour changes of food during processing. Unfortunately, the data given were not enough for determining the kinetic parameters. However, the results presented by Salunkhe et al (1978) on colour change during storage of various food were adequate. The scales were read from the Hunter-Colour and Colour-Difference Meter (Model D25D2, Hunter Association Laboratory, Inc. Fairfax, V.A.). The kinetic parameters were determined assuming first order kinetics and are shown in Table 2.5. The average activation energy for L, a, b was 63, 56 and 45 kJ mole^{-1}, respectively. Higher activation energy of 135 kJ mole^{-1} was found for the decrease in greeness of Brussels sprouts during storage (Tijskens et al, 1979). The rate of decrease which could probably be described by first order kinetics was 0.00112 x 10^{-4} s^{-1} at -4^{o}C.

TABLE 2.4 Reaction Rate Constants and Activation Energies for Chlorophyll Destruction

Reference	Food Product	pH	Temperature °C	Reaction Rate $k_{121.1^\circ C}$ x $10^4 s^{-1}$	Activation Energy kJ mole^{-1} (kcal mole^{-1})	Remark
Mackinney and Joslyn, 1941	Buffer solution,					
	chlorophyll a	-	0-50	-	32 (7.5)	
	chlorophyll b	-	0-50	-	38 (9.0)	
Epstein, 1959	Green peas;					
	chlorophyll a	-	121.1-148.9	-	52 (12.2)	no lag correction
	chlorophyll b	-	121.1-148.9	-	80 (19.0)	
Gold and Weckel, 1959	Peas;					
	blanched	-	115.6-137.8	27.41700	68 (16.1)	
	unblanched	-	115.6-137.8	27.61700	53 (12.6)	
Schanderl et al, 1962	In acid solution;					
	chlorophyll a	-	25-55	-	44 (10.4)	
	ethyl chlorophyllide a	-	25-55	-	44 (10.4)	
	methyl chlorophyllide a	-	25-55	-	44 (10.6)	
	free chlorophyllide a	-	25-55	-	45 (10.8)	
Gupte et al, 1964	Spinach puree;					
	chlorophyll a	6.5	126.7-148.9	-	65 (15.5)	
	chlorophyll b	5.5	126.7-148.9	-	32 (7.5)	
Dietrich et al, 1970	Green beans	Natural	87.8-100.0	38.00000	50 (12.0)	
Hermann, 1970	Spinach;					
	chlorophyll a	Natural	100-130	11.25000	53 (12.5)	
	chlorophyll b	Natural	100-130	7.95000	42 (10.0)	
Timbers, 1971	Peas	Natural	79.4-148.9	38.00000	50 (12.0)	
	Asparagus	Natural	79.4-148.9	4.85000	63 (15.0)	
	Green beans	Natural	79.4-148.9	25.58300	59 (14.0)	
	Spinach	Natural	79.4-148.9	18.28300	63 (15.0)	
Lenz and Lund, 1974	Pea puree	6.5	79.4-137.8	3.40000	92 (22.0)	
	Spinach puree	6.5	79.4-137.8	2.31700	80 (19.0)	

TABLE 2.5 Reaction Rate Constants and Activation Energies for Colour Change

Food Products	L-scale		a-Scale		b-Scale	
	$k_{37.8^oC}$ x 10^4 s^{-1}	Ea kJ mole^{-1} (kcal mole^{-1})	$k_{37.8^oC}$ x 10^4 s^{-1}	Ea kJ mole^{-1} (kcal mole^{-1})	$k_{37.8^oC}$ x 10^4 s^{-1}	Ea kJ mole^{-1} (kcal mole^{-1})
Ham and Chicken Loaf	0.00002	105 (25.1)	0.00007	-	0.00005	86 (20.4)
Frankfurters	0.00004	48 (11.5)	0.00006	70 (16.6)	0.00001	23 (5.4)
Beef steak	0.00002	54 (12.9)	0.00003	104 (24.8)	0.00001	21 (5.0)
Beef stew	0.00001	51 (12.1)	0.00003	36 (8.6)	0.00012	3 (0.8)
Cheese spread	0.00003	57 (13.6)	0.00005	51 (12.1)	0.00003	35 (8.3)
Pineapple	0.00008	67 (16.0)	0.00024	47 (11.1)	0.00008	84 (19.9)
Fruit cake	0.00006	61 (14.4)	0.00003	40 (9.5)	0.00009	64 (15.2)
Chocolate Brownies	0.00003	57 (13.6)	0.00004	43 (10.2)	0.00003	40 (9.6)

2.4.4 Viscosity

As the model system used, baby food, consisted of about 4.5% of various starches, wheat, barley and corn flour and 30% of potatoes in composition, the viscosity of the baby food depended on starch gelatinization.

Starch granules from different sources have different sizes, they vary between 3 and 30 mμ with respect to the average size of their largest diameter for wheat starch, corn and barley starch and between 10 and 100 mμ for root and tuber starch, as·potato starch. They are insoluble in cold water but swell with water when heated. The temperature at which granule swelling occurs varies with different starches. The gelatinization temperature ranges form 59.5-77.0°C depending on type of starch with the lowest temperature for barley starch and the highest for modified potato starch.

In terms of viscosity, it gradually increases with the increase in temperature. When the gelation temperature is reached, the viscosity will rise rapidly due to the resistance of the swollen starch granules to displacement. A dynamic situation eventually prevails in which some of the granules are still swelling while others are simultaneously disintegrating under the influence of continuous heating and stirring (Katz, 1938). Maximum viscosity is obtained when the increase in structural viscosity caused by swollen starch aggregates is counterbalanced by the decrease in viscosity resulting from disintegration and solubilization of the starch. As heating is continued, the viscosity decreases gradually due to the breakdown of starch structure. The change of viscosity during heating of the starch-water suspension can be followed on a recording viscometer (Anker and Geddes, 1944; Kesler and Bechtel, 1947; Crossland and Favor, 1948; Corn Starch, 1964; Knight, 1969). The pattern of viscosity change varied from one starch to another depending on the chemical property of the starch (Corn Starch, 1964). Starch concentration was also found to affect the pattern of viscosity change (Anker and Geddes, 1944).

Besides, there are other factors affecting the viscosity change which are (1) temperature (Corn Starch, 1964), (2) degree of agitation (Katz, 1938; Corn Starch, 1964), (3) pH of starch suspension (Corn Starch, 1964; Whistler and Paschall, 1965) and, (4) presence of chemicals (Whistler and Paschall, 1965). Higher temperature, higher agitation rate, pH higher than 7 and lower than 4, were found to accelerate gelatinization and subsequent breakdown during prolonged heating. Some ingredients had a retarding action such as sugar, dextrose and corn syrup.

As discussed before, prolonged heating can cause the change in viscosity which means a change in texture of the product. Luh et al (1964) studied the effect of conventional canning and UTST thermal processing on the viscosity change of food products. Unfortunately the data presented were inadequate for determination of kinetic parameters. In terms of consistency, a "z" of 23°C, 29°C and 20°C were found for fish pudding, liver paste and vanilla sauce during thermal processing (Ohlsson, 1980). These were equivalent to the approximate activation energies of 130, 103, 150 kJ mole^{-1}.

2.5 CONCLUSION

The changes in food during heat processing and storage were found to be described by either zero, first or second order kinetics. Zero order kinetics was found only at high concentrations and then it tended to change to first order kinetics as the concentration decreased. Second order kinetics were also found in some reactions. However, most of the changes in food could be described by first order kinetics.

There were a number of factors affecting the rate of change - temperature, pH, water activity, oxygen concentration and concentration of minor components e.g. Cu^{+2}. The temperature dependence of rate of change and in particular the destruction rate of nutrients was extensively studied and for most reaction rates the Arrhenius equation was found to adequately describe the temperature dependence.

Two heating procedures, steady-state and unsteady-state, can be used for estimation of the changes in food during processing. Calculation of kinetic parameters from the data obtained by the steady-state method is simple but only small food samples can be used. Unsteady-state procedure, where food is heated in a can, gives adequate sample size for eating quality determinations but the calculation is complex.

The rates of destruction of ascorbic acid and of changes in colour (browning reaction and chlorophyll destruction), and in viscosity were found to be mostly described by first order kinetics. For riboflavin, only the photodegradation rate was described by first order kinetics. The reaction rates reported were found to be in a wide range. The activation energy of ascorbic acid ranged from 14 to 172 kJ mole^{-1}. The range of 34-172 kJ mole^{-1} was reported for riboflavin. For browning reaction, chlorophyll destruction, total colour change and viscosity the range of activation energies were 87-223 kJ mole^{-1}, 32-92 kJ mole^{-1}, 45-63 kJ mole^{-1} and 103-150 kJ mole^{-1}, respectively.

3. INVESTIGATION OF TESTING METHODS AND DEVELOPMENT OF PROCESS

3.1 INTRODUCTION

The aim of the present research was to determine the kinetic parameters for the destruction of ascorbic acid and riboflavin and for the changes in colour and viscosity of foods during heating. As colour and viscosity required large sample size, the unsteady-state procedure of heating in can had to be used. Ascorbic acid and riboflavin were chosen because the analytical methods were simpler than for other vitamins and the kinetic parameters could be determined by either steady-state or unsteady-state heating procedure. The feasibility and accuracy of the computer model developed for the unsteady-state procedure (in cans), therefore, could be tested by comparison of the kinetic parameters determined for ascorbic acid and riboflavin from these two procedures-steady and unsteady-state . A baby food made from strained beef and mixed vegetables was used in this experimental work.

To determine the kinetic parameters, the concentration before and after heating for a specific time and temperature must be known, so the analytical methods were first studied to give assays of sufficient accuracy to follow the kinetics.

The preparation method for homogenized, strained baby food was also investigated to give standard raw material for all tests. The raw materials required were determined by setting the product characteristics required. As only one product composition was used in the study, frozen storage of the prepared raw baby food was necessary to provide exactly the same raw material for the heating tests.

Using the unsteady-state procedure where foods were heated in cans, the canning process - the preprocessing conditions, the retort operation, the processing conditions - was studied to obtain accurate control of the process.

Then, the preparation method, the final formulation, the pre-processing conditions and the processing conditions were finalized to give a heating process which could be accurately controlled and measured.

3.2 INVESTIGATION OF TESTING METHODS

The object of this part of study was to find the simplest method, using the equipment available, which would give the accuracy required. The method chosen for each quality characteristic will be discussed separately in the following section.

3.2.1 Ascorbic Acid

Specialised instruments such as autoanalyser, microfluorometer were not available, so a simple method of chemical titration with 2-6 dichloroindophenol was investigated. However, the colour interference of the samples made it difficult to achieve an accurate result. A colorimetric method of Pearson (1976) was tried. This method is based on the oxidation - reduction reaction of ascorbic acid and the indicator dye, 2-6 dichloroindophenol. The colour change was measured as absorbance by the Spectronic 20 spectrophotometer at wavelength 520 nm with the green filter. A standard curve was prepared using various concentrations of ascorbic acid solution showing the relationship between the concentration of ascorbic acid and the scale of the absorbance obtained. The concentration of ascorbic acid in the sample was directly calculated from the prepared standard curve.

It was found that this method could be used if the sample size was small enough to prevent the colour interference. Reproducible results were obtained where the total ascorbic acid content in the sample was more than 0.25 mg g^{-1} (Appendix 3.1a), and the sample size was approximately 8-10 g. The details of analytical method are in Appendix 3.2a.

3.2.2 Riboflavin

The fluorometric method (AOAC, 1977) was found to give duplicate results where the concentration was about 20-30 $\mu g\ g^{-1}$ (Appendix 3.1b). However, it was found that when measuring the fluorescence the samples had to be randomized as the instrument readings were drifting. Throughout all stages of the method, protection of solution from undue exposure to light was done by covering all glasswares with aluminium foil.
The details of the method are in Appendix 3.2b.

3.2.3 Colour

It is difficult to describe quantitatively what colour is, as what is actually seen is the overall appearance of the food which depends on more than the colour alone. Such qualities as surface texture, gloss, metallic characteristics, translucency and many more can contribute significantly to the total visual effect. In this study, an objective method was used in order to obtain simple quantitative data for describing the effect of heat on the colour change of the processed food.

A DU-colour instrument (Neotec Instruments, Inc. of Silver Spring, MD, 1971) was used. The measurement was read in the CIE system of X, Y, and Z as this system has achieved world wide acceptance and has been used essentially unchanged for many years (Billmeyer, 1968). Furthermore, the CIE chromaticity diagram is also available showing the colour of the sample on a two dimensional scale of x and y where $x = X/(X + Y + Z)$ and $y = Y/(X + Y + Z)$. That is, for any given colour in the colour space, it would be partially described by x and y and then a third number, the tristimulus value Y, must be cited to completely describe the colour as lightness or darkness.

One important parameter in measuring the colour of the sample by a reflectance method was the thickness of the sample on the glass window which must be controlled. A metal ring of about 1 cm depth was used. It was placed on the glass window, the sample was filled and the white cover was pressed against the ring to allow the excess sample to overflow.

3.2.4 Viscosity

Viscosity is a physical property which is related to texture of food. It was the object of this study to determine the change of the viscosity in processed foods which would relate to a change in the texture of the food. Since baby food is a non-Newtonian fluid, it is common practice to define a so-called apparent viscosity by using a shear rate selected to fall within a range of practical interest. The Brookfield Synchrolectric (LV type) was used.

The viscosity of non-Newtonian fluids depends on the rate of shear which is governed by the speed of rotation and size of spindle. Therefore, the speed of rotation of 0.5 s^{-1} and the spindle diameter of 0.3 cm (size 4), which had been found to give an adequate range of viscosity, were used. It was also found that the time of shear did effect the viscosity reading. So it was decided that the reading would be taken at 1 minute after starting. The temperature of the sample was exactly controlled at 25^{o}C as temperature affected the viscosity.

3.3 DEVELOPMENT OF PROCESS

The preparation of homogenized baby food and the canning process were studied.

3.3.1 Preparation of Baby Foods

The composition of the baby food used was based on the canned beef and vegetable baby food on the market. The approximate composition was found to be beef 5%, mixed vegetables 45%, flour, corn flour and barley flour 4.5%, yeast extract 0.4%, salt 0.4% and water 44.7%. The concentration of ascorbic acid in the existing canned product on the market was too low to determine so 2 mg of ascorbic acid per 100 g of raw material mixed was added. The following composition was used for this preliminary experiment.

Beef	5.0%
Carrots	14.0%
Peas	9.0%
Potatoes	22.0%
Flour	1.2%
Corn flour	2.5%
Barley flour	0.8%
Yeast extract	0.4%
Salt	0.4%
Water	44.7%

Beef was cut and minced through 1 cm, 0.4 cm and 0.25 cm diameter plates of a Kenwood mincer for 1, 2 and 2 times, respectively, as fine division was needed. Vegetables, except peas which were frozen, were washed, peeled, diced and then blanched in a steam blancher. A blanching time of 5 minutes was sufficient to destroy enzymes and therefore prevent enzymic browning reactions occurring. All raw materials including the dry ingredients and water were disintegrated under vacuum of 68.9 kPa pressure in the JEFFCO wet disintegrator (size 2 Model 291 DIMOCK MACHINE, Jeffress Bros. Ltd) for 3 minutes and then left under vacuum for another 2 minutes to draw out as much of the remaining air as possible. The vacuum disintegration was necessary so as to reduce the size of the food particles to a suitable size for the further steps in processing. To prevent blocking of the homogeniser, the slurry was screened through a 1 cm square screen before passing through the homogeniser. The homogeniser used was a "MINOR" homogeniser type K (APV Manton - Gaulin homogeniser) with two-stages where the slurry was forced through a small annulus at a pressure of 34500 kPa to create a very high velocity which broke down the particles into minute form. The homogeniser was preferred to the colloid mill as the strained baby food obtained from the latter entrapped a lot of air bubbles which could possibly effect the quality of the stored baby food.

The strained slurries were packed in SARAN bags under vacuum and frozen immediately in a plate freezer. The slurries were completely frozen within 2 hours. SARAN bags were used to prevent air/oxygen transmission into the bag. Rapid freezing was used to minimize the pre-heating destruction of the studied quality factors. The frozen baby food was stored at $-30^{o}C$ where the rate of destruction of most vitamins was negligible (Fennema, 1975).

As the initial product characteristics required for each run were the same, the raw baby food had to come either from the same batch of raw material slurry or the same proportion of various batches. However, because of the quantity of product required, it became obvious that one single batch could not be prepared for the whole study. Therefore a number of batches were made and equal amounts of each batch were mixed for each experiment. Sufficient batches were made to cover the whole study,with an adequate safety margin.

3.3.2 Preprocessing

3.3.2.1 Thawing

The raw strained baby food stored in frozen state was thawed prior to further preprocessing. During thawing, foods are subjected to damage by chemical, physical and microbial means although microbial problems are negligible in properly handled foods. High temperatures are detrimental to the quality of foods so mild temperature conditions should be used in thawing (Fennema, 1975).

Two different thawing conditions were studied, a $30^{o}C$ water bath and a water bath in a $25^{o}C$ controlled room. The thawing time was 1 hour in the $30^{o}C$ water bath and about 2 hours in the water bath held in $25^{o}C$ controlled room. As large amounts of frozen baby food were thawed, it was more difficult to control the condition of $30^{o}C$ as more than one water bath was required. Therefore, for convenience and more accurate temperature control, thawing in the water bath in $25^{o}C$ for 2½ hours was used.

3.3.2.2 Preheating

As the viscosity of baby food was related to gelatinization of starch, preheating to gelatinize the starch was necessary to give a consistent initial viscosity. Another purpose for preheating was to allow hot filling to be used providing a vacuum in the cans.

The temperature for preheating was chosen as 70°C to lie within the general gelatinization temperature range for starch of 59.5-77.0°C. The heating was carried out in a steam jacketed pan. A steam pressure in the jacket of 190 kPa was maintained and the product stirred by hand. The time required for heating to 70°C was 7 minutes and this condition was used in all experiments.

After preheating, the heated baby food was filled into the prepared cans with the minimum possible headspace being left so as to minimize can to can variations in the temperature responses of the samples. The filled cans were vacuum sealed and immersed in a water bath at 60°C. The time taken to reach a uniform temperature of 60°C was found to be 80 minutes.

3.3.3 Processing

The cans taken from the 60°C water bath were processed in a retort under different processing conditions. Temperature measurement and retort operation were studied. Processing conditions were set according to the existing retort.

3.3.3.1 Temperature Measurement

Standard 24 gauge (United States standard wire gauge) copper/constantan thermocouples were used and connected to a 12-point Honeywell-Brown recording potentiometer operating on a 72 second print cycle. A tension method of thermocouple mounting were used. Holes were located at diametrically opposite sides of the can and were pierced through the can wall with a sharp point. The copper and constantan wires were separated and threaded through holes from opposite sides of the can. They were then carefully joined and soldered. The junction point was made as small as possible to give the temperature measurement at the exact point in the can. The wires and junction point were held in position with adhesive tape on the outside of the can. Epoxy resin adhesive was applied on both sides of the hole and left overnight to complete hardening. For points near the can wall, following suggestions made by Packer (1967) the constantan wire was always the shorter within the can.

Anti-sulphur, lacquered cans of 7.4 cm diameter and 10.8 cm height were used. For each processing run, a can with thermocouples at five different points was filled with preheated baby food and heated in the retort. The temperature distribution through the food during processing was measured and recorded by the potentiometer. The thermocouple arrangement is shown in Figure 3.1 and Table 3.1.

3.3.3.2 Retort Operation

The retort used was a laboratory-scale, horizontal autoclave (locally made by Berry Engineering Ltd., Palmerston North, New Zealand). It was equipped with two venting valves, steam inlet, steam by-pass, cooling water inlet and drain water outlet, the steam pressure and temperature were controlled by an automatic pnuematic system. At the end of the 2 minutes venting period, the drain valve and two vent valves were closed. The required retort steam pressure was reached within a few seconds after closing vents and the steam temperature could be controlled for the required period. At the end of the holding period, the retort pressure was reduced slowly over 4 minutes. This step was necessary and had to be carefully controlled, as the high processing temperature involved may create very high pressures within the can of 200-300 kPa (Goldblith et al, 1961, p. 854). If the retort pressure was released too quickly, distortion or buckling of the can could occur.

Once the retort pressure was reduced to atmospheric, the cooling water was turned on and the retort was about 75% filled. This water level was maintained by continuous flow of cold water. The total cooling time was 40 minutes. The time taken to fill 75% of the retort was about 5 minutes.

3.3.3.3 Processing Conditions

The system on the retort used was limited to temperatures below 130^{o}C. In order to ensure satisfactory control at all times, the maximum retort temperature used was 129^{o}C.

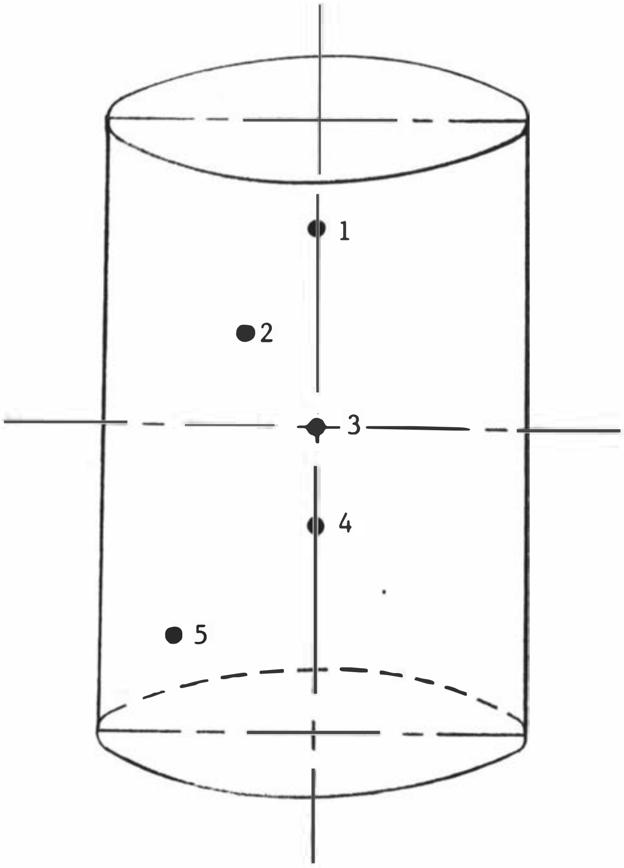


FIG. 3.1 Thermocouple Arrangement in a Can

TABLE 3.1 Distance from the Centre to the Measured Points

Point Number	r* cm	h* cm
1	0.0	3.6
2	1.2	1.8
3	0.0	0.0
4	0.0	1.8
5	2.5	3.6

* r is a distance from the centre of a can in diametral direction.

h is a distance from the centre of a can in axial direction.

For a low acid food of pH of 5.5-6.0, the $F^{10}_{121.1}$, which is the equivalent processing time in minutes at 121.1°C for "z" of 10°C, recommended is in the range of 10 to 15. It was decided to carry out the experiment at 129°C retort temperature for various processing times to obtain the $F^{10}_{121.1}$ of 5.0, 9.0, 13.0, 17.0 and 21.0

Heated samples were taken from the processed cans after cooling whereas control samples or zero time samples were taken randomly from the cans after removal from the 60°C water bath. Two samples of both the control and processed samples from each processing experiment were stored overnight in a chiller at 10°C prior to viscosity, colour, pH and dissolved oxygen measurements. All other control and processed samples were stored in -30°C frozen storage for vitamin analysis. The control and heated cans were completely thawed in an ambient temperature water bath. Then the can content was totally mixed before the samples were taken for analysis.

3.4 ADJUSTMENT OF PROCESS

The results from 3.3 suggested that adjustment of the process was necessary. Experiments were carried out and the results obtained were used to determine the final process.

3.4.1 Formulation

The ascorbic acid content in both control and heated samples was too low to obtain accurate results. The sample size required was large and caused colour interference in the ascorbic acid determination for the heated samples. The riboflavin concentration was also too low and a large sample size was needed causing an error from colour interference. Therefore, it was decided to add both ascorbic acid and riboflavin into the raw prepared baby food so as to reduce sample size and colour interference.

Using the measured temperature distribution at the centre and at the farthest point at the highest processing temperature of 129°C and the longest processing time ($F^{10}_{121.1}$ of about 21.0) with the kinetic reaction data from Chittaporn (1977), the average ascorbic acid retention at each point estimated from:

$$c_1 = c_o \exp(-k\Delta t)$$
$$c_1/c_o = \exp(-k \times 0.02)$$

where c_1 is the final concentration after one time interval Δt

k is the reaction rate calculated for various measured temperatures (h^{-1})

0.02 is the time interval, Δt(h), over which the temperature is assumed constant

c_o is the initial concentration

and this can be continued for c_2, c_3,...c_n for processing time of $n\Delta t$.

The average ascorbic acid retention of these two points was 69%. The necessary ascorbic acid to be added to give an accurate reading in the heated sample was calculated as 20 mg per 100 g of raw slurry. The riboflavin needed was calculated in a similar way as 2.5 mg per 100 g of raw slurry.

From the colour measurement, all the heated samples were darker than the control. As x and y could be calculated from X, Y and Z data Billmeyer (1968), it was found that there was a difference between x and y of the control and heated samples but the percentage change was the same for all heated samples subjected to various degrees of heat treatment. Therefore, it was concluded at this point that there was a change in colour during heat treatment but the change in x and y of the heated samples was the same, only the darkness (Y) of the samples changed. Only Y was therefore necessary to measure the change of colour during heating. The results of calculated x and y are shown in Appendix 3.3.

As the colour of the control samples was too dark, the composition of raw material was altered to produce a lighter colour in the control, thus providing more room for Y to change in the heated samples. The composition of mixed vegetables which governed the colour of the product as they were the main raw materials, were changed from 14% carrots, 9% peas, and 22% potatoes to 10% carrots, 5% peas and 30% potatoes. The experiments were repeated using the modified composition fortified with ascorbic acid and riboflavin. The analysis of both vitamins were found to be satisfactory. The colour of both control and heated samples were improved as Y obtained from a new control sample was

31-32 when the former control sample was 23-24.

Therefore, the final formulation was:

Beef	5.0%
Carrots	10.0%
Peas	5.0%
Potatoes	30.0%
Flour	1.2%
Corn flour	2.5%
Barley flour	0.8%
Yeast extract	0.4%
Salt	0.4%
Water	44.7%
Ascorbic acid	0.2 mg g^{-1}
Riboflavin	25.0 µg g^{-1}

3.4.2 Preprocessing Conditions

The viscosity of the control samples from various experimental runs were found to vary so that the change of viscosity with heat processing could not be predicted. As starch gelatinization depends on time and temperature of heating, rate of heating, degree of agitation, pH and other factors, it was difficult to obtain the same viscosity in the product unless all the factors involved were precisely controlled. Agitation by hand stirring may have been one of the important factors causing fluctuation in results in the preliminary experiment so a mechanical stirrer with controlled speed was used instead of hand stirring for later work.

Also, because of the complexity of the viscosity change of starch paste during heating and stirring, it was decided to control the viscosity of the control sample in each experimental run at about maximum viscosity, then any subsequent reduction in viscosity could be attributed to the effect of further heating.

The experiments were carried out at fixed steam pressure of 190-200 kPa in the jacket of the steam jacketed pan. The volume of material in the steam jacketed pan was fixed so that the rate of heating would be the same for all runs. Samples were taken at various times for viscosity measurement. The temperature and time of heating were recorded. From the results, the rates of heating were different and could not be controlled in the existing equipment. The viscosities of samples at various times were also different between experimental runs as a result of different rates of heating. This can be seen in Figure 3.2. However, the maximum viscosity was reached after the temperature of the baby food rose higher than 87°C and after a time of heating varying from 10 to 14 minutes. At this point, it was believed that all the starches were fully gelatinized. Therefore the preheating was designed to achieve this in all samples. The steam pressure was 190-200 kPa and the final temperature of the baby food had to be higher than 87°C. The time of heating could be flexible depending on the amount of baby food to be heated. As the initial temperature could affect the rate of heating so the thawed slurry had to be chilled for 45 minutes at 10°C before preheating.

3.5 FINAL PROCESS

The final formulation decided, was:

Beef	5.0%
Carrots	10.0%
Peas	5.0%
Potatoes	30.0%
Flour	1.2%
Corn flour	2.5%
Barley flour	0.8%
Yeast extract	0.4%
Salt	0.4%
Water	44.7%
Ascorbic acid	$0.2\ \mathrm{mg\ g^{-1}}$
Riboflavin	$25.0\ \mu\mathrm{g\ g^{-1}}$

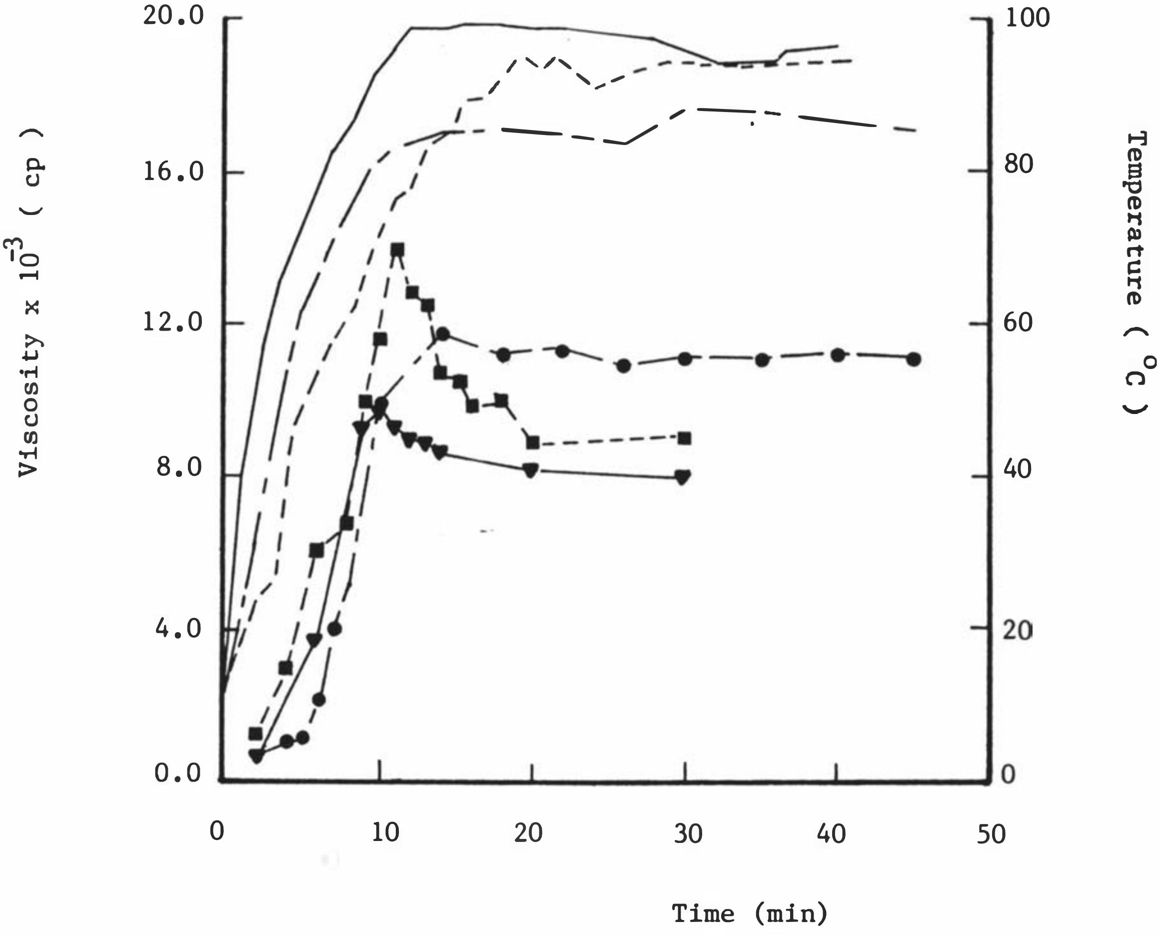


FIG.3.2 Time , Temperature and Viscosity Relationships During Preprocessing of Baby Food

—·— temperature-time relationships for experiment 1

—— temperature-time relationships for experiment 2

---- temperature-time relationships for experiment 3

●-·-● viscosity-time relationships for experiment 1

▼——▼ viscosity-time relationships for experiment 2

■---■ viscosity-time relationships for experiment 3

Frozen coarsely minced beef was minced again through the 0.25 cm diameter plate of a Kenwood mincer twice and put (about 500 g) in a plastic bag before storing at -10°C. Commercial frozen peas, carrot cubes and potato chips were used to ease the preparation step. Frozen minced beef was thawed, mixed with all frozen vegetables and other raw materials and 20 mg of ascorbic acid and 2.5 mg of riboflavin per 100 g of slurry, disintegrated under vacuum of 68.9 kPa pressure in a JEFFCO wet disintegrator for 3 minutes and then left under vacuum for another 2 minutes. This slurry was screened and passed through a MINOR-homogeniser which was operated at 34500 kPa pressure. The prepared slurry was vacuum packed in SARAN bags and frozen immediately in a plate freezer. The preparation of raw slurry was carried out in 16 kg batches providing enough slurry for all experimental runs. The frozen prepared slurry was kept at -30°C and thawed in a water bath held in a 25°C controlled room for 2½ hours before further processing. Exactly 800 g of thawed slurry from each batch was mixed and chilled at 10°C for 45 minutes giving exactly 12 kg for preheating.

Preheating was carried out in a MERCER steam jacketed pan (30 cm diameter, maximum capacity of 12,000 cm^3) with a Pioneer mixer model 2600 (Premier Colloid Mills Ltd.) at high speed of 50 s^{-1} and the steam pressure in the jacket of 190-200 kPa until the temperature of the baby food reached 87°C. Lacquered cans were then filled with hot baby food with minimum possible headspace and immediately vacuum sealed. The cans of baby food were then immersed in a 60°C water bath for 80 minutes before processing in the retort. Eight control cans were randomly taken, 2 cans were kept at ambient temperature for viscosity and colour analysis, the remaining cans were kept at -10°C for ascorbic acid and riboflavin analysis.

The remaining cans taken from the 60°C water bath were processed in a retort. One of the cans was equipped with 5 thermocouple junctions (Figure 3.1). The retort was closed, and the thermocouple ends were connected to a 12-point Honeywell-Brown recording potentiometer. Retort operation was exactly the same as described in 3.3.3.2. The temperature used and duration of processing were varied.

After cooling, two of the heated cans were kept at ambient temperature for viscosity and colour measurement, and the rest kept at $-10^{o}C$. Viscosity and colour measurement were carried out in the same day. Frozen control and heated cans for each experimental run were thawed in the ambient temperature water bath at the same time. The can content was mixed, then the sample was taken for analysis.

4. TEMPERATURE DISTRIBUTION IN A CAN DURING PROCESSING

4.1 INTRODUCTION

A major objective of this study was to establish a calculation procedure which, given the processing conditions, could be used to predict the extent of processing of the various critical components of the food. Before describing the detail, it may be helpful to set out the sequence of this part of the investigation.

First, in order to have a basis for comparison a careful series of experimental tests were carried out. Because of the temperature sensitivity of the reaction rates, temperatures should be known accurately within $\pm 0.25^{\circ}$C. And because temperatures varied with position, as well as with time, it was necessary to be able to predict temperatures at all positions within the can. For testing purposes, four points were considered sufficient. If these could be fitted then the others would presumably conform to the geometrical pattern.

For prediction two broad approaches were used, one based on an analytical solution and the other using a numerical finite difference method, to the heat conduction equations. Because of the many calculations needed, both were carried out by computer.

Thermal properties of the material were needed for these calculations, and they were estimated from the experimental results.

The predictions from the two calculation approaches were compared with the experimental results. In general both approaches, when the best thermal data were used, gave a very good fit and thus confidence to the prediction procedure, except for a consistent irregularity in the early stages of the cooling phase. This was not fully explained but some suggestions are advanced to account for it and modifications to the cooling calculations allow for its effects.

These procedures led finally to a calculation method which was sufficiently accurate for the kinetic predictions.

4.2 EXPERIMENTAL DETERMINATION OF TEMPERATURE DISTRIBUTION

The prepared, preheated baby food was filled and sealed in the prepared cans as described in Chapter 3. Two different retort temperatures were used, 120^o and 129^oC, and the canned baby food was processed for various times to get an approximate microbiological lethality number ($F_{121.1}^{10}$) of 5,9,13,17 and 21 min. The experimental runs were randomly performed. The detailed processing conditions together with the run number of each experiment performed in this study are shown in Table 4.1.

The retort operation was the same as described in section 3.3.3.2. The temperature distribution in the can was measured at various points by thermocouples connected to the Honeywell-Brown recording potentiometer as described in Table 3.1. The recorded temperatures at points 1,2,3 and 4 are shown in Figures 4.9 and 4.10.

TABLE 4.1 Experimental Run Number and Processing Conditions

Run No.	Initial temperature °C	Retort* temperature °C	Heating** time s	Cooling* water temperature °C	Cooling*** time s	Approximate $F_{121.1}^{10}$ intended min
7	60.0	120.2	3816	19.4	2400	5
4	60.0	119.6	5112	21.3	2400	13
9	61.0	120.0	5256	19.9	2400	17
2	60.3	119.8	6120	20.8	2400	21
6	61.0	129.1	2952	20.8	2400	5
1	58.8	128.7	3384	20.6	2400	9
8	60.2	128.6	3456	22.0	2400	13
5	61.0	129.2	3744	20.2	2400	17
10	59.0	129.1	3816	20.0	2400	21

* Average temperature calculated from the recorded temperatures obtained from each experimental run.

** The interval between the time when the required retort temperature was reached to the time when the cooling water was turned on.

*** The interval between the time when the cooling water was turned on to the end of cooling.

4.3 COMPUTER PROGRAMS FOR TEMPERATURE DISTRIBUTION CALCULATION

Two computer programs based on the analytical solution and the numerical finite difference method were studied and compared with the experimental measurements; the programs were written in FORTRAN IV language and run on a Burroughs B6700 computer.

4.3.1 Analytical Solution Method

The content of the can are a finite cylinder at an initial temperature, TI, and with thermal diffusivity, α. When the can is put in a medium at temperature, TA, there is heat transfer in all three directions. From heat transfer theory, this complex three dimensional heat transfer can be broken down into the radial heat transfer and infinite slab heat transfer.

If YC is the solution for radial heat transfer
YL is the solution for infinite slab heat transfer.

For a short cylinder

$$\frac{T - TA}{TI - TA} = (YC)(YL) \tag{4.1}$$

where T is the temperature of any point at time, t.

From Carslaw and Jaeger (1959, p.199 and p.100), where heat diffusivity is constant,

$$YC = 2\sum_{n=1}^{\infty} \frac{J_o(\beta_n r/a)}{\beta_n J_1(\beta_n)} \cdot e^{(-\beta_n^2 \alpha t/a^2)} \tag{4.2}$$

where a is cylinder radius
r is distance from the centre in radial direction
β_n is n^{th} positive root of $J_o(\beta) = 0$
t is time

$$YL = \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{(-1)^m}{(2m+1)} \cos \frac{(2m+1)\pi x}{2h} e^{-(2m+1)^2\pi^2\alpha t/4h^2} \tag{4.3}$$

where h is half-height of the cylinder

x is the distance from the centre in the axial direction.

Where $\alpha t/a^2$ is less than 0.02 and r/a is not too small, the series is slow to converge but a short term approximation exists (CARSLAW and JAEGER, 1959, p.330).

$$YC = 1-(\frac{a^{0.5}}{r^{0.5}} \text{ erfc } (z) + \frac{(a-r)(\alpha ta)^{0.5}}{4ar^{1.5}} \text{ ierfc } (z) +$$

$$\frac{(9a^2 - 7r^2 - 2ar)\alpha t}{32a^{1.5}r^{2.5}} i^2 \text{ erfc } (z)) \tag{4.4}$$

where z is $\dfrac{(a-r)}{2(\alpha t)^{0.5}}$

For the same reason, where $\alpha t/h^2$ is small, equation (4.5) has to be used instead of equation (4.2) (CARSLAW and JAEGER, 1959, p.309).

$$YL = 1-(\sum_{n=0}^{\infty} (-1)^n \text{ erfc } (\frac{(2n+1)h-x}{2(\alpha t)^{0.5}}) +$$

$$\sum_{n=0}^{\infty} (-1)^n \text{ erfc } (\frac{(2n+1)h+x}{2(\alpha t)^{0.5}})) \tag{4.5}$$

In the canning process, temperature distribution in both heating and cooling phases is required. In the heating phase, the temperature distribution can be calculated by

$$T = (TA-TI)\phi(r,x,t) + TI \tag{4.6}$$

where $\phi(r,x,t)$ is 1-(YC)(YL) at the point (r,x) at time, t

YC is the solution calculated by equation (4.2) or (4.4)

YL is the solution calculated by equation (4.3) or (4.5)

T is the temperature at (r,x) at time, t

TA is the retort temperature

TI is the initial temperature

a is the can radius
h is the half of can height
r is a distance from the centre of the can in the radial direction
x is a distance from the centre of the can in the axial direction
t is the total time from the beginning of the heating phase
β_n is the n^{th} positive roots of $J_o(\beta) = 0$.

In the cooling phase, if the temperature of the whole can content at the beginning of cooling is assumed to be uniform and equal to the retort temperature (Hicks, 1951), then the temperature distribution can be calculated by

$$T = (TA-TI)\phi(r,x,t) + (TC-TA)\phi(r,x,t-t_1) + TI \qquad (4.7)$$

where TC is the cooling water temperature
t_1 is the heating time.

The computer program was constructed based on the above theory; equations (4.1) to (4.7) were used. For equation (4.1) and (4.2), 6 terms in each series were calculated as Fleming (1971) stated that up to 3 terms of the series must be evaluated. Equation (4.4) and (4.5) were used where $\alpha t/a^2$ was less than 0.02; r/a was more than 0.1 and $\alpha t/h^2$ was less than 0.3 (Fleming, 1971). Where r/a was less than 0.1, the value of YC was set equal to zero. The flow chart of the computer program and the details of the program are in Appendix 4.1.

The calculated temperatures from the computer program were compared with the ones calculated by hand calculator based on the processing conditions of run no. 6 for the heating phase to check the accuracy of the constructed program, and it was found that the calculated temperatures were identical (Table 4.2).

TABLE 4.2 Comparison of the Calculated Temperatures at the Centre of the Can

Time s	Fo_c*	Fo_h*	CALCULATED TEMPERATURE °C	
			Computer	Hand Calculator
0	0	0	61.00	61.00
360	0.0404	0.0189	61.26	61.26
720	0.0807	0.0379	66.79	66.78
1080	0.1211	0.0569	77.06	77.05
1440	0.1615	0.0759	87.60	87.61
1800	0.2018	0.0948	96.75	96.74
2160	0.2422	0.1138	104.18	104.17
2520	0.2826	0.1328	110.03	110.03
2880	0.3229	0.1517	114.57	114.56

* Fo_c is the Fourier number of the radial direction which is equal to $\alpha t/a^2$.

Fo_h is the Fourier number in the axial direction which is equal to $\alpha t/h^2$.

4.3.2 Numerical Finite Difference Method

The general heat transfer equation for unsteady-state in a finite cylinder is

$$C\frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + \lambda \frac{\partial^2 T}{\partial r^2} + \frac{\lambda}{r} \frac{\partial T}{\partial r} \qquad (4.8)$$

where C is heat capacity on a volumetric basis

λ is thermal conductivity which is assumed to be constant

Using the numerical finite difference method, equation (4.8) becomes

$$\frac{T^{i+1}_{m,n} - T^{i}_{m,n}}{\Delta t} = \frac{\lambda}{C}\left(\frac{T^{i}_{m+1,n} - 2\,T^{i}_{m,n} + T^{i}_{m-1,n}}{(\Delta x)^2}\right) + \frac{\lambda}{C}\left(\frac{T^{i}_{m,n+1} - 2\,T^{i}_{m,n} + T^{i}_{m,n-1}}{(\Delta r)^2}\right) + \frac{\lambda}{C}\cdot\frac{1}{r}\left(\frac{T^{i}_{m,n+1} - T^{i}_{m,n-1}}{2\Delta r}\right) \qquad (4.9)$$

$$= \alpha(A) + \alpha(B) + \alpha(C)$$

where r is $(n-1)\Delta r$

x is $(m-1)\Delta x$

T^{i} represents temperature at time, t

T^{i+1} represents temperature at time $t + \Delta t$

α is the thermal diffusivity which is λ/C.

At the centre, where n=1, equation (4.9) was modified by Albasiny (1960) as

$$\lim_{r\to 0} \frac{1}{r}\frac{\partial T}{\partial r} = \frac{\partial^2 T}{\partial r^2}$$

$$\frac{\lambda}{r}\frac{\partial T}{\partial r} = \lambda\frac{\partial^2 T}{\partial r^2}$$

then $$C\frac{\partial T}{\partial r} = \lambda\frac{\partial^2 T}{\partial x^2} + 2\lambda\frac{\partial^2 T}{\partial r^2}$$

so $$\frac{T^{i+1}_{m,1} - T^{i}_{m,1}}{\Delta t} = \alpha\left(\frac{T^{i}_{m+1,1} - 2\,T^{i}_{m,1} + T^{i}_{m-1,1}}{(\Delta x)^2}\right) + 2\alpha\left(\frac{T^{i}_{m,2} - 2\,T^{i}_{m,1} + T^{i}_{m,0}}{(\Delta r)^2}\right) \qquad (4.10)$$

Assuming that the temperature at the point below the centre line is equal to the temperature at the corresponding point above the line, the temperature at the centre (m=1, n=1) and the temperature along the height and the radius can be calculated by (4.11), (4.12) and (4.13), respectively.

$$\frac{T^{i+1}_{1,1} - T^{i}_{1,1}}{\Delta t} = 2\alpha\left(\frac{T^{i}_{2,1} - T^{i}_{1,1}}{(\Delta x)^2}\right) + 4\alpha\left(\frac{T^{i}_{1,2} - T^{i}_{1,1}}{(\Delta r)^2}\right) \qquad (4.11)$$

$$\frac{T^{i+1}_{m,1} - T^{i}_{m,1}}{\Delta t} = 2\alpha\left(\frac{T^{i}_{m+1,1} - T^{i}_{m,1}}{(\Delta x)^2}\right) + 4\alpha\left(\frac{T^{i}_{m,2} - T^{i}_{m,1}}{(\Delta r)^2}\right) \qquad (4.12)$$

$$\frac{T^{i+1}_{1,n} - T^{i}_{1,n}}{\Delta t} = 2\alpha\left(\frac{T^{i}_{2,n} - T^{i}_{1,n}}{(\Delta x)^2}\right) + \alpha(B) + \alpha(C) \qquad (4.13)$$

The computer program was constructed based on the above equations by assuming the initial temperature at all points was equal throughout the can, while the temperature at the surface was equal to the retort temperature during heating and equal to the cooling water temperature during cooling. The details of the program are in Appendix 4.2.

Using this program, the degree of accuracy of temperature distribution prediction was dependent on the number of time increments, Δt, and dimensional increments, Δr and Δx. The dimensional increments, Δr and Δx, of less than 0.008 and 0.010 m and the time increments of 7.5 seconds should be used (Teixeira, 1971). The dimensional increments, Δr and Δx of 0.0037 and 0.0054 m and the time increment of 6 seconds were used in this study.

4.4 THERMAL PROPERTY DETERMINATION

To use the two programs to find the temperature distribution, only one thermal property, the thermal diffusivity, α is needed. This property can be calculated from the experimental temperature data using the analytical solution of the heat transfer equation.

The analytical solution for heat transfer can be re-expressed as:

$$\frac{T - TI}{TA - TI} = 1-Ae^{-Fo_c\beta_n^2}\ Be^{-Fo_x\pi^2/4} \qquad (4.14)$$

where A is $2\sum_{n=1}^{\infty} \frac{J_o(\beta_n r/a)}{\beta_n J_1(\beta_n)}$

B is $\frac{4}{\pi}\sum_{m=0}^{\infty} \frac{(-1)^m}{(2m+1)} \cos \frac{(2m+1)\pi x}{2h}$

If Y is (T - TI)/(TA - TI), where T is the centre temperature, and only one term in each series is considered, equation (4.14) simplifies to:

$$\ln Y = \ln A + \ln B + (-Fo_c\beta_1^2 - Fo_x\frac{\pi^2}{4})$$

$$\ln Y = \text{constant} - t(\frac{\alpha\beta_1^2}{a^2} + \frac{\alpha\pi^2}{4h^2}) \qquad (4.15)$$

From a plot of ln Y against time, t, the slope of the regression line on the straight part will be equal to $-(\alpha\beta_1^2/a^2 + \alpha\pi^2/4h^2)$. Knowing $\beta_1 = 2.4048$ and the dimensions of the can used, a = 0.037 m, h = 0.054 m, the thermal diffusivity can be calculated as illustrated in equation (4.16).

$$-\alpha\left(\frac{(2.4048)^2}{(0.037)^2}+\frac{\pi^2}{4(0.054)^2}\right)=\text{slope}$$

$$\alpha=\frac{-\text{slope}}{5070.4568}\ \text{m}^2\text{s}^{-1} \qquad (4.16)$$

This method has been used by other workers (Olson and Jackson, 1942; Teixeira, 1969). The graph plotted of ln Y versus time is a straight line, after the initial heating lag period, and only one term in the summation is adequate (Hicks, 1951). Therefore, the above method should result in an accurate thermal diffusivity calculation as long as the temperature measurement is accurate.

In the preliminary experiments, the canned baby food was processed under various temperatures and the centre temperature was measured with time. The thermal diffusivity was calculated from the slope obtained. The results are shown in Table 4.3. The average thermal diffusivity was found to be 1.5737 x 10^{-7} m^2s^{-1} with the standard deviation of 0.0678 x 10^{-7} m^2s^{-1}. This value of "α" was similar to data given by Teixeira (1975), Crumpton and Treadgill (1977) and Lenz and Lund (1977a) for other food systems. Crumpton and Treadgill (1977) stated in their study that the retort temperature had less effect on thermal diffusivity than the physical state of the material. The above results agreed with Crumpton and Treadgill's study as the deviation of calculated thermal diffusivities at different retort temperatures was less than the deviation of calculated thermal diffusivities of various experimental runs at the same retort temperature. This may have resulted from the variation in the contents from can to can, which was significant in other studies. The variation of thermal diffusivity between cans was 6.46% (Hurwitcz and Tischer, 1956) and 10-15% in work carried out by Jackson and Olson (1940). Heterogeneous packs were found to result in even greater variations (Esselen, 1951). Therefore, it was concluded that it was valid to use the average thermal diffusivity for all processing temperature conditions studied, as the baby food was homogeneous and the experimental variation small.

TABLE 4.3 Diffusivities of Baby Food at Various Temperatures

Retort Temperature ^{o}C	Diffusivity x 10^{7} $m^{2}s^{-1}$	Correlation Coefficient R^2
128.3	1.5717	0.999
	1.5359	1.000
	1.6229	0.999
	1.4677	0.999
	1.5465	0.999
120.6	1.5456	0.999
120.0	1.6101	0.999
111.1	1.5564	0.998
	1.7064	0.999

Some of the raw materials were changed in state so as to save time in preparation (section 3.5), frozen potato chips and carrot cubes and also frozen minced beef were used instead of the fresh ones. The thermal diffusivity of the baby food was redetermined and found to be 1.5429 x 10^{-7} $m^{2}s^{-1}$ with the standard deviation of 0.0196 x 10^{-7} $m^{2}s^{-1}$ at 120^{o}C and 1.5277 x 10^{-7} $m^{2}s^{-1}$ with the standard deviation of 0.0318 x 10^{-7} $m^{2}s^{-1}$ at 129^{o}C. The difference between these two means was tested and found to be insignificant. Details of the measurements and analysis are shown in Appendix 4.3. Therefore, the mean thermal diffusivity of 1.5353 x 10^{-7} $m^{2}s^{-1}$ with standard deviation of 0.0261 x 10^{-7} $m^{2}s^{-1}$ was used for all the processing conditions studied.

4.5 COMPARISON BETWEEN PREDICTED TEMPERATURES FROM THE TWO COMPUTER PROGRAMS - ANALYTICAL SOLUTION AND NUMERICAL FINITE DIFFERENCE

The predicted temperatures from both programs based on 3 points in the can of run no. 6 were almost identical (Table 4.4). The differences in temperatures were mostly about 0.1 to 0.2°C in both heating and cooling phases. In the heating phase, the predicted temperature by the numerical finite difference program was higher than the predicted temperature by the analytical solution program while in the cooling phase, the numerical finite difference program gave a lower predicted temperature. The difference was greater at the outside point than the centre of the can in the beginning of both heating and cooling phases. The greatest difference was 0.4°C for the centre and 0.9°C for the outside point in the heating phase. This difference could be due to the slower convergence in the heating phase of the analytical solution. Also, as the temperature gradients were high at the beginning, the temperatures of the can contents changed rapidly, thus smaller time steps should have been used to obtain more accurate approximation in the numerical finite difference program. In the cooling phase, the differences were larger, these could be due to the assumption made in the analytical solution program that the initial temperatures of the can contents were uniform and equal to the retort temperature; this resulted in higher predicted temperatures.

The differences in predicted temperatures by these two programs based on run no.6 are also shown in Figures 4.1and 4.2 for the centre point and the outside point, (r/a, x/h) of (2/3, 2/3). The residuals (predicted temperatures by analytical solution - predicted temperatures by numerical finite difference method) were calculated for both the centre point and the outside point. The calculation was done at 1.2 minute intervals, the distribution of residuals is shown in Figure 4.3. The mean residual was 0.07°C with a standard deviation of 0.34°C for the centre point and 0.07°C with a standard deviation of 0.54°C for the outside point. These differences were small and could be considered insignificant. Therefore, to test the accuracy of predictions, only predicted temperatures from the analytical solution program were compared with the experimental temperatures.

TABLE 4.4 Comparison of Temperatures Predicted by the Analytical Solution and the Numerical Finite Difference Programs

Time s	Fo_c	Fo_x	TEMPERATURE ^oC					
			at the centre		at r/a = 1/3, x/h = 1/3		at r/a = 2/3, x/h = 2/3	
			Analytical	Finite	Analytical	Finite	Analytical	Finite
Heating								
0	0	0	61.00	61.00	61.00	61.00	61.00	61.00
72	0.0081	0.0038	61.00	61.00	61.00	61.00	61.74	62.64
144	0.0162	0.0076	61.00	61.00	61.02	61.09	66.76	68.16
216	0.0242	0.0114	60.99	61.02	61.29	61.50	73.46	74.68
288	0.0323	0.0152	61.05	61.13	62.05	62.36	79.86	80.79
360	0.0404	0.0189	61.26	61.43	63.34	63.77	85.44	86.14
720	0.0807	0.0379	66.79	67.24	74.11	74.60	103.17	103.35
1080	0.1211	0.0569	77.06	77.44	86.04	86.38	111.97	112.04
1440	0.1615	0.0759	87.60	87.88	96.15	96.36	117.13	117.17
1800	0.2018	0.0948	96.75	96.93	104.09	104.21	120.48	120.50
2160	0.2422	0.1138	104.18	104.29	110.16	110.23	122.79	122.80
2520	0.2826	0.1328	110.03	110.09	114.78	114.81	124.43	124.43
2880	0.3229	0.1517	114.57	114.60	118.27	118.28	125.61	125.61
2952	0.3311	0.1554	115.34	115.36	118.86	118.87	125.81	125.81
Cooling								
72	0.0081	0.0038	116.07	116.09	119.41	119.42	124.82	123.38
144	0.0162	0.0076	116.77	116.78	119.90	119.81	117.01	114.78
216	0.0242	0.0114	117.44	117.41	119.98	119.65	106.51	104.57
288	0.0323	0.0152	117.98	117.85	119.23	118.69	96.49	95.00
360	0.0404	0.0189	118.23	117.96	117.63	116.94	87.75	86.64
720	0.0807	0.0379	111.96	111.24	102.39	101.60	60.16	59.87
1440	0.1615	0.0759	82.22		69.83			
2160	0.2422	0.1138	57.80		48.97			

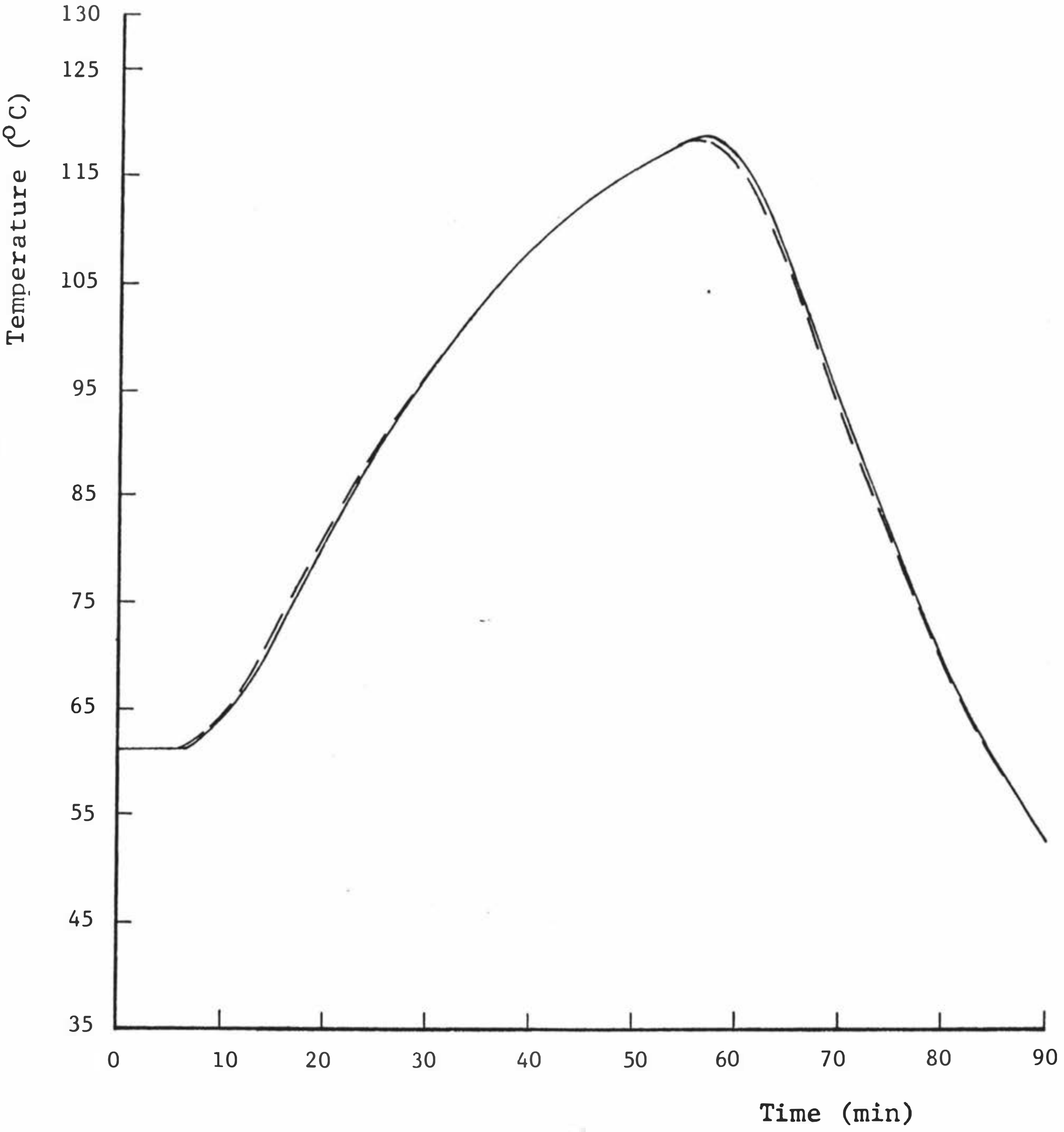


FIG. 4.1 Comparison of Predicted Temperatures from the Computer Programs at (r/a, x/h) of (0.0, 0.0)

(————) predicted temperatures from the analytical solution computer program

(—— ——) predicted temperatures from the numerical finite difference method program

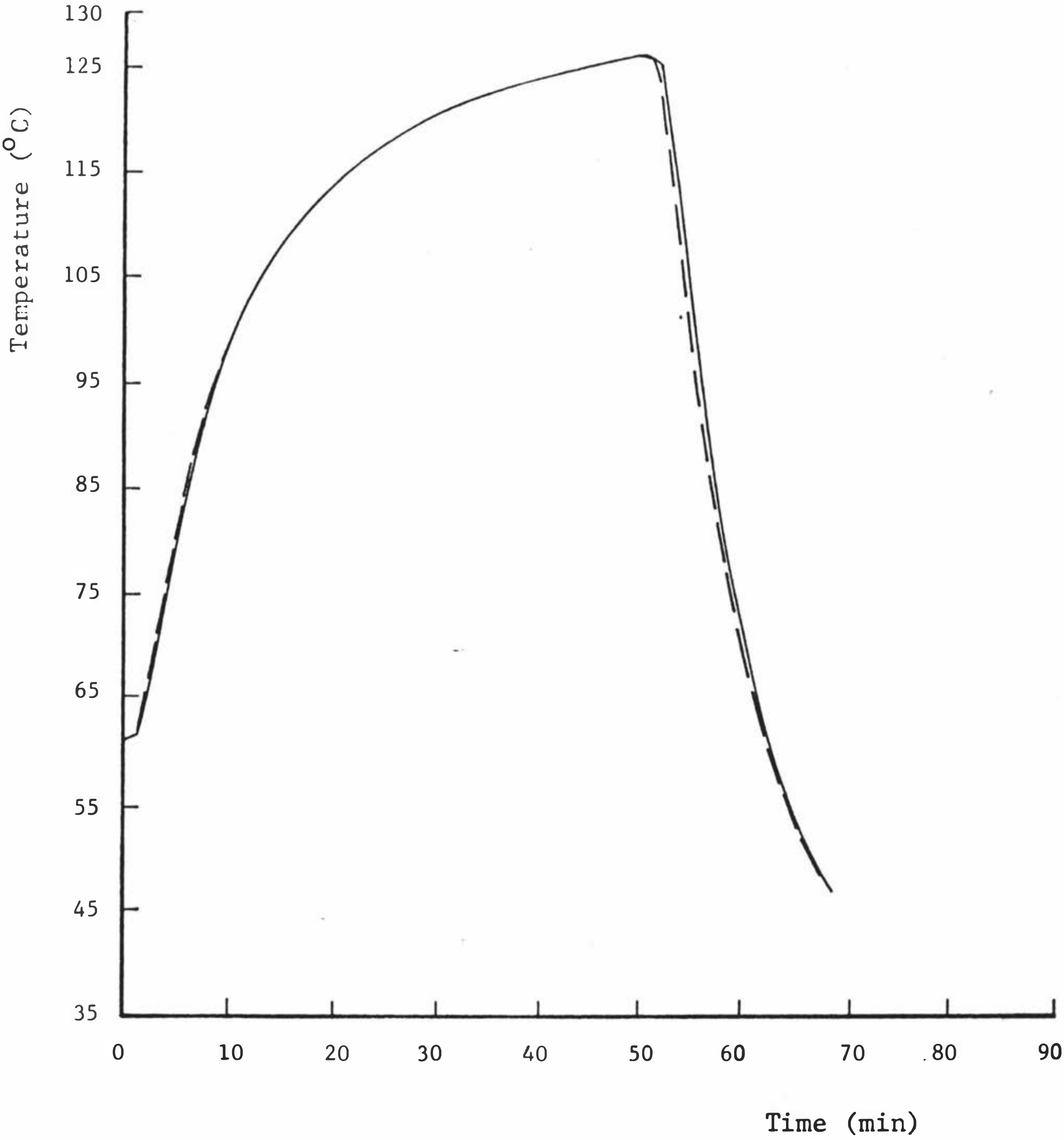


FIG. 4.2 Comparison of Predicted Temperatures from the Computer Programs at (r/a, x/h) of (2/3, 2/3)

(————) predicted temperatures from the analytical solution program

(—— ——) predicted temperatures from the numerical finite difference program

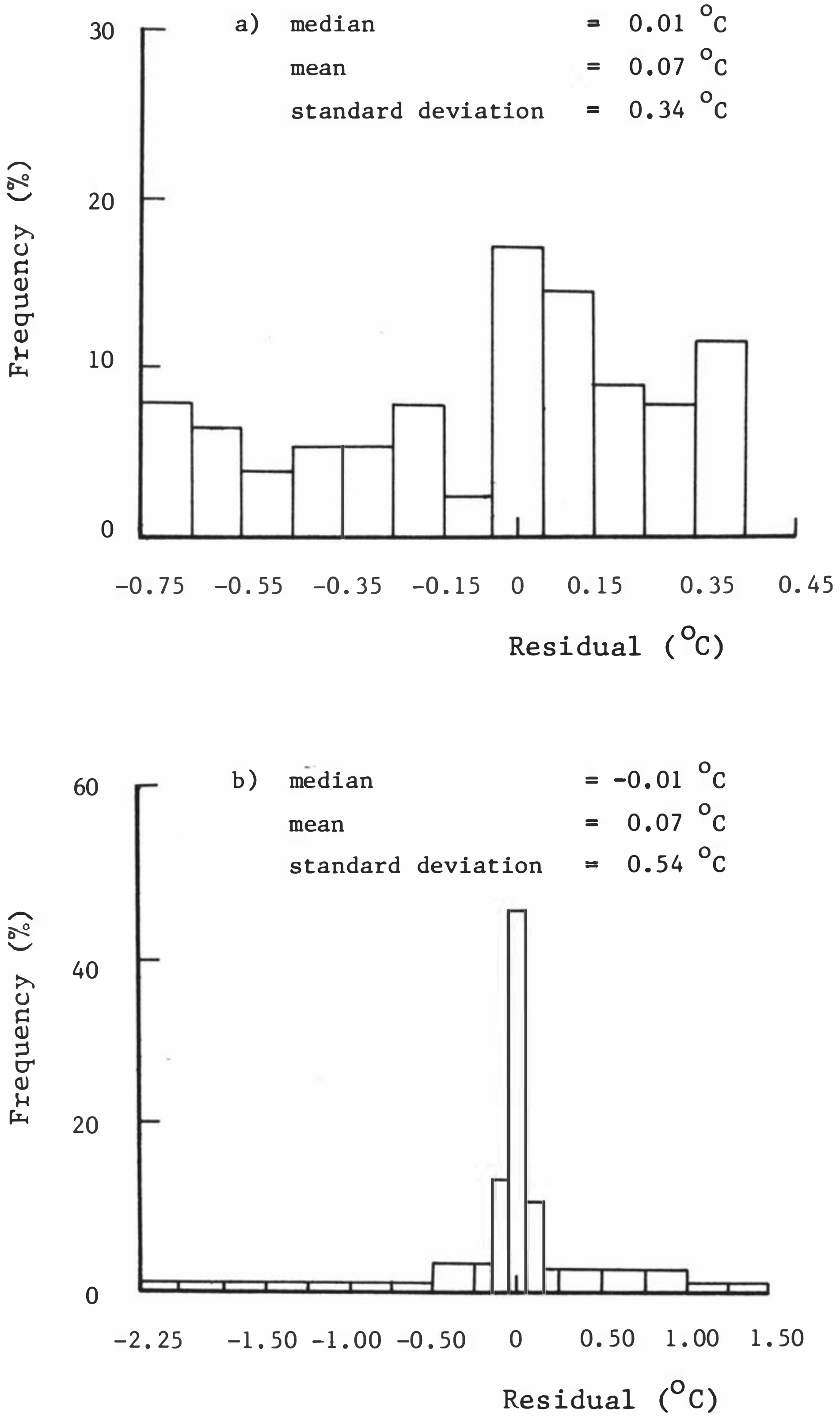


FIG. 4.3 Distribution of Residuals for Comparison of the Analytical Solution and the Numerical Finite Difference Method for Run no.6

a) at the centre point, (r/a, x/h) of (0.0, 0.0)

b) at the point (r/a, x/h) of (2/3, 2/3)

Theoretically, in the heating phase, the analytical solution could give more accurate prediction than the numerical finite difference method as it was based on the exact heat transfer for the uniform initial temperatures while the numerical finite difference was an approximate prediction. In the cooling phase, the temperature predicted by the numerical finite difference method should be more accurate as the actual predicted temperatures at the end of the heating phase were used. In the analytical solution, the initial temperature of the can contents in the cooling phase was assumed to be uniformly equal to the retort temperature and this may result in inaccurate prediction, especially for a short heating time process.

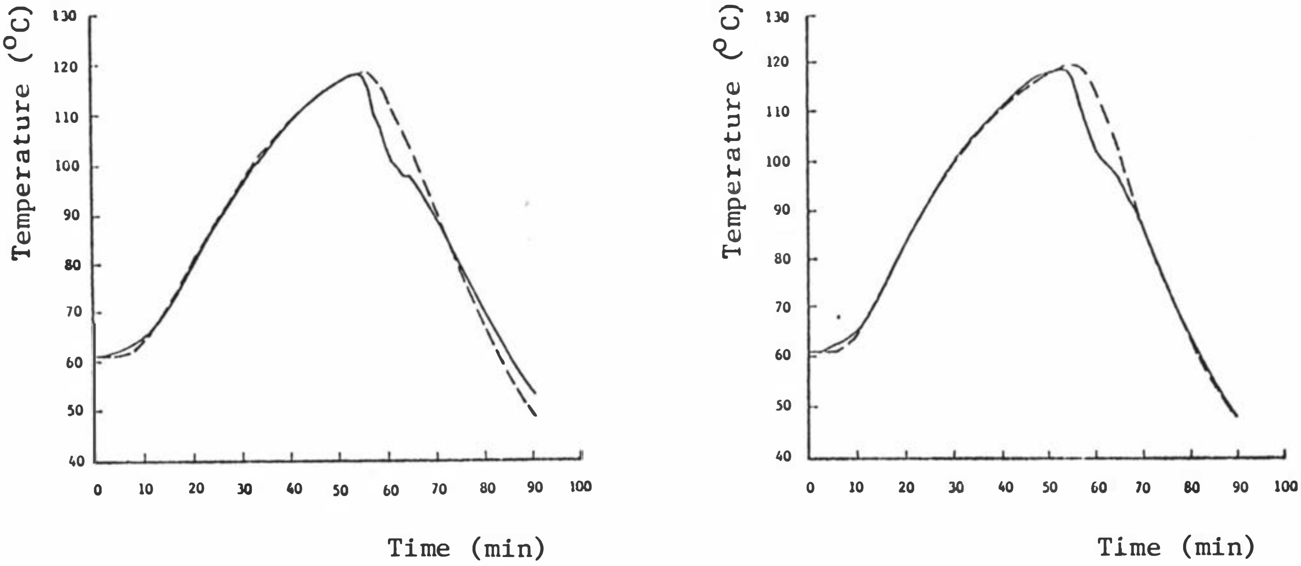
The time consumed by these two programs was found to be dependent on the number of points and the time increment required. Where only a few points are required in temperature prediction, the analytical solution method will take less time than the finite difference method program. Where a large number of points are required, the finite difference method will consume less time and should be used as it will be cheaper.

4.6 COMPARISON OF THE PREDICTED TEMPERATURES FROM THE ANALYTICAL SOLUTION PROGRAM AND THE EXPERIMENTAL TEMPERATURES

The comparison of experimental temperatures and the analytical solution predicted temperatures was done on 4 points in the can for the processing conditions of runs no.6 and no.7. The mean value of the thermal diffusivity of $1.5353 \times 10^{-2}\ m^2 s^{-1}$ was used for all the processing conditions.

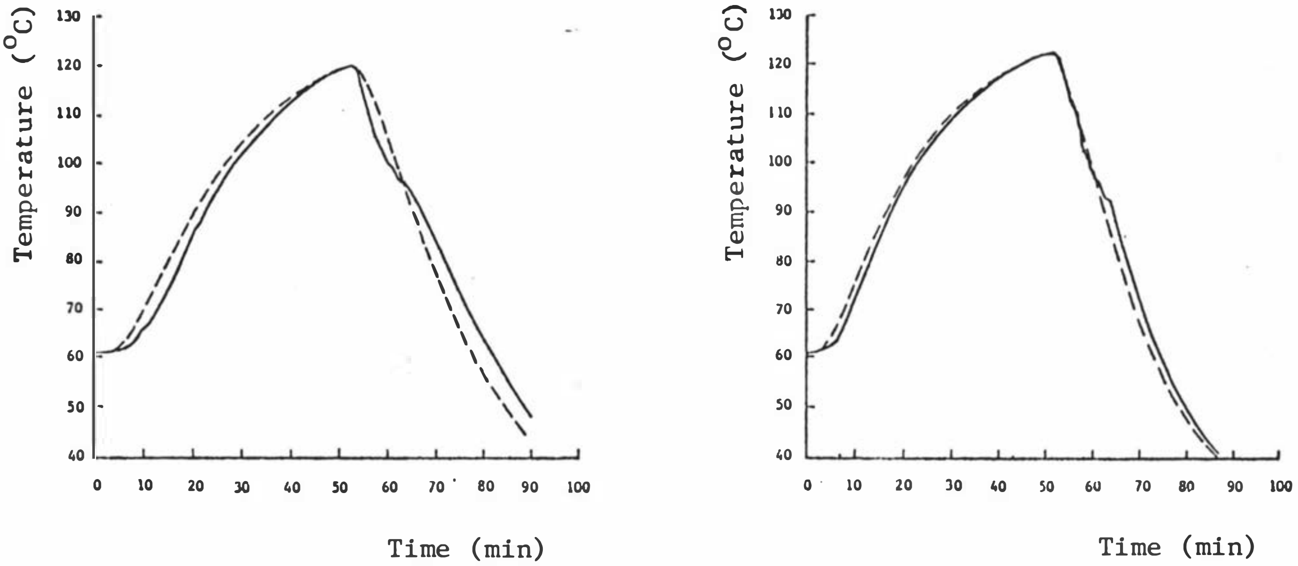
4.6.1 Comparison of Temperatures in the Heating Phase

As can be seen from Figures 4.4 and 4.5, the calculated temperatures were close to the measured temperatures in the heating phase. The temperature difference was in the range of 0.5-1.0^{o}C at the beginning where the temperature was lower than 100^{o}C, then, it decreased to 0.2-0.5^{o}C where the heating times were longer and temperatures were higher.



(a) at r/a = 0.0 , x/h = 0.0

(b) at r/a = 0.0 , x/h = 1/3



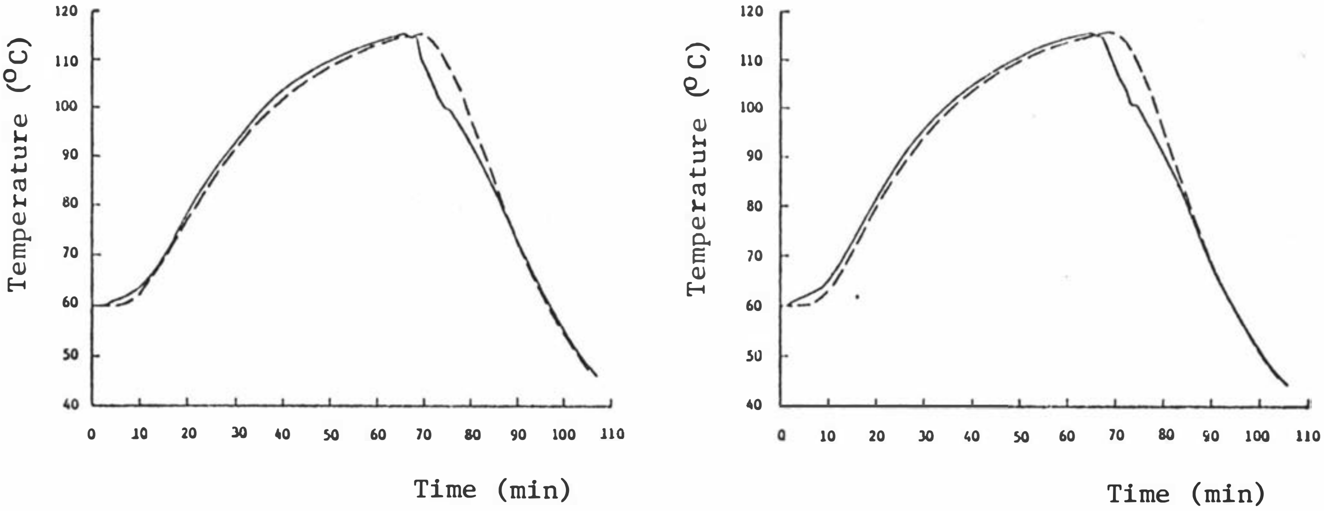
(c) at r/a = 1/3 , x/h = 1/3

(d) at r/a = 0.0 , x/h = 2/3

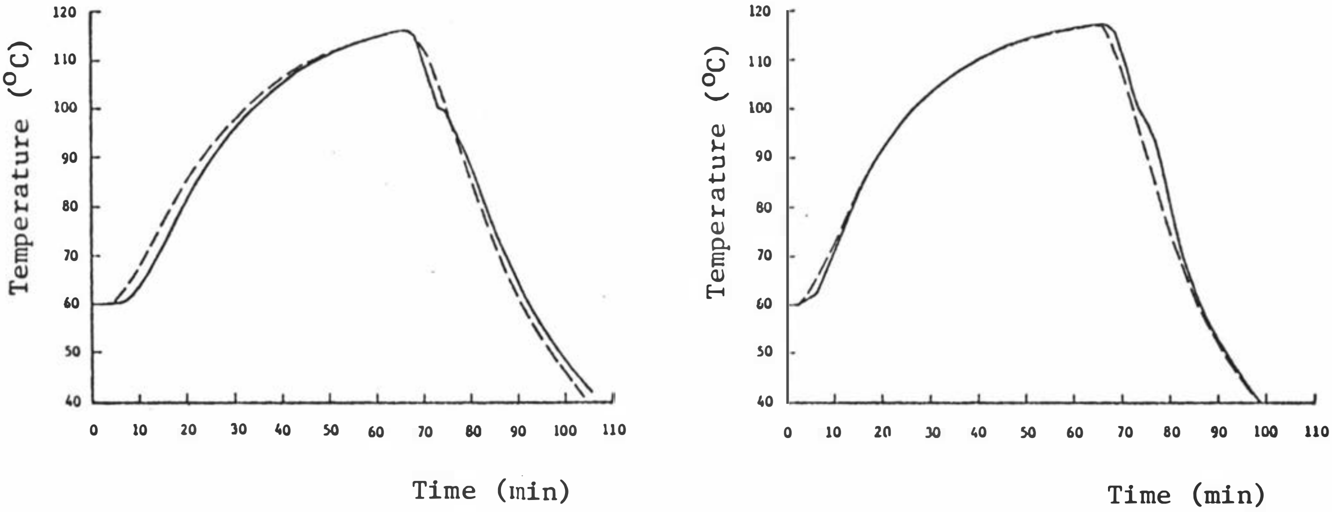
FIG.4.4 Comparison of Experimental Temperatures and Predicted Temperatures from the Analytical Solution Computer Program for Run no.6 (retort temperature was 129^oC)

(————) experimental temperatures

(—— ——) predicted temperatures



(a) at r/a = 0.0 , x/h = 0.0 (b) at r/a = 0.0 , x/h = 1/3



(c) at r/a = 1/3 , x/h = 1/3 (d) at r/a = 0.0 , x/h = 2/3

FIG. 4.5 Comparison of Experimental Temperatures and Predicted Temperatures from the Analytical Solution Computer Program for Run no.7 (retort temperature was 120°C)

(————) experimental temperatures

(—— ——) predicted temperatures

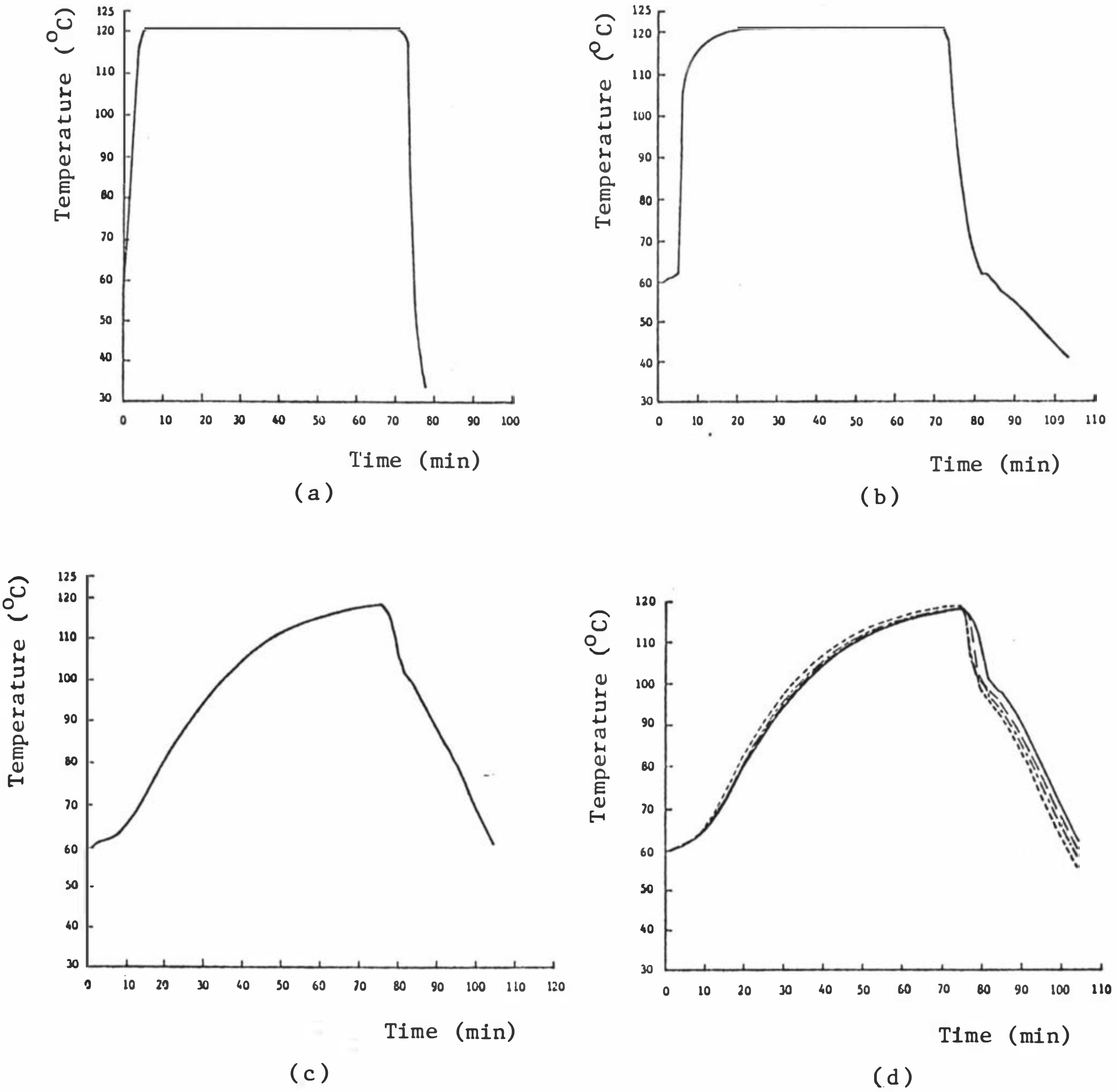
The larger difference at the beginning of heating could have resulted from the equations used. When time was small, the value of $\phi(r,x,t)$ in equation (4.6) was zero. Therefore, the predicted temperatures were equal to or nearly equal to the initial temperature. The deviation of the predicted temperatures from the experimental temperatures could also have been caused by the errors in the thermocouples. These errors were firstly the inaccuracy of placing the thermocouple junctions as only one millimetre could effect the temperature, and secondly the conduction through the thermocouple wires which could be high at the beginning of heating phase as the temperature difference between outside and the junction is high. This conduction also depended on the thermal diffusivity of the food. Therefore, the calculated temperatures could possibly be more accurate than the experimental temperatures.

The residual (i.e. the experimental temperature - the predicted temperature) was calculated for the centre point and shown in Appendix 4.4(a) for runs no.6, 7, 8 and 9. The distribution of the residuals was the normal distribution. The residual mean varied from run to run, from -1.1 to 0.4°C, with the residual standard deviation from ± 0.4 to ± 0.8°C. This standard deviation was less than the 1.7°C found by Lenz (1977) which was described as resulting from the biological variability of the physical constants.

4.6.2 Comparison of Temperatures in the Cooling Phase

An irregular phenomenon was found in the cooling phase (Figures 4.4 and 4.5). The temperature rapidly decreased to 100 ± 5°C and sometimes held there for 1-2 minutes, then, gradually decreased again. This irregular cooling curve was also found by other workers (Powers et al, 1952; Board et al, 1960) Powers et al (1952) explained in their study that the rapid cooling occurred because the home-type canning jars used could vent during processing and a high vacuum could ensue, which, in turn, led to vigorous boiling during cooling when the headspace steam condensed causing rapid cooling of the contents. In 1949 Townsend et al in their comparative heat penetration study in jars and cans, found that the contents of jars occasionally cooled faster than those of cans although the later heated faster. They attributed the rapid cooling to the contents being stirred by "boiling". Board et al (1960) also found this rapid cooling phenomenon in cans. The cooling curves obtained when the retort pressure was reduced to 608 kPa or less during cooling showed faster cooling than that calculated for the conduction mechanism and also some of them showed irregular fluctuations in rate of cooling. They concluded that the mechanism of cooling appeared to depend on whether cooling was predominately by conduction or if it was accelerated by movement of the contents of the can. Cooling by conduction was found in most of the cans where they were cooled under 1620 kPa superimposed pressure. It was also stated that in the more viscous products, such as baked beans, cream style corn and solid meat, boiling with consequent movement of materials in the can was probably the main cause of non-conductive cooling. The phenomenon of boiling of the can content when the pressure was released was also found by Hemler et al (1952). The residuals were calculated as in 4.5.1, the residual distribution is shown in Appendix 4.4 (b) for experimental runs no.6, 7, 8, and 9. The residual mean and the residual standard deviation were calculated by assuming that the residual distribution was a normal distribution. The residual mean varied from -0.9 to -3.3°C with the standard deviation varying from ± 2.2 to ± 4.5°C. The residual medians were -0.6 to -2.7°C. This indicated that the predicted temperatures were 0.9 to 3.3°C higher than the experimental temperatures. The residual standard deviation found was higher than those stated by Lenz (1977) and could not be treated as the result of the biological variability of the physical constants. These higher values were due to the irregular cooling curve found in the present experiments.

Experiments were performed with different materials in the can, namely, water, starch solution at the same concentration as in the baby food (4.2%), vegetable puree and the homogenised baby food. The other materials were filled into the cans without any headspace as before. The baby food was filled into the cans with different headspaces - 0, 0.6, 1.3 and 1.9 cm. The heat penetration curves and the cooling curves are shown in Figure 4.6. In the can of water, convective heat transfer occurred in both heating and cooling. Starch solution also showed a similar heating and cooling pattern except that it was slower in heating and had a break point in the cooling curve at the temperature of 60°C which could be explained by the change in



(a)

(b)

(c)

(d)

FIG. 4.6 Heat Penetration Curves for Different Can Contents and Different Headspaces

(a) for water in a can without any headspace,

(b) for starch solution in a can without any headspace,

(c) for vegetable puree in a can without any headspace,

(d) for baby food in a can with,

(———) no headspace

(— —) 0.6 cm headspace

(—.- —) 1.3 cm headspace

(-----) 1.9 cm headspace.

the state of the starch paste. For puree and baby food with no headspace, similar heating and cooling patterns were found as before (in section 4.5), with the irregular cooling curve phenomenon. With different headspaces, the irregular cooling curve still occurred.

From the results obtained, the irregular cooling curve might be caused by boiling and steam condensation in the can. When the pressure was released, boiling could have occurred and the temperature in the can would have decreased rapidly because of loss of latent heat due to evaporation of water. When the pressure in the can was reduced to the atmospheric pressure and the temperature was lower than 105°C, boiling stopped, steam in the can condensed giving the latent heat to the system and the temperature was held there for 1-2 min , and then the can contents were further cooling by the conduction heat transfer. This phenomenon created two parts in the cooling phase involving two different thermal diffusivities. Therefore, in the cooling phase, the assumption of constant thermal diffusivity was invalid.

It might be possible to follow this irregular cooling curve by using the numerical finite difference method. However, it would be very complicated as the thermal diffusivity cannot be assumed constant. Further experimental investigation was needed in estimating the extent of boiling and the change in thermal diffusivity where λ and C had to be determined separately. But there was no equipment available for measuring the λ and C, therefore, it was not possible to use this method to follow the irregular cooling curve in this study. However, the predicted temperatures from the analytical solution program and the numerical finite difference method program were identical (in section 4.5) so it was considered valid to modify the analytical solution program so that the cooling curve of the predicted temperatures fitted the cooling curve of the experimental temperatures.

4.6.3 Comparison of Temperatures in the Overall Process

The residual distribution, the residual mean and the residual standard deviation were also calculated for the overall process. The same method as described in section 4.5 was used. The residual distribution is shown in Appendix 4.4(c) for run no.6,8, 7 and 9. The residual means for the overall process varied from -0.4 to -1.2 °C with standard deviation varying from ± 2.5 to ± 3.4 °C. As the standard deviation found in the heating phase described in section 4.6.1 was fairly small, this high standard deviation was mainly due to the high deviation between the predicted temperatures and the experimental temperatures in the cooling phase described in section 4.6.2 as a result of the irregular cooling phenomenon.

Therefore the analytical solution program could be used for the heating phase but had to be modified for the cooling phase.

4.7 MODIFICATION OF THE ANALYTICAL SOLUTION PROGRAM

The two parts of the cooling phase were referred to as the "beginning of the cooling stage" and the "later cooling stage", where the beginning of the cooling stage was defined as a stage starting from the time when cooling water was turned on to the time when the temperature reached 105°C and then the later cooling stage started at 105°C and continued to the end of cooling phase. This is shown in Figure 4.7.

4.7.1 The Beginning of the Cooling Stage

As higher thermal diffusivity used in the cooling phase would result in lower predicted temperatures, the thermal diffusivities of 1.5353×10^{-7}, 2.0×10^{-7}, 2.2×10^{-7}, 2.5×10^{-7} m^2s^{-1} were used in the analytical solution. The predicted temperatures were compared with the experimental temperatures for five different experimental runs.

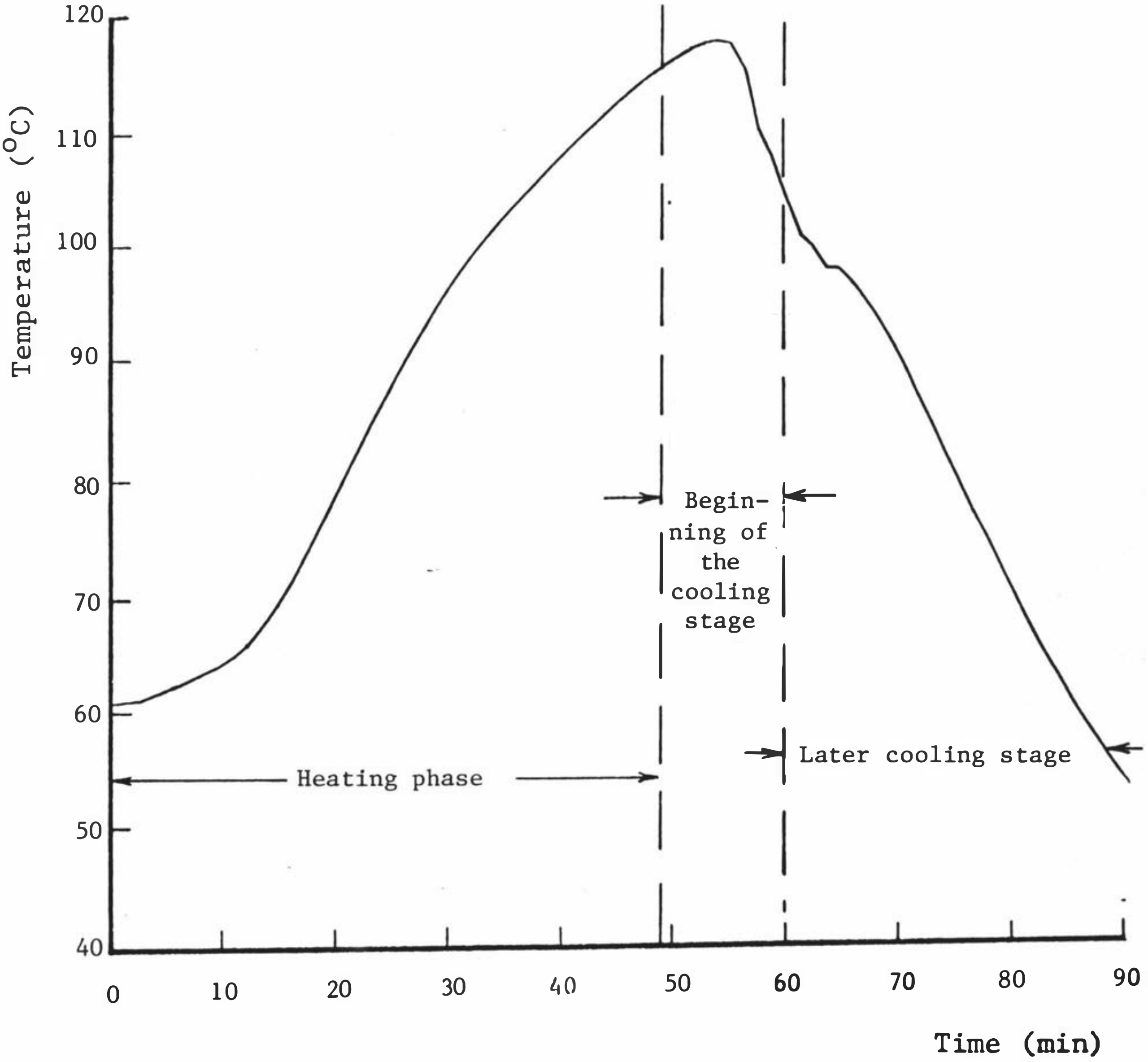


FIG. 4.7 Diagram Showing Different Parts in Heat Processing

The thermal diffusivity of $2.2 \times 10^{-7}\ m^2s^{-1}$ was found to give the best approximation at the centre and at (r/a, x/h) of (0, 1/3) and (1/3, 1/3). The variances of the predicted temperatures at the centre, using various thermal diffusivities of 1.5353×10^{-7}, 2.0×10^{-7}, 2.2×10^{-7}, and $2.5 \times 10^{-7}\ m^2s^{-1}$, from the experimental temperatures were determined using 1.2 minute intervals. The plot of variance versus thermal diffusivity is shown in Figure 4.8. The thermal diffusivity of $2.2 \times 10^{-7}\ m^2s^{-1}$ was found to give minimum variance. Thus, this thermal diffusivity would give the best approximation of temperature at the centre of the can.

Where r/a was more than 1/3 and x/h was more than 1/3, it was found that thermal diffusivity of $2.2 \times 10^{-7}\ m^2s^{-1}$ could not be applied. The lower value of $1.5353 \times 10^{-7}\ m^2s^{-1}$ gave a better approximation in this area.

The temperatures at (r/a, x/h) of (0, 0), (1/9, 0) and (2/9, 0) were measured experimentally to determine the extent of r where x was equal to 0 at which the thermal diffusivity of $2.2 \times 10^{-7} m^2s^{-1}$ could be used. The experimental temperatures were compared with the predicted temperatures calculated with thermal diffusivities of 2.2×10^{-7} and $1.5353 \times 10^{-7}\ m^2s^{-1}$. It was found that neither of these thermal diffusivities gave well fitted predicted temperatures at (1/9, 0.0), and (2/9, 0.0) points. The higher thermal diffusivity of $2.2 \times 10^{-7}\ m^2s^{-1}$ was found to result in the lower predicted temperatures while the lower thermal diffusivity of $1.5353 \times 10^{-7}\ m^2s^{-1}$ gave higher predicted temperatures than the experimental temperatures. Therefore, the thermal diffusivity of $2.2 \times 10^{-7}\ m^2s^{-1}$ should be used to prevent an overestimation of microbiological lethality factor.

In conclusion, the thermal diffusivity of $2.2 \times 10^{-7}\ m^2s^{-1}$ was used for temperature calculation of all points in the centre area where r/a and x/h were less than or equal to 1/3. Where r/a and x/h were more than 1/3, the thermal difffusivity of $1.5353 \times 10^{-7}\ m^2s^{-1}$ was used.

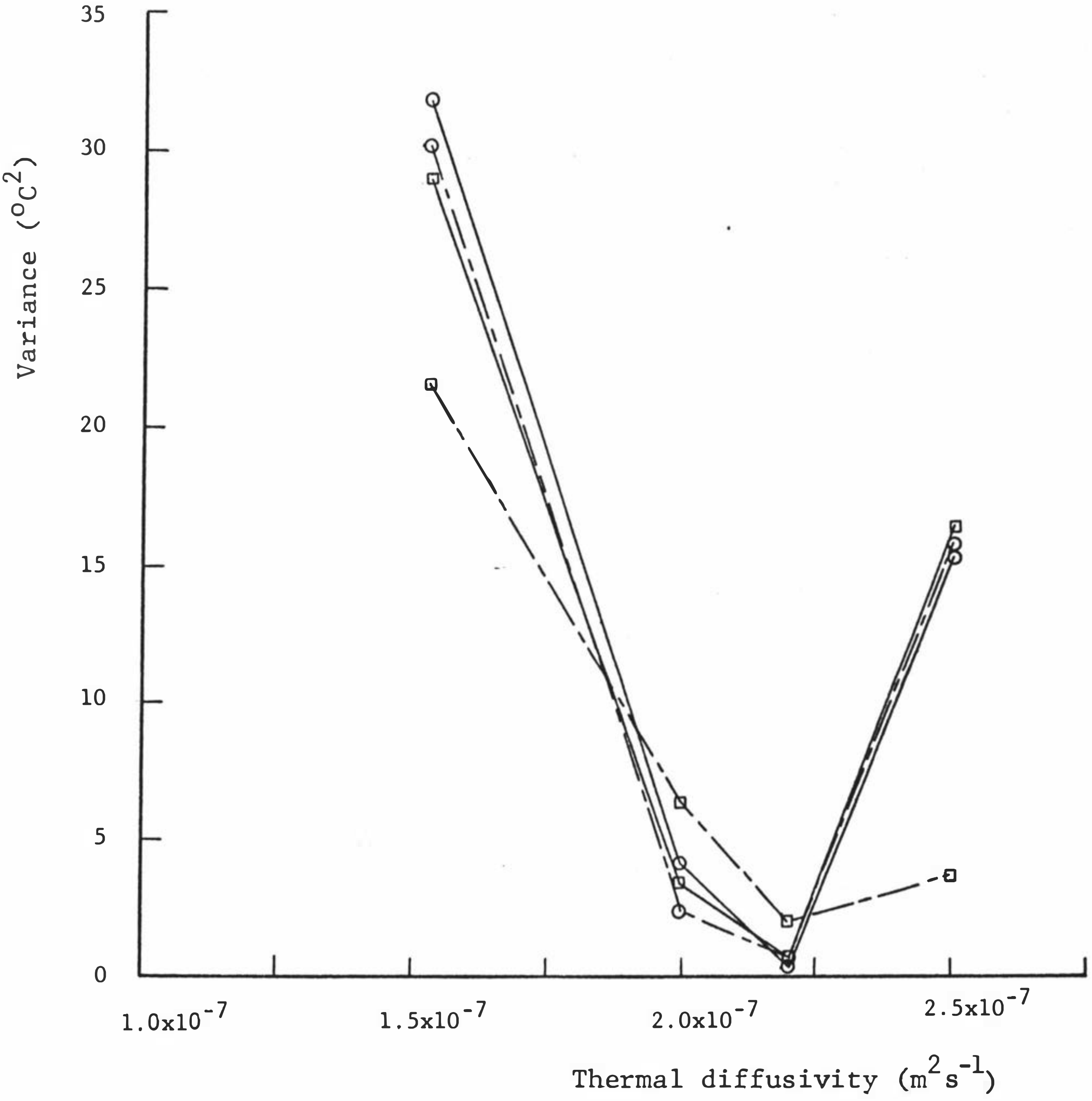


FIG. 4.8 Variance versus Thermal Diffusivity.

(○——○) run no.6

(□—‑—□) run no.7

(□——□) run no.8

(○‑ ‑ ‑○) run no.9

4.7.2 The Later Cooling Stage

When the temperature of the food reached 100 ± 5°C, the temperature was found to decrease much more slowly. Thus, the computer model had to be further modified by setting the temperature at which the smaller thermal diffusivity would be used. Again the thermal diffusivity in this stage and the significant temperature for the beginning of this stage were determined by trial and error. It was found that the temperature should be set at 105°C with a thermal diffusivity of 1.32 x 10^{-7} m^2s^{-1}.

Therefore, the computer program was constructed for the early cooling stage using the thermal diffusivity of 2.2 x 10^{-7} m^2s^{-1} for the centre area of $r \leq a/3$ and $x \leq h/3$, the thermal diffusivity of 1.5353 x 10^{-7} m^2s^{-1} for the outside area where $r/a > 1/3$ and $x/h > 1/3$ and in the later cooling stage the thermal diffusivity was set at 1.32 x 10^{-7} m^2s^{-1}, for every point in the can where the temperature was lower than 105°C.

In the centre area, where the thermal diffusivity used in the calculation was changed from 2.2 x 10^{-7} m^2s^{-1} in the beginning of the cooling to 1.32 x 10^{-7} m^2s^{-1} in the later stages, it was found that the calculated temperatures using 1.32 x 10^{-7} m^2s^{-1} for the first few minutes were higher than the earlier predicted temperatures causing fluctuation in the cooling curve and deviation from the experimental temperatures. Therefore, further modification of the computer model was required. However, in the outside region where the thermal diffusivity changed from 1.5353 x 10^{-7} m^2s^{-1} to 1.32 x 10^{-7} m^2s^{-1}, the results obtained were reasonable and modification was not necessary.

The computer model was further modified for the centre area by assuming that the temperature at every point in this area at the beginning of the later cooling stage were uniform and equal to the set temperature of 105°C. The heat transfer equations applied in this later cooling stage were simulated from the heating phase, TA and TI in equation (4.6) were substituted by TC and TLIMIT giving:

$$T = YCOOL(TLIMIT - TC) + TC \qquad (4.17)$$

where YCOOL is (YC)(YL)

TLIMIT is a set temperature which was 105°C in this study

TC is a cooling water temperature.

This equation was used to predict the temperatures in the later cooling stage for all points in the centre area where r/a was less than or equal to 1/3 and x/h was less than or equal to 1/3 with the thermal diffusivity of $1.32 \times 10^{-7}\ m^2s^{-1}$.

4.7.3 Conclusion

A modified computer program was constructed providing the opportunity to use any three thermal diffusivities in each part of processing and to vary the can size, the time and distance increment, the processing temperature and processing time, the set temperature.

The temperature distribution in the can in the heating phase was calculated by the following equations, using "α" of $1.5353 \times 10^{-7}\ m^2s^{-1}$.

For the heating phase,

where $\alpha t/a^2$ was less than 0.02 and r/a was not less than 0.1:

$$YC = 1-\left(\frac{a^{0.5}}{r^{0.5}}\,\mathrm{erfc}\,(z) + \frac{(a-r)(\alpha ta)^{0.5}}{4ar^{1.5}}\,\mathrm{ierfc}\,(z) + \frac{(9a^2 - 7r^2 - 2ar)\alpha t}{32a^{1.5}\ r^{2.5}}\,i^2\mathrm{erfc}\,(z)\right) \qquad \text{(a)}$$

where r/a was less than 0.1:

$$YC = 0.0 \qquad \text{(b)}$$

where $\alpha t/h^2$ was less than 0.3:

$$YL = 1-\left(\sum_{n=0}^{\infty}(-1)^n \mathrm{erfc}\left(\frac{(2n+1)h-x}{2(\alpha t)^{0.5}}\right)+\sum_{n=0}^{\infty}(-1)^n \mathrm{erfc}\left(\frac{(2n+1)h+x}{2(\alpha t)^{0.5}}\right)\right) \quad \text{(c)}$$

where $\alpha t/a^2$ was more than 0.02:

$$YC = 2\sum_{n=1}^{\infty}\frac{J_o(\beta_n r/a)}{\beta_n J_1(\beta_n)}\, e^{(-\beta_n \alpha t/a^2)} \quad \text{(d)}$$

where $\alpha t/h^2$ was more than 0.3:

$$YL = \frac{4}{\pi}\sum_{m=0}^{\infty}\frac{(-1)^m}{(2m+1)}\cos\left(\frac{(2m+1)\pi x}{2h}\right) e^{-(2m+1)^2\pi^2\alpha t/4h^2} \quad \text{(e)}$$

then:

$$T = (TA-TI)(1-(YC)(YL)) + TI \quad \text{(f)}$$

For the beginning of the cooling stage,

where r/a and x/h were less than or equal to 1/3:

$$T = (TA-TI)\phi(r,x,t) + (TC-TA)\phi(r,x,t-t_1) + TI \quad \text{(g)}$$

where $\phi(r,x,t)$	was $1-(YC)(YL)$
YC, YL	were calculated from equations (d) and (e) using "α" of $1.5353 \times 10^{-7}\ m^2 s^{-1}$
$\phi(r,x,t-t_1)$	was $1-(YC)_{t-t_1}\ (YL)_{t-t_1}$
$(YC)_{t-t_1}$	was calculated from equation (a), (b) or (d) using α_2 instead of α depending on the value of $\alpha_2(t-t_1)/a^2$
$(YL)_{t-t_1}$	was calculated from equation (c) or (e) using α_2 instead of α depending on the value of $\alpha_2(t-t_1)/h^2$
α_2	was $2.2 \times 10^{-7}\ m^2 s^{-1}$.

where r/a and x/h were more than 1/3, the temperatures were calculated by equation (g) using α_2 of $1.5353 \times 10^{-7}\ m^2s^{-1}$.

For the later cooling stage,

where r/a and x/h were more than 1/3 the temperatures were calculated by equation (g) using α_2 of $1.32 \times 10^{-7}\ m^2s^{-1}$,

where r/a and x/h were less than or equal to 1/3:

$$T = YCOOL(TLIMIT-TC) + TC \qquad (h)$$

where YCOOL was $(YC)_{t-t_1}\ (YL)_{t-t_1}$

$(YC)_{t-t_1}$ was calculated from equation (a), (b) or (d) using α_3 instead of α depending on the value of $\alpha_3(t-t_1)/a^2$

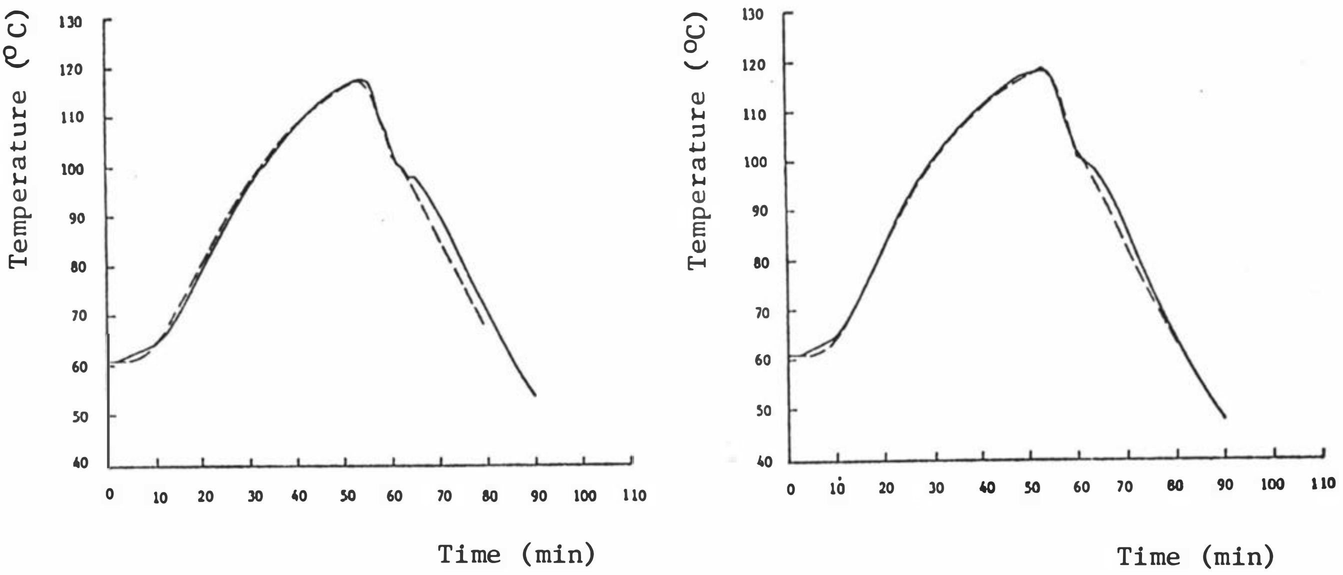
$(YL)_{t-t_1}$ was calculated from equation (c), or (e) using α_3 instead of α depending on the value of $\alpha_3(t-t_1)/h^2$

α_3 was $1.32 \times 10^{-7}\ m^2s^{-1}$.

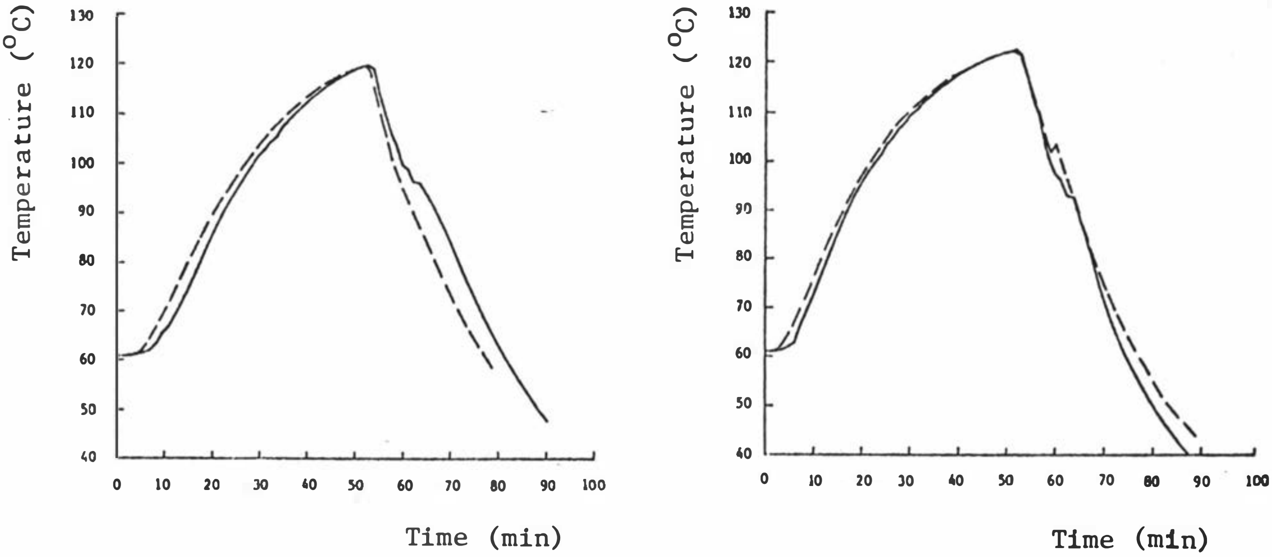
The flow chart of this modified program and the computer program are shown in Appendix 4.5. The predicted temperatures were then compared with the actual temperatures. The details of the comparison are discussed in the following section.

4.8 COMPARISON OF THE EXPERIMENTAL TEMPERATURES AND THE PREDICTED TEMPERATURES FROM THE MODIFIED ANALYTICAL SOLUTION PROGRAM

As can be seen in Figures 4.9 and 4.10 for runs no.6 and 7, the predicted temperatures from the modified computer program were much closer to the experimental temperatures, especially in the beginning of the cooling. However, a larger difference in the later part of cooling was found in some experiments, but the effect of these differences was much lower than the differences in the higher temperatures in terms of microbiological lethality and therefore could be neglected in this study. The comparison of experimental and predicted temperatures are also shown in Appendix 4.6 for runs no.8 and 9.



(a) at r/a = 0.0 , x/h = 0.0 (b) at r/a = 0.0 , x/h = 1/3

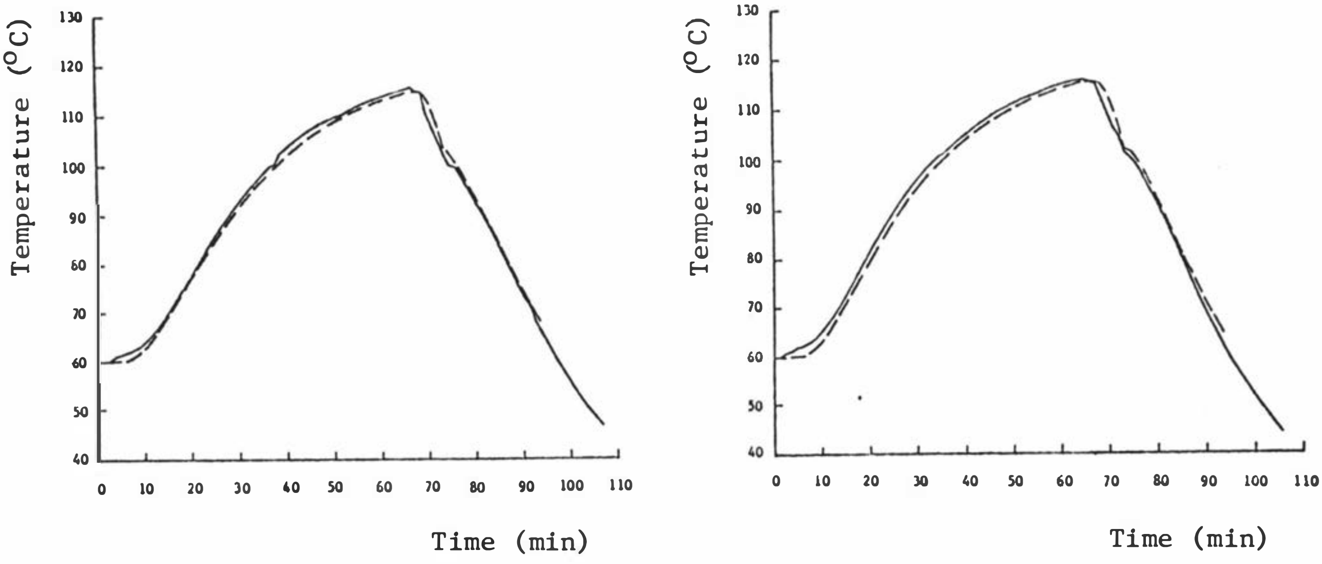


(c) at r/a = 1/3 , x/h = 1/3 (d) at r/a = 0.0 , x/h = 2/3

FIG. 4.9 Comparison of Experimental Temperatures and Predicted Temperatures from the Modified Analytical Computer Program for Run no.6 (retort temperature was 129^{o}C)

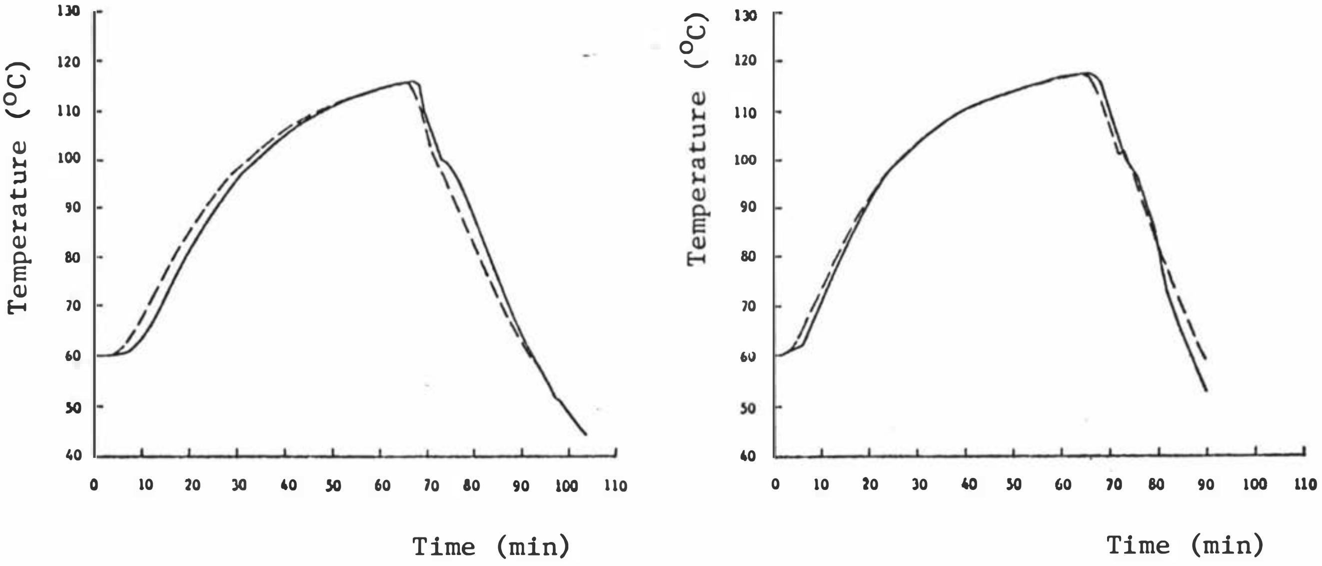
(————) experimental temperatures

(—— ——) predicted temperatures



(a) at r/a = 0.0 , x/h = 0.0

(b) at r/a = 0.0 , x/h = 1/3



(c) at r/a = 1/3 , x/h = 1/3

(d) at r/a = 0.0 , x/h = 2/3

FIG. 4.10 Comparison of Experimental Temperatures and Predicted Temperatures from the Modified Analytical Solution Computer Program for Run no.7 (retort temperature was 120^{o}C)

(————) experimental temperatures

(—— ——) predicted temperatures

The lethality, $F_{121.1}^{10}$ at the points of (r/a, x/h) of (0.0, 0.0) and (0.0, 1/3) for experimental runs no.6 and 7 was calculated using temperatures data from the experiments and computer program. The method of calculation is described and shown in Appendix 4.7. An example of the calculation and the result is shown in Appendix 4.8 for the centre point based on the predicted temperatures for run no.6. The $F_{121.1}^{10}$ calculated from the experimental temperature data were higher than the $F_{121.1}^{10}$ calculated by predicted temperature data. The difference between experimental and calculated $F_{121.1}^{10}$ for micro-organisms for run no.6 and run no.7, were 5.44% and 9.28% respectively at (0.0, 0.0) and 1.76% and 11.21% respectively at (0.0, 1/3) respectively. The difference in $F_{121.1}^{10}$ for ascorbic acid, using the k and Ea determined by Chittaporn (1977), was lower, 4.25 and 3.58% at (0,0) and 3.14 and 4.43% at (0.0, 1/3) for runs no.6 and 7 respectively. In terms of concentration, the final concentration calculated based on the experimental temperature data was lower than the final concentration calculated based on the predicted temperature data. The percentage difference between these calculated final concentrations ($(x_1 - x_2)/x_2$ where x_1 is a calculated final concentration based on predicted temperature data and x_2 is a calculated final concentration based on experimental temperature data) was 0.6, 0.5% for run no.6 and 0.6, 0.8% for run no.7 at (0.0, 0.0) and (0.0, 1/3) respectively. These differences were less than the chemical analytical errors.

The differences between the predicted temperatures obtained from the modified computer program and the experimental temperatures were less for the point on the axis where r/a was equal to zero than other points where r/a was increased. At r/a equal to 1/3, the differences were higher, this could be explained by the error in placement of the thermocouples. Where r/a was equal to 1/3, the equivalent distance from the centre of the can was 1.233 cm but the placement distance used in the study was 1.2 cm. A difference of 0.033 cm in the experiment could have resulted in the slower heating and cooling rates which were found in the results shown in Figures 4. 9 (c) and 4.10 (c).

At the change from the first to the second stage of cooling, the predicted temperatures at the outside points rose slightly (Figures 4.9 (d) and 4.10 (d)). This could be explained as a result of changing the thermal diffusivity from $1.5353 \times 10^{-7}\ m^2s^{-1}$ to $1.32 \times 10^{-7}\ m^2s^{-1}$. However, it was considered to be the best approximation of the temperature distribution that could be made.

The residual distribution for both the overall process and the cooling phase were determined for each experiment using 1.2 minute intervals. The same method as described in section 4.5 was used. The distribution is shown in Appendix 4.9a,b for the overall process and for the cooling phase for runs no.6, 8, 7 and 9. The distribution was a normal distribution. The residual means varied for the overall process from 0.1 to 0.7°C with the standard deviations varying from 1.0 to 1.9°C and for the cooling phase from 0.9 to 1.7°C with the standard deviations varying from 1.2 to 2.3°C. These residual standard deviations were lower than those found from the unmodified computer program in section 4.6.2.

For the overall process, the residual standard deviation found was in the range accepted as the biological variability by Lenz (1977). Therefore, the overall predicted temperatures by this modified computer model were considered to give the best approximation for temperature distribution during processing.

4.9 CONCLUSION

The computer model was finally constructed for the temperature distribution calculation in the can of food based on the analytical solution. Some modification was found to be necessary. The thermal diffusivity could not be assumed to be constant for the whole processing system because an irregular cooling curve occurred during cooling. The average thermal diffusivity of $1.5353 \times 10^{-7}\ m^2s^{-1}$ was used for the heating phase, and also for the beginning of cooling where r/a and x/h were higher than 1/3. The thermal diffusivity of $2.2 \times 10^{-7}\ m^2s^{-1}$ was used for the area in the can where r/a and x/h were less than or equal to 1/3 at the beginning of cooling. When the temperature was less than 105°C, the second phase of cooling started and the thermal diffusivity of 1.32×10^{-7} $m^{2}s^{-1}$ was used. The equation was also modified for the area of r/a and x/h less than or equal to 1/3. The program was written providing the opportunity to use any processing conditions, can size, time and dimensional increments, thermal diffusivities, set temperature. Comparison between the predicted temperatures and the experimental ones was found to be satisfactory. Therefore, this model was used for further calculation of quality retention in the determination of kinetic parameters.

However, it is worthwhile to state here that this constructed model can be used only for a similar processing operation where the irregular cooling phenomenon does occur and if the thermal diffusivities in different parts of the processing are determined. For the process operation where the can is cooled under pressure and there is no irregular cooling phenomenon, it is believed that the un-modified programs constructed in section 4.3 (using the analytical solution and the numerical finite difference method) could be used ~~giving~~ to give satisfactory results.

5. DETERMINATION OF KINETIC PARAMETERS BY UNSTEADY-STATE PROCEDURE

5.1 INTRODUCTION

The rate of changes in food during processing can be expressed either by a first-order rate constant (k) or a decimal reduction time (D) but "k" is more frequently used for describing the changes in nutrients and quality factors and therefore " k " was used in this study. There were many factors affecting " k " (sections 2.2.2 and 2.2.3) but only the temperature factor was studied. The Arrhenius equation was found to adequately describe the temperature dependence of the rate and this was expressed in terms of " Ea ". For purposes of comparison it is convenient to convert rate constants to those at a standard temperature, in this study chosen as k_{129^oC} as 129°C was the maximum temperature involved. The value of " k " at any temperature in the temperature range of this study (60 - 129°C) could then be determined if " Ea " was known.

To determine these parameters, Ea and k_{129^oC}, the initial concentration of reactant e.g. nutrients and quality factors, and the concentration of reactant after processing were measured in the total can contents, using the unsteady-state procedure. The calculation of the kinetics was therefore based on mass average prediction for the whole can. The temperature distribution in the can during heating was determined using the modified analytical solution program and from this the overall quality retention was determined. Where the kinetic parameters were unknown, a method for their determination was developed based on trial and error comparison of the experimental and the predicted concentrations. The computer program was constructed and the kinetic parameters for ascorbic acid, riboflavin, colour and viscosity were determined.

5.2 EXPERIMENTAL ANALYSIS OF QUALITY RETENTION

The control and heated canned baby food was sampled from each experimental run described in section 4.2. All the samples were analysed at least in duplicate by the methods in Chapter 3. The results obtained from the analysis of the control samples represent the initial concentration or quality. The final concentration or quality of each experimental run was obtained from the analysis of the heated samples. The mean initial and final concentration/quality from each experimental run, are shown in Table 5.1. Details of the analytical results are in Appendix 5.1.

For colour, it was found that only Y represented the change during heating as can be seen in Appendix 5.1 (c). The loss in ascorbic acid ranged from 6.0 to 16.0%. For riboflavin, the loss was less than ascorbic acid ranging from 2 to 7%. The change in colour (Y) and viscosity ranged from 13 to 23%, 10 to 26%, respectively.

5.3 QUALITY RETENTION CALCULATION

The following discussion involves the theory of the quality retention calculation, the computer program constructed and the effect of the size of the time increment and the dimension increment.

5.3.1 Theory of Quality Retention Calculation

Assuming that the changes in food qualities such as vitamins and sensory qualities can be described by first order kinetics, the concentration change will be

$$\frac{dc}{dt} = -kc \qquad (5.1)$$

where c is the concentration

k is the reaction rate coefficient

t is the time.

After time, t, the final concentration can be determined by integration of equation (5.1).

$$\frac{c_n}{c_o} = \exp\left(-\int_o^t k\,dt\right) \qquad (5.2)$$

For unsteady-state heat transfer, the temperatures of the can contents change with time and position. Therefore, the effect of temperature on k must be taken into account. This relationship can be

TABLE 5.1 The Mean Initial and Final Quality on Heat Processing

RETORT TEMPERATURE ^{o}C	129					120			
$F^{10}_{121.1}$ min	5.0	9.0	13.0	17.0	21.0	5.0	13.0	17.0	21.0
Details Run No.	6	1	8	5	10	7	4	9	2
Ascorbic acid x10 ^{2}, mg g^{-1}									
initial	25.68	23.89	25.29	24.82	23.29	24.50	26.14	25.95	24.16
final	24.10	21.84	23.04	22.56	20.95	22.46	23.83	23.60	21.71
Riboflavin, μg g^{-1}									
initial	25.28	25.70	25.40	26.21	26.15	25.41	25.59	26.06	25.94
final	24.74	24.63	24.06	24.65	24.46	24.65	24.35	24.64	24.24
Colour, Y									
initial	30.5	30.3	30.4	30.2	30.9	30.3	31.0	30.1	30.6
final	26.1	25.4	24.9	23.5	23.8	26.9	26.4	25.1	24.1
Colour, X									
initial	30.2	30.4	29.8	29.9	30.3	29.8	31.0	30.3	30.2
final	26.3	26.1	25.0	23.9	24.2	27.2	27.4	25.6	24.5
Colour, Z									
initial	8.0	8.2	8.0	7.9	8.9	8.0	8.6	8.4	8.4
final	6.7	6.6	6.4	6.1	6.5	6.9	7.1	6.7	6.3
Viscosity Reading									
initial	70.1	72.4	67.4	64.3	75.6	66.7	62.7	60.0	65.2
final	60.0	57.3	52.4	48.8	55.6	60.1	54.9	49.6	50.1

described by equation (5.3) (Lund, 1975).

$$k = k_{Tr} e^{-\frac{Ea}{R}(\frac{1}{T} - \frac{1}{Tr})} \tag{5.3}$$

Then equation (5.2) can be substituted

$$\frac{c_n}{c_o} = \exp\left(-\int_o^t k_{Tr} e^{-\frac{Ea}{R}(\frac{1}{T} - \frac{1}{Tr})} dt\right) \tag{5.4}$$

As the temperatures in the can vary from position to position and also from time to time, to calculate the overall quality retention after time "t", integration of equation (5.4) over the total volume of the can is necessary.

Therefore, the final total concentration can be determined from

$$\frac{c_f}{c_o} = {}_o\int^v \exp\left(-{}_o\int^t k_{Tr} e^{-\frac{Ea}{R}(\frac{1}{T} - \frac{1}{Tr})} dt\right) dv \tag{5.5}$$

where c_f is the final total concentration

c_n is the concentration after time $n\Delta t$ where $n=1,2,3...$

c_o is the initial concentration

k_{Tr} is the reaction rate constant at reference temperature, Tr

Ea is the activation energy

T is the average temperature over Δt and Δv

v is a volume

Δt is a time increment

Δv is a volume increment

R is the gas constant.

As can be seen, the equation (5.5) is complex and takes a long time for calculation, especially where dt and dv are very small, so a computer program was constructed to calculate the quality retention from equation (5.6), where Tr was 129°C and k_{Tr} was k_{129^oC}:

$$\frac{c_f}{c_o} = {}_o\!\int^v \exp\left({}_o^{-}\!\!\int^t k_{129^oC}\, e^{-\frac{Ea}{R}\left(\frac{1}{T} - \frac{1}{402}\right)} dt\right) dv \qquad (5.6)$$

where Ea is the activation energy (kJ $mole^{-1}$)
R is the gas constant and equal to 0.0083 (kJ $mole^{-1}\ {}^oK^{-1}$)
T is absolute temperature (^oK)

5.3.2 Computer Program for Quality Retention Calculation

From equation (5.5), the numerical integration technique over Δv and Δt could be used in the calculation by the computer program. Other mathematical methods could also be used, namely, Simpson's rule which was used by Hicks (1951) in his calculation for the cooling phase and a weighted-residual technique which was used by Hayakawa (1969). However, these methods are more complicated than the graphical integration method. Therefore, the numerical integration technique was used.

From equation (5.6), assuming that dt and dv are small, so T can be regarded as constant. The final concentration of the vitamin or the quality after time, Δt, of the small volume, Δv, can be calculated from

$$c_f = c_o \exp\left(-k_{129^oC}\, e^{-\frac{Ea}{R}\left(\frac{1}{T} - \frac{1}{402}\right)} \Delta t\right)\Delta v \qquad (5.7)$$

where T is the average temperature over the increment volume, Δv, over the time increment, Δt.

The computer program was constructed based on equation (5.6), c_f which is the final concentration in a small volume of Δv at the end of time, Δt, was calculated to then become the initial concentration in this small volume for the next Δt. The calculation was repeated until the end of the total time.

The size of the small volume will depend on the distance increment size used and can be calculated by:

$$\Delta v = \pi(r_2^2 - r_1^2)\Delta x \qquad (5.8)$$

where r_1 and r_2 are the radii and $r_2 = r_1 + \Delta r$.

Therefore, the computer program constructed in chapter 4 was extended for the quality retention calculation using equation (5.6). The flow chart of the extended program used is shown in Figure 5.1. The detail of the computer program is shown in Appendix 5.2.

5.3.3 Size of Time Increment and Dimension Increment

The computer program was run through the Burroughs B6700 computer and the result obtained was expressed in terms of final concentration or final quality value. Different sizes of time increments and dimension increments were tried and the final concentrations and the processing time consumed by the computer were compared. Using the same processing conditions, the results obtained are shown in Table 5.2. The dimension increment was expressed in term of (number of increments on the radius x number of increments in the half-height).

TABLE 5.2 Effect of Size of Increment on Quality Retention Calculation

DIMENSION INCREMENT	TIME INCREMENT s	FINAL ASCORBIC ACID CONCENTRATION x 10^2 mg g^{-1}	COMPUTER PROCESSING TIME s
5 x 5	72	18.07	84.86
10 x 10	72	17.95	254.00
15 x 15	72	17.93	562.00
10 x 10	36	17.93	526.39

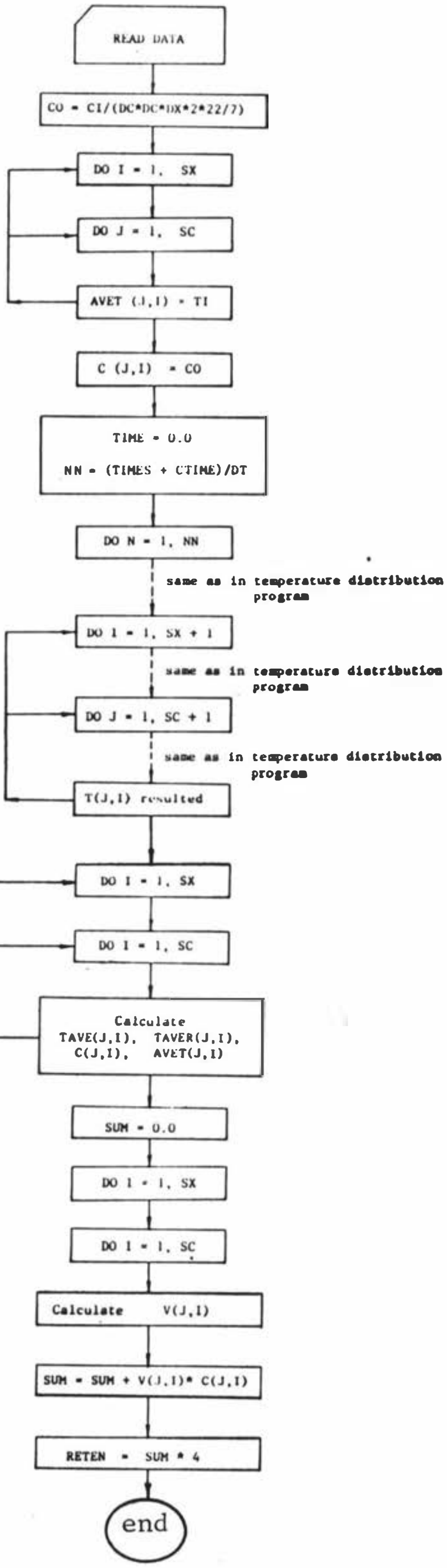


FIG. 5.1 Flow Chart for Quality Retention Calculation Program

As can be seen, the smaller the increment size, the longer the processing time required by the computer which means that the cost of calculation is higher. Considering the results obtained, the dimension increment of 5 x 5 with 72 s time increment which required the least time resulted in a final concentration which was higher than the others. When either the dimension increment of 15 x 15 with 72 s time increment or the dimension increment of 10 x 10 with 36 s time increment was used, the time consumed in calculation was double the time consumed when the dimension increment of 10 x 10 with 72 s time increment was used. But the results obtained were almost the same, the difference in calculated concentration was only 0.01 - 0.02 mg/100 g which was about 0.1%. Therefore, the increment size of 10 x 10 with 72 s time increment were used for the rest of the study.

5.4 DETERMINATION OF KINETIC PARAMETERS

As the only results that could be determined from the experiments were the initial concentration and the final concentration of the quality in the baby food heated at a specified temperature for a specific time (section 5.2), the computer program for the quality retention calculation was used to determine the final concentration (section 5.3). Unfortunately, the quality retention cannot be predicted by this computer program unless the kinetic parameters, k_{129^oC} and Ea, for that quality are known. Therefore, these parameters, k_{129^oC} and Ea, had to be assumed, the final concentration calculated and then the calculated final concentration compared with the experimental result. This trial and error method was used to determine the k_{129^oC} and Ea which would give the closest approximation of the experimentally determined final quality. However, this method consumed a lot of computer time. Therefore, in this study, k_{129^oC} and Ea were systematically tested in the calculation. The residual which is the difference between the actual c/c_o and the calculated c/c_o was calculated for various levels of assumed k_{129^oC} and Ea for each experimental run. The calculated c/c_o for each processing run was dependent on only k_{129^oC} and Ea, so the residual was also dependent on only k_{129^oC} and Ea. Therefore, to determine the actual k_{129^oC} and Ea of each quality, the relationship between the residual and k_{129^oC} and Ea was evaluated using multiple regression analysis to obtain a second order response surface model and then the residual was minimized by the differentiation of the empirical relationship. The details of the study are discussed in the following sections.

5.4.1 The Design

To fit a second order response surface, at least three levels of each variable are required. Orthogonal composite design was used as it involves three levels of each variable. In this study, k_{129^oC} and Ea were the two variables involved. The design is shown in Figure 5.2, where X1 is a coded variable of k_{129^oC} and X2 is a coded variable of Ea.

5.4.2 The Analysis

Using the k_{129^oC} and Ea at various points in the design, the final concentration of the quality of each experimental run was calculated from the quality retention program. The absolute residual was then calculated for all points in the experimental design, the absolute residual (Q) was defined as:

$$\text{absolute residual} = \left| \left(\frac{c}{c_o}\right)_{exp} - \left(\frac{c}{c_o}\right)_{cal} \right|$$

where $\left(\frac{c}{c_o}\right)_{exp}$ is $\frac{c}{c_o}$ obtained from measured c and c_o

$\left(\frac{c}{c_o}\right)_{cal}$ is $\frac{c}{c_o}$ obtained from calculated c and measured c_o

c is the final concentration

c_o is the initial concentration.

The residuals were averaged for each temperature (120^o and 129^oC) for each value of k_{129^oC} and Ea. From these calculated residuals, the quadratic equation was fitted by multiple linear regression. Then, the k_{129^oC} and Ea were determined by minimizing the residual.

The regression equation was fitted using both the average residuals and the individual residuals. The resulting equations were slightly different but the minimization of the residual (Q) gave almost the same k_{129^oC} and Ea. This was true for all four qualities - ascorbic acid,

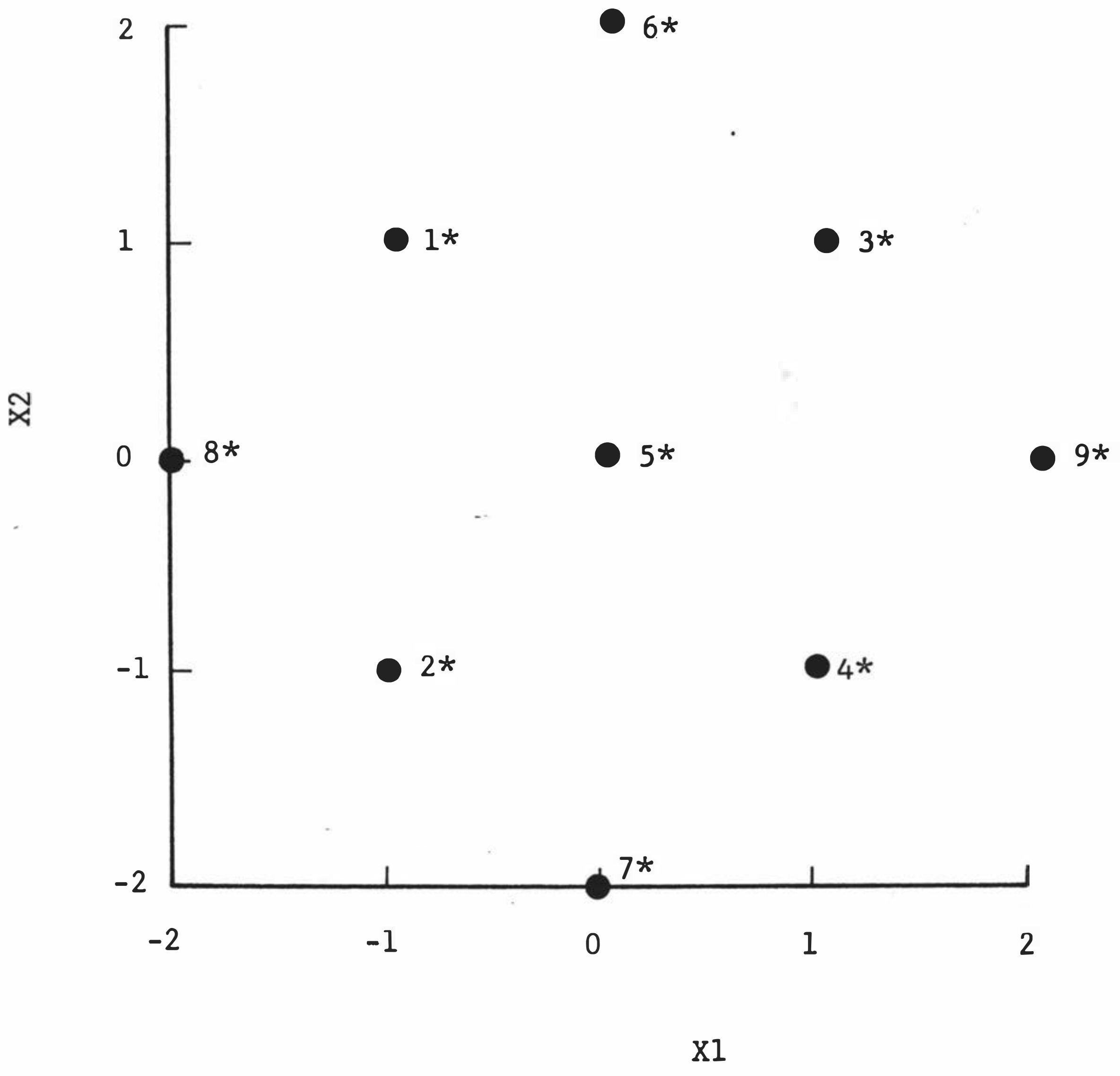


FIG. 5.2 An Orthogonal Central Composite Design to Fit a Second Order Response Surface

riboflavin, colour (Y) and viscosity as shown below.

For ascorbic acid:

the regression equation (R^2 = 83.1%) resulting from using average absolute residual at each process temperature was:

$$Q = |0.01225 - 0.00400X1 + 0.00151X2 + 0.00435X1^2 - 0.00484X1X2| \quad (5.9)$$

the regression equation (R^2 = 56.1%) resulting from using individual absolute residuals:

$$Q = |0.01183 - 0.00392X1 + 0.00145X2 + 0.00444X1^2 - 0.00475X1X2| \quad (5.10)$$

minimization of Q gave the k_{129^oC} and Ea from equation (5.9) of $0.4352 \times 10^{-4}\ s^{-1}$ and 80.7 kJ $mole^{-1}$ and from equation (5.10) of $0.4348 \times 10^{-4}\ s^{-1}$ and 80.9 kJ $mole^{-1}$.

For riboflavin:

the regression equation (R^2 = 92.3%) resulting from using average absolute residuals was:

$$Q = |0.00770 + 0.00148X1 - 0.00112X2 + 0.00524X1^2 - 0.00375X1X2| \quad (5.11)$$

the regression equation (R^2 = 61.3%) resulting from using individual absolute residuals was:

$$Q = |0.00795 + 0.00150X1 - 0.00106X2 + 0.00520X1^2 - 0.00358X1X2| \quad (5.12)$$

minimization of Q gave the k_{129^oC} and Ea from equation (5.11) of $0.2361 \times 10^{-4}\ s^{-1}$ and 79.0 kJ $mole^{-1}$ and from equation (5.12) of $0.2363 \times 10^{-4}\ s^{-1}$ and 78.9 kJ $mole^{-1}$.

For colour, Y:

the regression equation (R^2 = 88.5%) resulting from using average absolute residuals was:

$$Q = |0.02592 + 0.01579X1 - 0.01226X2 + 0.01104X1^2 - 0.01416X1X2| \quad (5.13)$$

the regression equation (R^2 = 80.6%) resulting from using individual absolute residuals was:

$$Q = |0.02641 + 0.01615X1 - 0.01209X2 + 0.01106X1^2 - 0.01360X1X2| \quad (5.14)$$

minimization of Q gave the k_{129^oC} and Ea from equation (5.13) of $1.2403 \times 10^{-4}\ s^{-1}$ and 122.1 kJ $mole^{-1}$ and from equation (5.14) of $1.2333 \times 10^{-4}\ s^{-1}$ and 121.7 kJ $mole^{-1}$.

For viscosity:

the regression equation (R^2 = 64.4%) resulting from using average residuals was:

$$Q = |0.02020 - 0.00766X2 + 0.01282X1^2 + 0.00530X2^2 - 0.01464X1X2| \quad (5.15)$$

the regression equation (R^2 = 49.1%) resulting from using individual absolute residuals was:

$$Q = |0.01963 - 0.00686X2 + 0.01313X1^2 + 0.00509X2^2 - 0.01445X1X2| \quad (5.16)$$

minimization of Q gave the k_{129^oC} and Ea from equation (5.15) of $1.724 \times 10^{-4}\ s^{-1}$ and 155.4 kJ $mole^{-1}$ and from equation (5.16) of 1.742×10^{-4} and 156.5 kJ $mole^{-1}$.

Therefore, only the average absolute residuals were used in the analysis. An example of the complete method of determination of residuals, determination of empirical equations by multiple regression, the decoding of the regression equation, the minimization of residual and, then determination of k_{129^oC} and Ea is shown in Appendix 5.3. The program for contour plots and an example of a contour plot are also shown in Appendix 5.3.

5.5 DETERMINATION OF KINETIC PARAMETERS FOR ASCORBIC ACID

5.5.1 Determination of the Range of k_{129^oC} and Ea

Using the k_{129^oC} and Ea reported by Chittaporn (1977) of 2.33 x 10^{-4} s^{-1} and 84.2 kJ $mole^{-1}$, the calculated final concentration of ascorbic acid based on the processing conditions of run no.6 was 17.95 x 10^{-2} mg g^{-1} which was much lower than the 24.16 x 10^{-2} mg g^{-1} determined from the experiment. To increase the calculated concentration, the k_{129^oC} and/or the Ea would have to be changed. From the literature review, it appeared that the Ea was in the right range but it was necessary to determine the possible range for the k_{129^oC}.

Rough estimation of the possible k_{129^oC} of ascorbic acid was carried out by averaging the measured temperatures at all 5 points of run no.6. Using the approximate average temperature of 110°C, the k_{129^oC} was calculated as 0.4115 x 10^{-4} s^{-1} (Appendix 5.4). Then this k_{129^oC} was used to calculate the final concentration from the computer program based on the processing conditions of runs no.6 and 10. The equivalent processing times at 129°C were calculated from the predicted concentrations and k_{129^oC} of 0.4115 x 10^{-4} s^{-1} and then plotted against the measured ln (c/c_o). The new k_{129^oC} of 0.5641 x 10^{-4} s^{-1} was obtained from the slope of the lines. This gave the possible range for k_{129^oC} for use in the systematic calculation of k_{129^oC} and Ea by use of the experimental design.

These two k_{129^oC} (0.4115 x 10^{-4} and 0.5641 x 10^{-4} s^{-1}) were used in the design as the coded variable X1 at levels of -1 and +1, as the actual k_{129^oC} was likely to fall in this range. Then the highest and lowest levels of k_{129^oC} (+2 and -2) were calculated from these two k_{129^oC} to obtain an orthogonal design which should cover the possible range of k_{129^oC} for ascorbic acid.

Therefore, the kinetic reaction rate at 129°C at each level was coded by:

$$X1 = \frac{k_{129^oC} - 0.4878 \times 10^{-4}}{0.0763 \times 10^{-4}}$$

The activation energies of 63 and 83 kJ mole^{-1} were used as X2 of respectively -1 and +1

$$X2 = \frac{Ea - 73}{10}$$

The absolute residuals were calculated for points, 1,2,3,4,5,6 and 8 (Figure 5.2). The k_{129^oC} and Ea at each point are shown in Figure 5.3 with the average absolute residual and the standard deviation shown in the bracket. It was found that the Ea levels used were too low as the absolute residual was lowered where the Ea was increased (point 5 and 6) whereas the k_{129^oC} of 0.5641×10^{-4} s^{-1} gave the highest absolute residual indicating that the actual k_{129^oC} of ascorbic acid would be in the lower range of k_{129^oC} rather than in the higher range.

Therefore the levels of the k_{129^oC} and Ea were reconsidered. Most of the previous results obtained were used to minimize the computation cost.

5.5.2 A Model for Ascorbic Acid for Determination of Kinetic Parameters

The final orthogonal design for ascorbic acid is shown in Table 5.3. Using the k_{129^oC} and Ea at various points in the design, the absolute residuals were determined and are shown in Figure 5.4. From these calculated residuals, a quadratic model was fitted by multiple linear regression. The coefficient terms of higher than 80% significance were taken into the final model.

The regression equation (R^2 = 83.1%) resulting from using average absolute residual at each process temperature was:

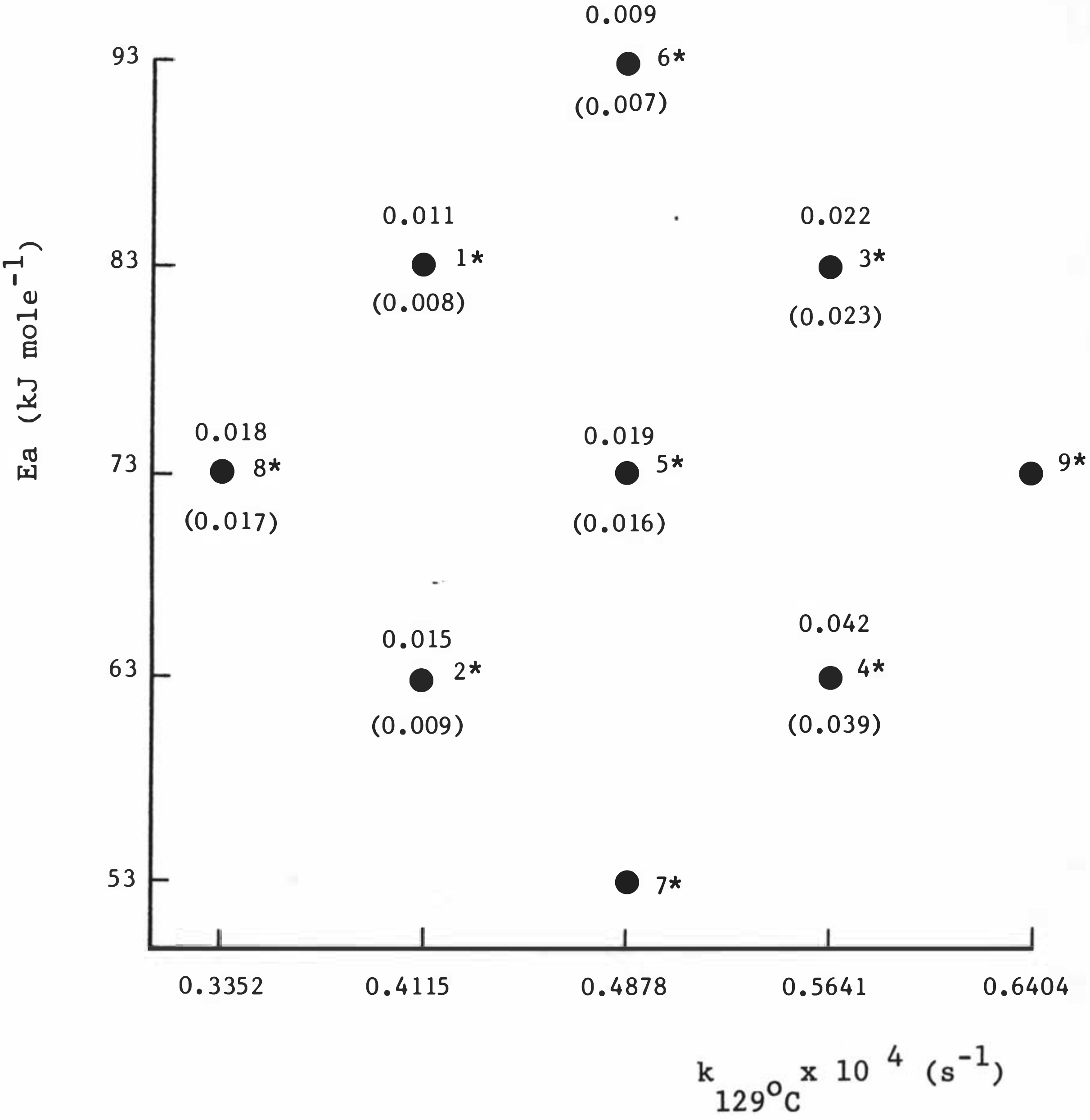


FIG. 5.3 First Design for Ascorbic Acid with Calculated Average Absolute Residuals and their Standard Deviations

TABLE 5.3 Level of the k_{129^oC} and the Ea in the Orthogonal Composite Design for Ascorbic Acid

Point	X1*	k_{129^oC} s^{-1}	X2*	Ea kJ $mole^{-1}$
1	-1	0.3352×10^{-4}	+1	93
2	-1	0.3352×10^{-4}	-1	73
3	+1	0.4878×10^{-4}	+1	93
4	+1	0.4878×10^{-4}	-1	73
5	0	0.4115×10^{-4}	0	83
6	0	0.4115×10^{-4}	2	103
7	0	0.4115×10^{-4}	-2	63
8	-2	0.2589×10^{-4}	0	83
9	+2	0.5641×10^{-4}	0	83

$$* \quad X1 = \frac{k_{129^oC} - 0.4115 \times 10^{-4}}{0.0763 \times 10^{-4}}$$

$$X2 = \frac{Ea - 83}{10}$$

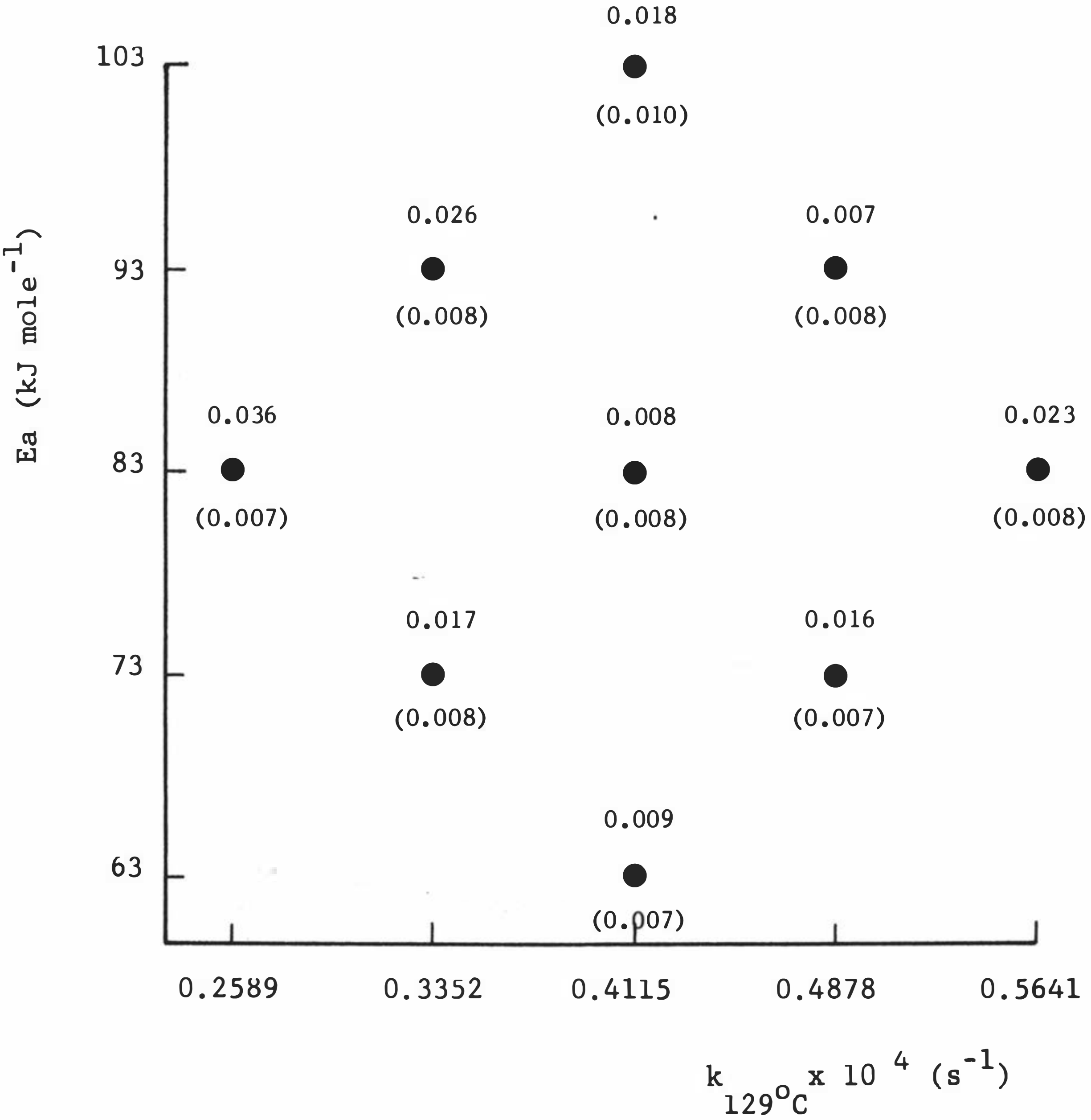


FIG. 5.4 Orthogonal Design for Ascorbic Acid with Calculated Average Residuals and their Standard Deviations

$$Q = |0.01225 - 0.00400X1 + 0.00151X2 + 0.00435X1^2 - 0.00484X1X2| \quad (5.17)$$

The equation was decoded and minimization of Q was done by the differential method and is shown in Appendix 5.3. The decoded equation was

$$Q = |-0.0651 - 1.4904\text{x}10^3\ k_{129^oC} + 2.6995\text{x}10^{-3}\ Ea + 7.4652\text{x}10^7\ k^2_{129^oC} - 62.0238\ k_{129^oC}\ Ea| \quad (5.18)$$

Minimum Q was obtained where k_{129^oC} was $0.4352\text{x}10^{-4}\ s^{-1}$ and Ea was 80.7 kJ mole^{-1}. Contour plot of this equation was also made using the computer program (Appendix 5.3(e)) and is shown in Appendix 5.3(f). The optimum point obtained as the stationary point in the plot was found approximately at k_{129^oC} of $0.43 \times 10^{-4}\ s^{-1}$ and Ea of 81 kJ mole^{-1}.

The minimum average absolute residual calculated for all experimental runs, where the k_{129^oC} was $0.43 \times 10^{-4}\ s^{-1}$ and the Ea was 81 kJ mole^{-1}, was 0.006 with the standard deviation of 0.007.

5.6 DETERMINATION OF KINETIC PARAMETERS FOR RIBOFLAVIN

From the k_{129^oC} and Ea obtained for ascorbic acid, the k_{129^oC} and Ea of riboflavin were calculated (Appendix 5.5(a)). The calculation was based on the determination of equivalent processing times using the known kinetic reaction of ascorbic acid at each temperature, 129°C and 120°C. These calculated equivalent processing times were plotted against ln (c/c_o) found from the analysis for riboflavin of control and heated samples. The k_{129^oC} and k_{120^oC} for riboflavin were obtained from linear regression analysis. Assuming a linear relationship of ln k and 1/T, the activation energy was calculated. It was found that the kinetic reaction rate of riboflavin at 129°C was $0.246 \times 10^{-4}\ s^{-1}$ and the activation energy was 87 kJ mole^{-1}. The average absolute residual from the quality retention calculation was 0.006 with the standard deviation of 0.005.

The experimental design method used for determination of kinetic parameters for ascorbic acid was also used. The ranges of the k_{129^oC} and Ea were chosen to cover the values calculated by the equivalent processing time method but, wherever possible, points used for ascorbic acid were put into the design to save computation time. The design is shown in Table 5.4.

TABLE 5.4 Orthogonal Composite Design for Riboflavin

Point	X1**	k_{129^oC} s^{-1}	X2**	Ea kJ $mole^{-1}$
*1	-1	0.1826×10^{-4}	1	93
*2	-1	0.1826×10^{-4}	-1	73
3	1	0.3352×10^{-4}	1	93
4	1	0.3352×10^{-4}	-1	73
5	0	0.2589×10^{-4}	0	83
*6	0	0.2589×10^{-4}	2	103
*7	0	0.2589×10^{-4}	-2	63
*8	-2	0.1063×10^{-4}	0	83
9	2	0.4115×10^{-4}	0	83

* Denotes the extra points needed for calculation

** $$X1 = \frac{k_{129^oC} - 0.2589 \times 10^{-4}}{0.0763 \times 10^{-4}}$$

$$X2 = \frac{Ea - 83}{10}$$

The final concentration was calculated by the quality retention program and the absolute residual was calculated for each run at each k_{129^oC} and Ea level. The multiple linear regression was carried out as in Appendix 5.3.

Taking only the terms of higher than 80% significance, the regression equation ($R^2 = 92.3\%$) was:

$$Q = |0.00770 + 0.00148X1 - 0.00112X2 + 0.00524X1^2 - 0.00375X1X2| \quad (5.19)$$

Minimum Q was obtained where the k_{129^oC} and the Ea were 0.236 x 10^{-4} s^{-1} and 79.0 kJ $mole^{-1}$. These k_{129^oC} and Ea were used in the quality retention calculation, the average residual was calculated and is shown in Table 5.5 with the average residual from the processing time method and from another point in the orthogonal design.

TABLE 5.5 Average Absolute Residuals and their Standard Deviations Resulting from Different Levels of k_{129^oC} and Ea

$k_{129^oC} \times 10^4$ s^{-1}	Ea kJ $mole^{-1}$	Average Absolute Residual	Standard Deviation
0.246	87	0.006	0.005
0.236	80	0.006	0.005
0.259	83	0.005	0.006

From Table 5.5, the average residuals and the standard deviations were almost the same but it was decided to do another design to see whether a lower average absolute residual could be obtained. The new design is shown in Figure 5.5 with the average absolute residuals and their standard deviations.

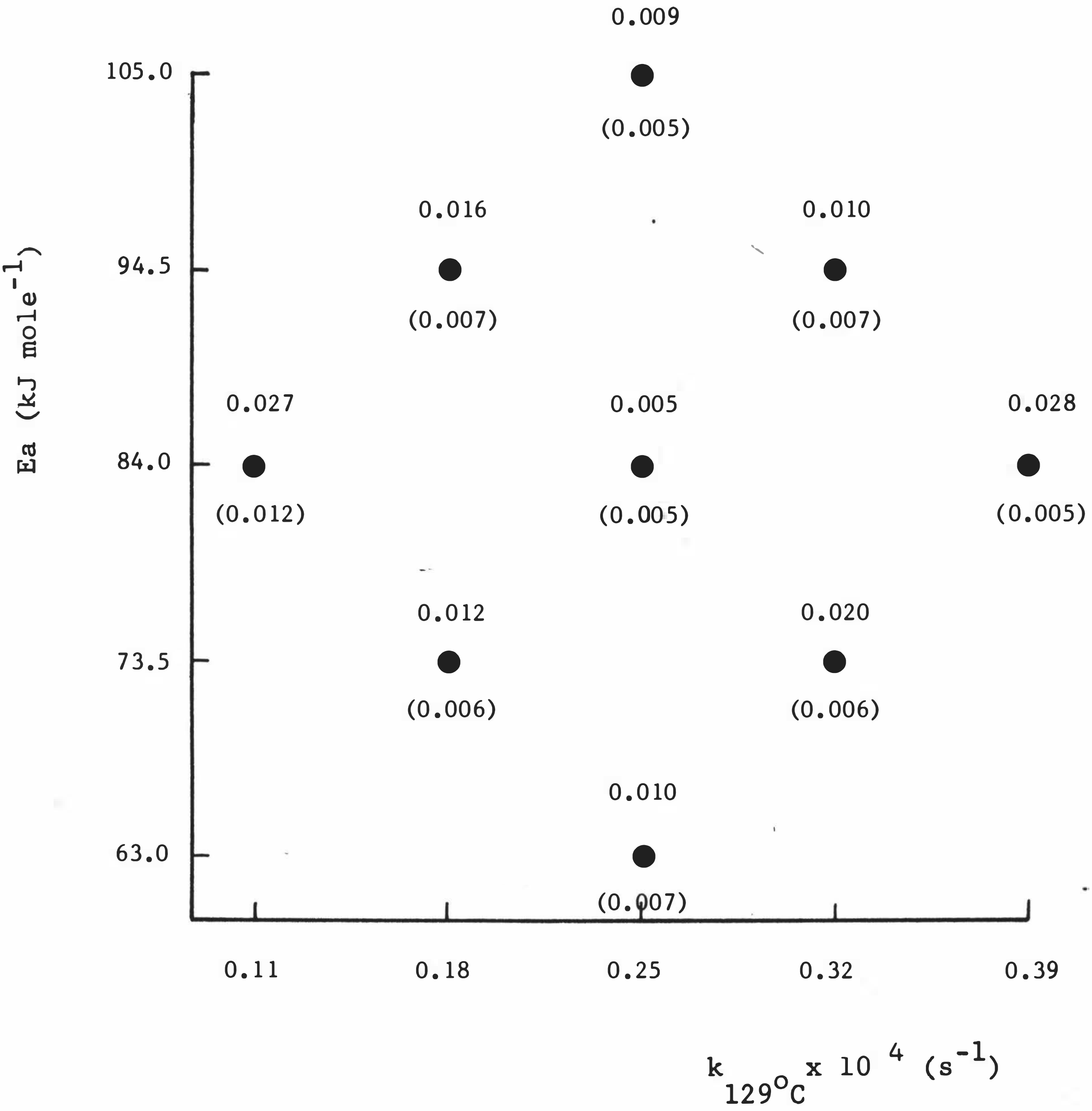


FIG. 5.5 Second Orthogonal Composite Design for Riboflavin with Average Absolute Residuals and their Standard Deviations

Taking only the terms of higher than 80% significance, the regression equation (R^2 = 93.4%) was:

$$Q = |0.00754 + 0.00508X1^2 - 0.00368X1X2| \qquad (5.20)$$

Minimum residual was found, where the k_{129^oC} was 0.250×10^{-4} s^{-1} and the Ea was 84 kJ $mole^{-1}$, to be 0.005 with the standard deviation of 0.005.

Therefore, it was concluded that the k_{129^oC} and the Ea of riboflavin were 0.250×10^{-4} s^{-1} and 84 kJ $mole^{-1}$.

5.7 DETERMINATION OF KINETIC PARAMETERS FOR COLOUR

As in section 5.5, the kinetic parameters found for ascorbic acid in section 5.4 were used for calculating the equivalent processing times. The approximate kinetic parameters for colour were found to be 1.063 $\times 10^{-4}$ kJ $mole^{-1}$ and 120.9 kJ $mole^{-1}$. The calculation is in Appendix 5.5(b).

The composite orthogonal design shown in Figure 5.6 was also used, the k_{129^oC} ranged from 0.900×10^{-4} to 2.100×10^{-4} s^{-1} and the Ea ranged from 92.4 to 159.6 kJ $mole^{-1}$. The residuals were calculated and the multiple linear regression was carried out as in Appendix 5.3 where X1 and X2 were defined as:

$$X1 = \frac{k_{129^oC} - 1.5 \times 10^{-4}}{0.3 \times 10^{-4}}$$

$$X2 = \frac{Ea - 126.0}{16.8}$$

The average residual at each point in the design is shown in Figure 5.6. Taking only terms of higher than 90% significance, the multiple regression equation (R^2 = 88.5%) was:

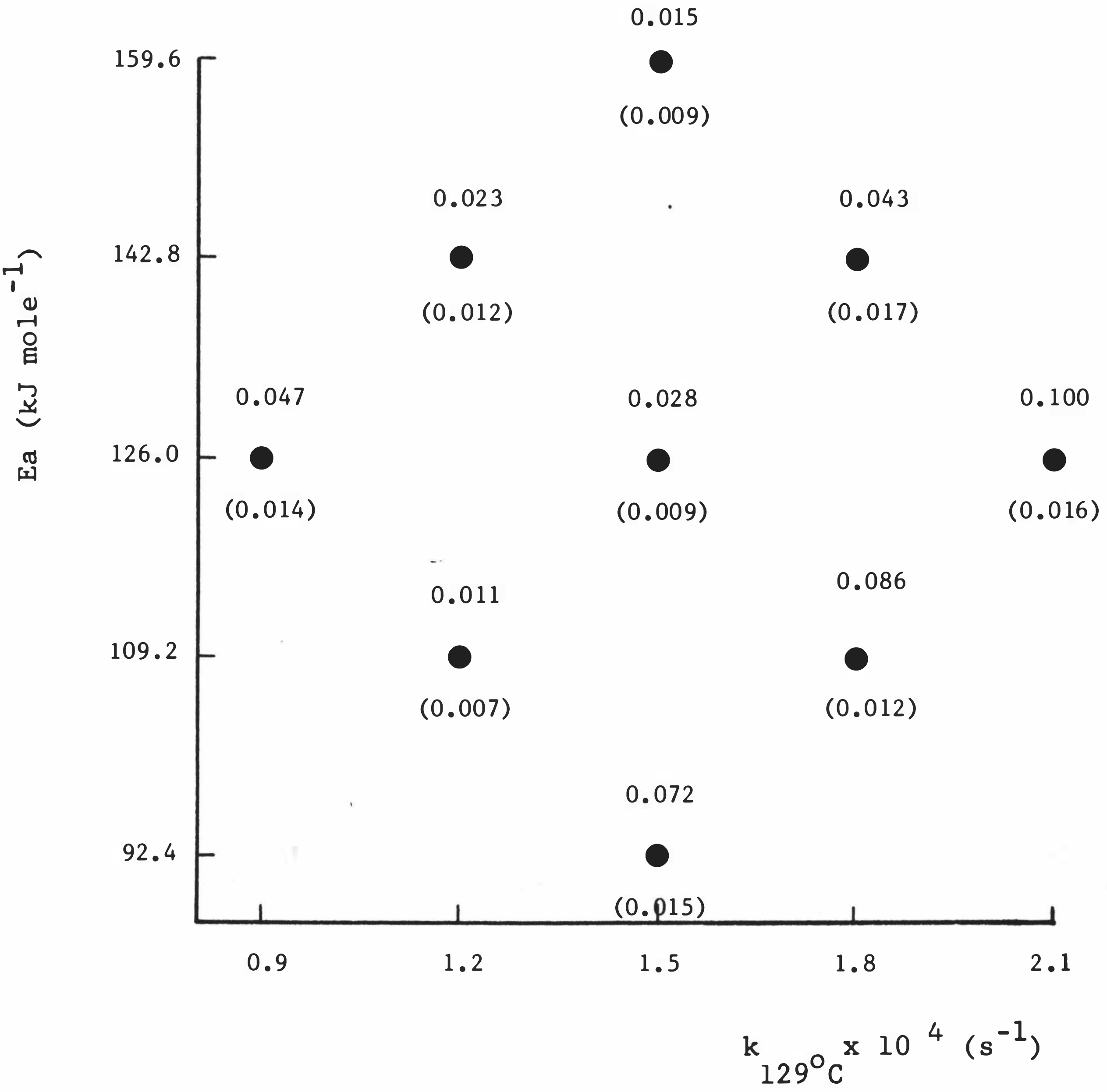


FIG. 5.6 First Orthogonal Composite Design for Colour, Y, with Average Absolute Residuals and their Standard Deviations

$$Q = |0.02592 + 0.01579X1 - 0.01226X2 + 0.00104X1^2 - 0.01416X1X2| \quad (5.21)$$

Minimization of Q gave the k_{129^oC} of $1.240 \times 10^{-4}\ s^{-1}$ and the Ea of 122.1 kJ $mole^{-1}$. To get closer estimation of the k_{129^oC} and Ea, the design in Figure 5.7 was used. The absolute residual and the standard deviation were calculated for each point and are shown in Figure 5.7.

Taking only terms higher than 90% significance, the multiple regression equation (R^2 = 77.6%) was:

$$Q = |0.00762 + 0.00459X1^2 + 0.00449X2^2 - 0.00850X1X2| \quad (5.22)$$

Minimization of Q gave the k_{129^oC} of $1.200 \times 10^{-4}\ s^{-1}$ and the Ea of 121.8 kJ $mole^{-1}$. The average absolute residual using these k_{129^oC} and Ea was 0.007 with the standard deviation of 0.006.

Therefore, the k_{129^oC} and Ea of colour, Y, were $1.200 \times 10^{-4}\ s^{-1}$ and 122 kJ $mole^{-1}$.

5.8 DETERMINATION OF KINETIC PARAMETERS FOR VISCOSITY

The equivalent processing time method was also used for calculation of the k_{129^oC} and Ea for viscosity (Appendix 5.6(c)). The k_{129^oC} and the Ea of $1.2348 \times 10^{-4}\ s^{-1}$ and 143.6 kJ $mole^{-1}$ were found.

The design in Figure 5.8 was first used and the average absolute residual at each point are shown in Figure 5.8. Taking only terms higher than 80% significance, the regression equation (R^2 = 64.4%) was:

$$Q = |0.02020 - 0.00766X2 + 0.01282X1^2 + 0.00530X2^2 - 0.01464X1X2| \quad (5.23)$$

Minimization of Q gave the k_{129^oC} of $1.724 \times 10^{-4}\ s^{-1}$ and the Ea of 155.4 kJ $mole^{-1}$. To find a closer approximation of the k_{129^oC} and Ea

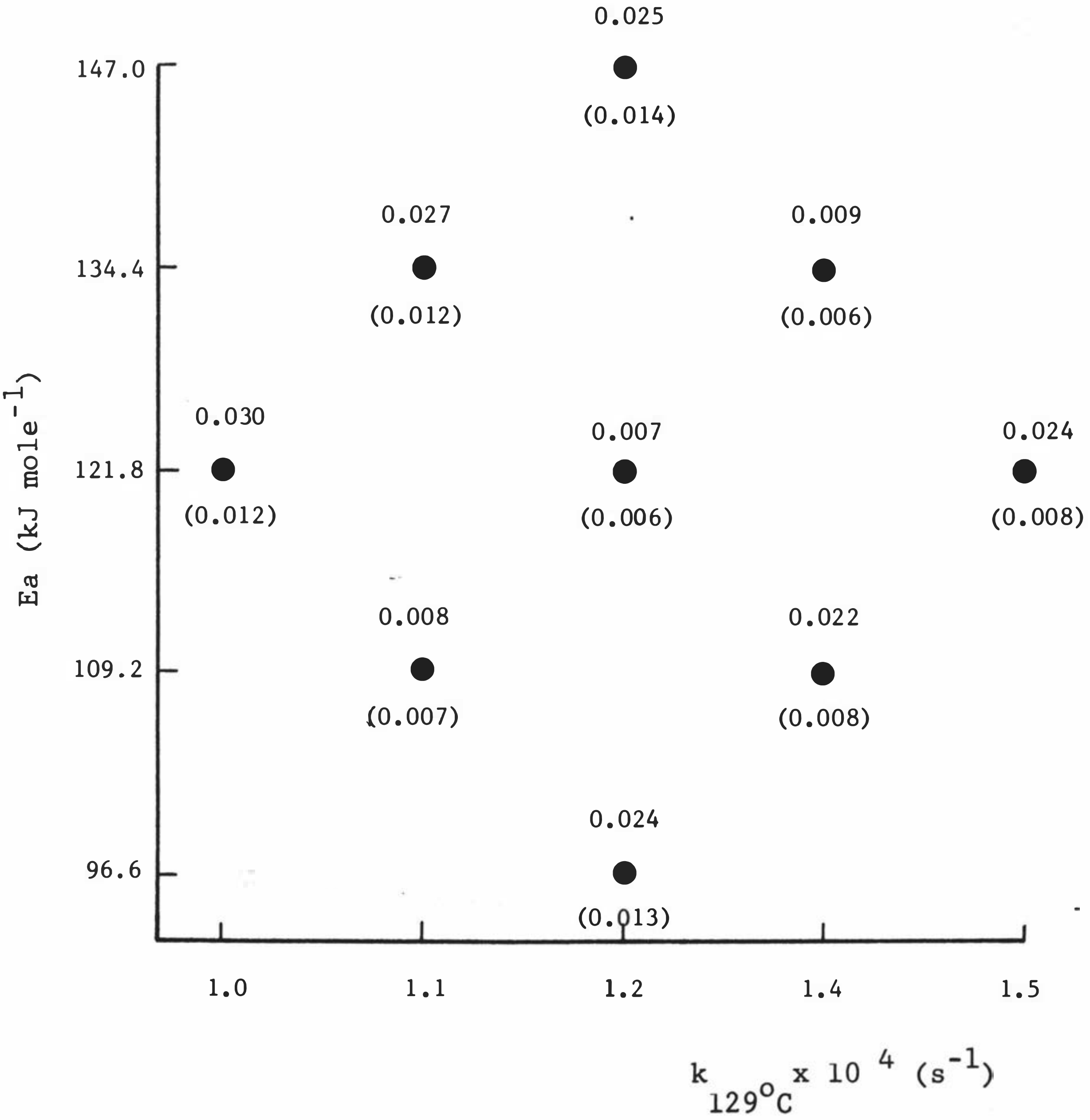


FIG. 5.7 Second Orthogonal Composite Design for Colour, Y, with Average Absolute Residuals and their Standard Deviations

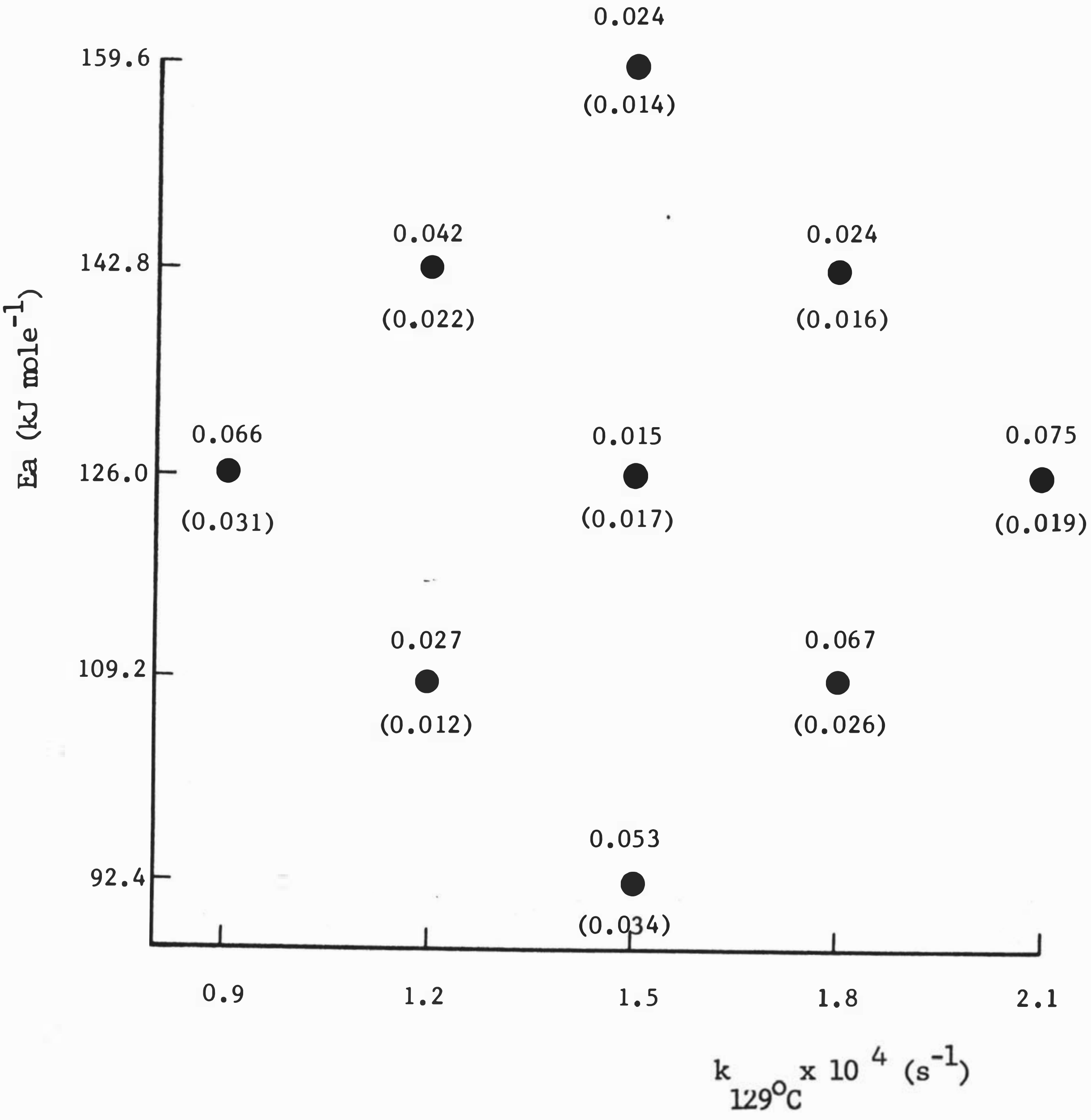


FIG. 5.8 First Orthogonal Composite Design for Viscosity with Average Absolute Residuals and their Standard Deviations

of viscosity, the design in Figure 5.9 was used. The absolute residual at each point was calculated and is shown in Figure 5.9.

Taking only terms of higher than 80% significance, the regression equation (R^2 = 15.4%) was:

$$Q = |0.01193 + 0.00164X2^2| \qquad (5.24)$$

Minimization of Q gave the k_{129^oC} of 1.650 x 10^{-4} s^{-1} and the Ea of 151.2 kJ $mole^{-1}$. These k_{129^oC} and Ea gave the lowest average absolute residual (Figure 5.9) of 0.011 with the standard deviation of 0.010.

Therefore the k_{129^oC} and Ea of viscosity were 1.650 x 10^{-4} s^{-1} and 152 kJ $mole^{-1}$.

5.9 CONCLUSION

The final computer program was developed for determining the quality retention of food in the can after heat processing by extending the temperature distribution calculation program developed in Chapter 4. As the purpose of the study was to determine the kinetic parameters, k_{129^oC} and Ea, which were unknowns in the program, so this program was written providing the opportunity to use any value of k and Ea. The time and dimension increment sizes were studied as they could effect the accuracy of quality retention calculation and it was found that a time increment of 72 seconds and a dimensional increment of 10 x 10 were the best to use.

The kinetic parameters were determined roughly by using an equivalent processing time method and then the ranges of k_{129^oC} and Ea were finally determined for an orthogonal composite design to systematise the trial and error method. Using various k_{129^oC} and Ea in the design, the absolute residual was determined for each processing condition at each k_{129^oC} and Ea level. The residuals were averaged for each temperature (120^o and 129^oC) for each level of k_{129^oC} and Ea. The multiple linear regression of residuals (Q) to both kinetic parameters, k_{129^oC} and Ea, was carried out using the average absolute residuals. The

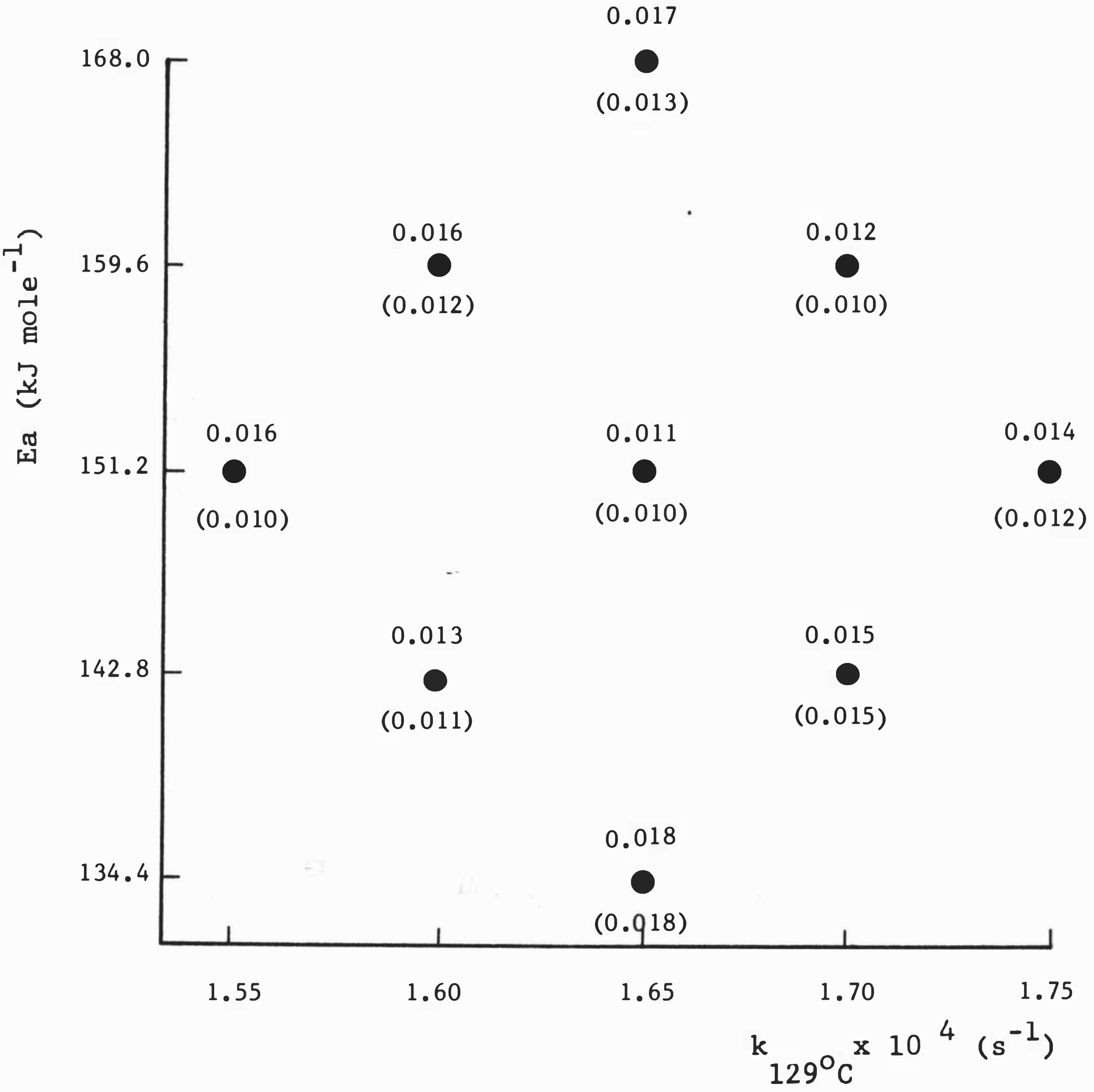


FIG. 5.9 Second Orthogonal Composite Design for Viscosity with Average Absolute Residuals and their Standard Deviations

actual k_{129^oC} and Ea were obtained from arithmetic optimization of Q.

For ascorbic acid the range was roughly estimated from the data obtained by Chittaporn (1977). By use of one orthogonal design, the kinetic parameters were found to be k_{129^oC} of 0.435×10^{-4} s^{-1} and Ea of 81 kJ $mole^{-1}$.

For riboflavin, colour and viscosity, the kinetic parameters were first roughly estimated by using the kinetic parameters obtained for ascorbic acid in calculating the equivalent processing time. Then the ranges of k_{129^oC} and Ea were used in orthogonal composite designs, one to two designs being necessary to find the k_{129^oC} and Ea. The k_{129^oC} and Ea was found to be 0.250×10^{-4} s^{-1} and 84 kJ $mole^{-1}$, 1.200×10^{-4} s^{-1} and 122 kJ $mole^{-1}$, and 1.650×10^{-4} s^{-1} and 151 kJ $mole^{-1}$ for riboflavin, colour and viscosity, respectively.

6. KINETIC PARAMETER DETERMINATION BY STEADY-STATE PROCEDURE

6.1 INTRODUCTION

As stated before, there are two procedures for determining the kinetic parameters for thermal degradation of food quality: steady-state and unsteady-state. Chapter 5 dealt with an unsteady state procedure where the food in a can was subjected to different degrees of heating. The computer program was constructed to determine the changes in temperature throughout the can and from this the overall change in the quality, assuming that the change on heat processing of the food qualities studied followed a first order reaction.

In this chapter, a steady-state procedure, where food was heated in tubes, was studied to determine the order of the degradation reactions of ascorbic acid and riboflavin on heat processing and the kinetic parameters, as well as to compare the kinetic parameters obtained with those in Chapter 5.

6.2 EXPERIMENTATION

6.2.1 Sample Preparation

The sample was prepared in exactly the same way as had been done for the unsteady-state procedure in the can. The frozen, homogenised strained beef and mixed vegetables baby food prepared for the experiment in Chapter 5 was thawed for 2½ hours in a 30^{o}C water bath, then, it was heated with hand stirring, to 87^{o}C for gelatinization. Some ascorbic acid had been lost during storage, so ascorbic acid was therefore added to make the concentration high enough for accurate analysis and in the same range as before. Readjustment was unnecessary for riboflavin because no loss of riboflavin was found during storage at -10^{o}C.

About 0.8 - 0.9 g of preheated baby food was filled into borosilicate glass vials of 3 mm internal diameter, 1 mm thick and 130 mm long by using a 25 ml syringe. The tubes were heat-sealed under vacuum by heating the top part of the tubes to expel the air and create a vacuum (Wilkinson et al, 1980). The temperature of the flame used for sealing the tubes must be carefully controlled. Improperly sealed tubes may result if the temperature is too high and this can lead to higher oxygen content in the tube and explosion of the baby food when it is heated. The prepared vials were kept in the dark at -10°C before heating.

6.2.2 Thermal Processing System

The same thermostatically controlled oil bath ± 0.2°C used by Wilkinson et al (1980) was used. The vials were heated at specified temperatures, 110, 120, 129 and 139°C. It was found by Wilkinson et al (1980) that on heating liver in this system, the temperature difference between the centre of the liver in the tube and the glass-liver interface during the initial heating period was ca 20°C after three seconds and ca 3°C after 30 seconds, therefore, in 15 seconds, 90% of the desired temperature was reached. So Wilkinson et al (1980) concluded that there was effectively instantaneous heating and cooling. As the same oil bath, size and type of vials and range of temperatures were used, this was assumed to be true for the similar heating of the baby food.

Four heating times at each temperature were studied for each vitamin (Table 6.1). As the sample sizes required for analysis of the two vitamins were different, 4 vials for ascorbic acid and 2 vials for riboflavin were randomly removed at the specified heating time. The removed vials were immediately cooled in a crushed ice/water bath. After cooling, the vials were washed with ethanol and stored in the dark at -10°C until analysis. Control samples which were not heated were treated in a similar manner.

TABLE 6.1 Heating Temperatures and Times for Steady-State Heating Method

Temperature °C	Heating Time (minutes)							
	Ascorbic Acid				Riboflavin			
110	210	450	690	1140	240	510	840	1200
120	110	240	370	-	120	270	420	600
129	40	85	135	195	70	150	240	340
139	35	75	125	175	40	80	130	180

6.2.3 Determination of Ascorbic Acid and Riboflavin

The sample vials were taken from the storage and cut at both ends. The sample in the vial was blown out by compressed air into the weighed 10 ml volumetric flask for ascorbic acid analysis and into the weighed 250 ml erlenmeyer flask for riboflavin analysis, then the sample was weighed. Duplicate analysis of each sample was carried out by the method described in Appendix 3.2.

6.3 DESTRUCTION OF ASCORBIC ACID AND RIBOFLAVIN ON HEATING

The average concentrations of ascorbic acid and riboflavin before and after heating are shown in Table 6.2.

TABLE 6.2 Concentration of Ascorbic Acid and Riboflavin Before and After Heating

Ascorbic Acid			Riboflavin		
Temperature °C	Time min	Concentration x 10^{2} mg g^{-1}	Temperature °C	Time min	Concentration μg g^{-1}
110	0	36.77	110	0	26.11
	210	31.74		240	25.00
	450	27.74		510	24.39
	690	20.64		840	23.24
	1150	15.72		1200	22.77
120	0	21.57	120	0	26.75
	110	18.37		120	25.30
	240	15.45		270	23.71
	370	13.59		420	23.08
				600	22.16
129	0	31.29	129	0	25.85
	40	29.02		70	23.90
	85	24.87		150	22.86
	130	21.77		240	22.16
	195	16.91		340	21.73
139	0	38.76	139	0	26.27
	35	30.59		40	24.37
	75	26.83		80	23.51
	125	24.95		130	22.69
	175	22.08		180	21.74

84%.

6.4 DETERMINATION OF THE ORDER OF REACTION

As discussed in Chapter 2, most degradation on heat processing of vitamins in foods was found to follow a first order reaction, so in Chapter 5, where the order of reaction could not be determined, degradation was assumed to follow a first order reaction. However, in this section, the order of reaction could be determined by regressing different forms of concentration against time.

For zero order reaction:

$$\frac{dc}{dt} = -k \qquad (6.1)$$

$$c - c_o = -kt \qquad (6.2)$$

plotting $c - c_o$ against time, t, will give a straight line of slope,-k.

For a first order reaction:

$$\frac{dc}{dt} = -kc \qquad (6.3)$$

$$\ln \frac{c}{c_o} = -kt \qquad (6.4)$$

plotting $\ln(c/c_o)$ against time, t, will give a straight line of slope, -k.

For a second order reaction:

$$\frac{dc}{dt} = -kc^2 \qquad (6.5)$$

$$\frac{1}{c} - \frac{1}{c_o} = kt \qquad (6.6)$$

plotting $1/c - 1/c_o$ against time, t, will give a straight line of slope, k.

Linear regression of $(c_o - c)$, $\ln(c/c_o)$ and $(1/c - 1/c_o)$ against time for all the concentrations in Table 6.2 gave the correlation coefficients (R^2) shown in Table 6.3. Statistically, the higher correlation coefficient indicates a higher consistency in the data at that order of reaction.

For ascorbic acid, the correlation coefficients were very high except at 139°C. However, for all 4 temperatures, the first order relationship gave the highest average R^2 and the lowest standard deviation which indicated that over the temperature range studied the kinetics of ascorbic acid degradation in baby food were consistent with the first order kinetics. As can also be seen in Figure 6.1, the first order relationship, $-\ln(c/c_o)$ versus time did give a reasonable approximation of the experimental results.

The correlation coefficients for riboflavin were lower than the ones for ascorbic acid for all orders studied and were more difficult to interpret. The second order reaction did give slightly higher correlation coefficients. But as can be seen in Figures 6.2 and 6.3, at the temperature of 120°C, neither first or second order gave a good fit of the experimental results. This could be due to the only small amounts of riboflavin destroyed.

Therefore, it was concluded that the degradation under these heat processing conditions of ascorbic acid was best described by the first order kinetics and that the kinetic parameters would be determined based on first order kinetics. For riboflavin, both first order and second order kinetics were studied for determination of k_{129^oC} and Ea as the experimental results did not adequately distinguish between first and second order kinetics.

TABLE 6.3 Correlation Coefficients of Regression Analysis of Concentration of Ascorbic Acid and Riboflavin with Time of Heating

TEMPERATURE °C	CORRELATION COEFFICIENT		
	ZERO ORDER	FIRST ORDER	SECOND ORDER
Ascorbic Acid			
110	0.987	0.990	0.970
120	0.988	0.993	0.999
129	0.991	0.980	0.940
139	0.934	0.953	0.970
AVERAGE	0.975	0.979	0.970
STANDARD DEVIATION	0.027	0.018	0.024
Riboflavin			
110	0.967	0.969	0.971
120	0.956	0.956	0.956
129	0.935	0.940	0.946
139	0.963	0.966	0.970
AVERAGE	0.955	0.958	0.963
STANDARD DEVIATION	0.014	0.013	0.012

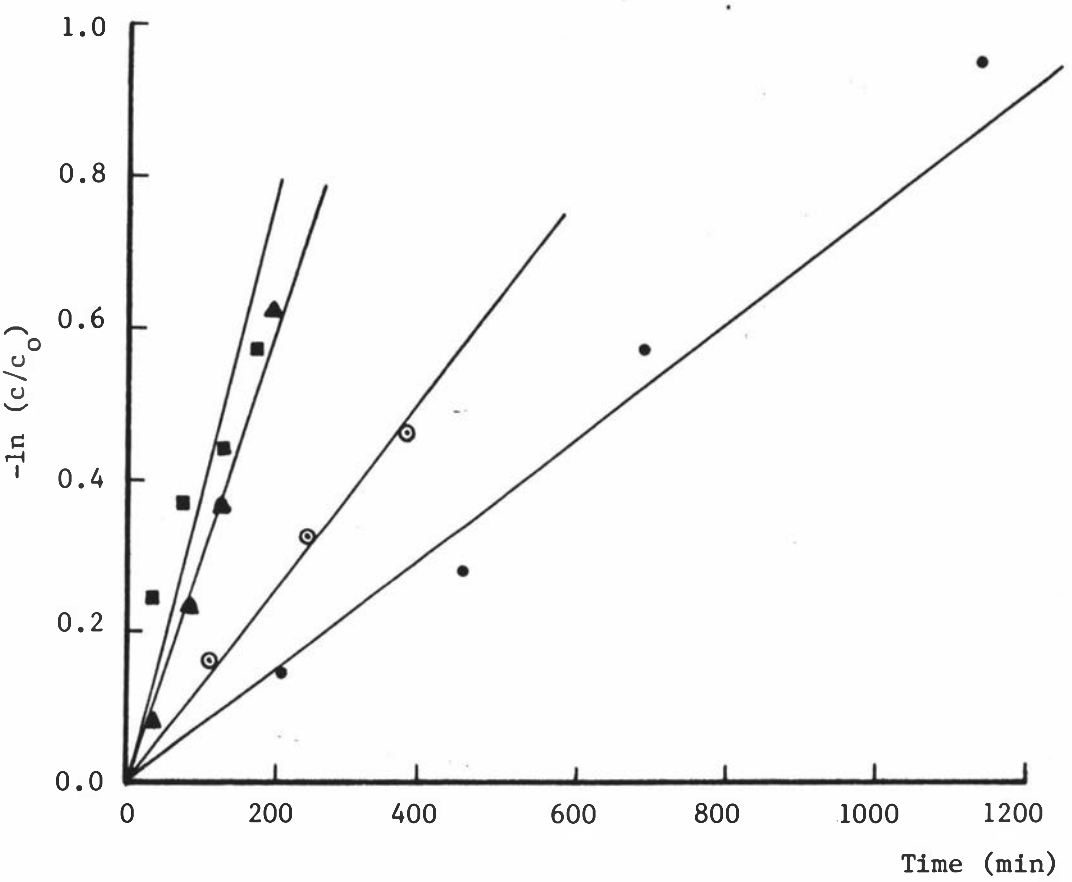


FIG. 6.1 Degradation Rate for Ascorbic Acid in Baby Food on Heating Described by First Order Kinetics

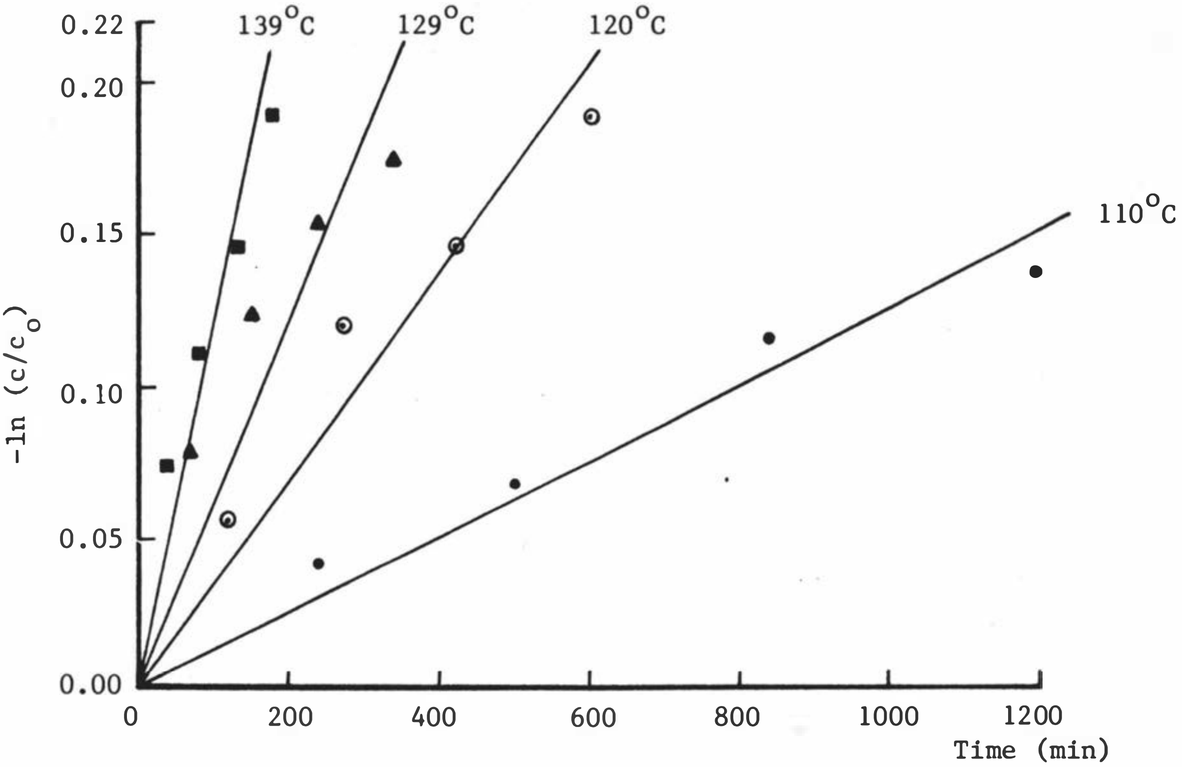


FIG. 6.2 Degradation Rate for Riboflavin in Baby Food on Heating Described by First Order Kinetics

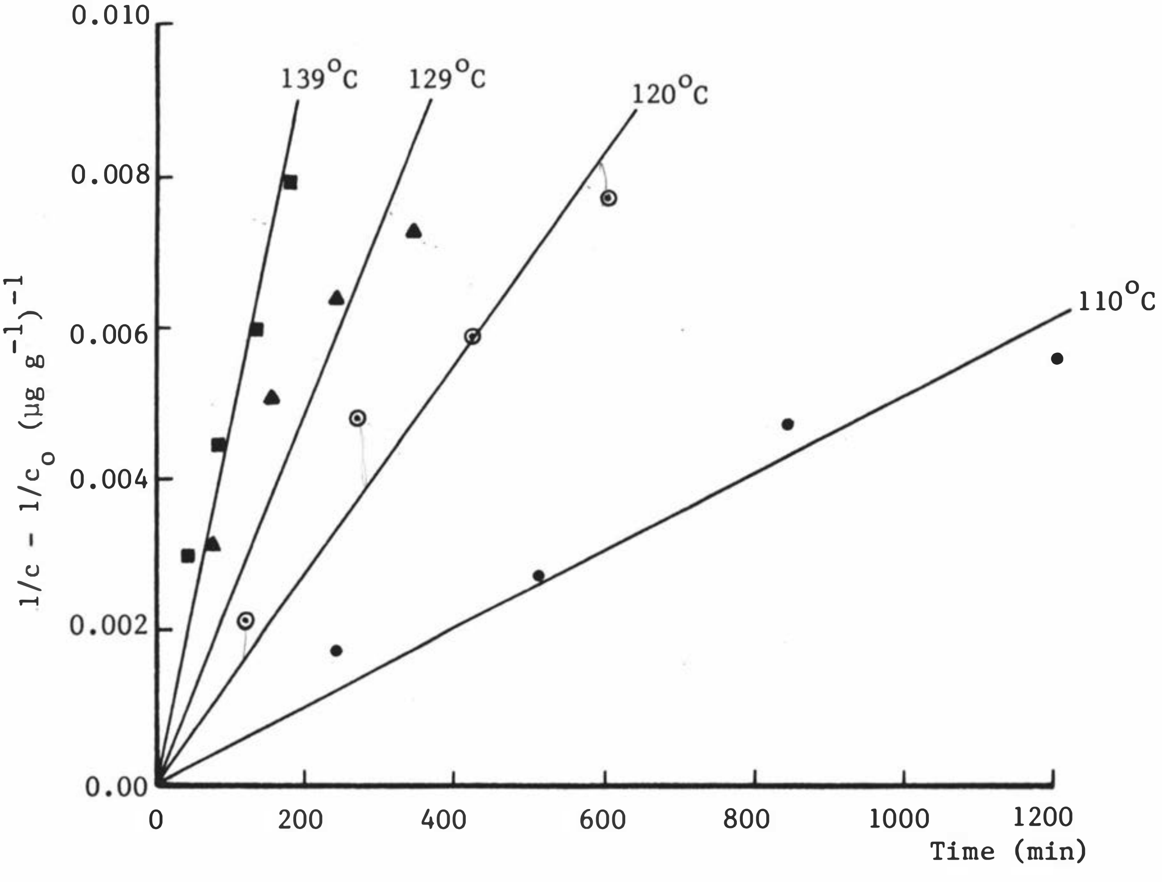


FIG. 6.3 Degradation Rate for Riboflavin in Baby Food on Heating Described by Second Order Kinetics

6.5 KINETIC PARAMETERS DETERMINATION

6.5.1 Calculation of Kinetic Parameters for First Order Reaction

For a first order reaction, the kinetic reaction rate at each temperature was determined from the regression analysis of $-\ln(c/c_o)$ against heating times, forcing the line through zero as instantaneous heating and cooling was assumed. Then, the temperature dependence of the rates was determined from the regression analysis of ln k against the inverse of absolute temperature as:

$$k = Ae^{-Ea/Rt} \qquad (6.7)$$

$$\ln k = \ln A - \frac{Ea}{RT} \qquad (6.8)$$

where A is the frequency factor (s^{-1})
Ea is the activation energy (kJ $mole^{-1}$)
R is the gas constant (kJ $mole^{-1}\ {}^{o}K^{-1}$)
T is the absolute temperature (^{o}K).

The k_{129^oC} and Ea could also be determined by linear regression of $\ln(\ln(c_o/c))$- ln t against the inverse of absolute temperature as:

$$\ln(\frac{c_o}{c}) = kt \qquad (6.4)$$

substituting "k" by equation (6.7), giving

$$\ln(\frac{c_o}{c}) = Ae^{-Ea/Rt}\ t$$

therefore

$$\ln(\ln(\frac{c_o}{c}) - \ln t) = \ln A - \frac{Ea}{RT} \qquad (6.9)$$

Linear regression of$(\ln(\ln(c_o/c))- \ln t)$ against the inverse of absolute temperatures would give a slope of -Ea/R and an intercept of ln A. So using all data obtained at various heating temperatures and times, the k_{129^oC} and Ea could be determined.

To distinguish between these two methods, the first method using equation (6.8) was called the two-step method and the second method using equation (6.9) was called the one-step method.

6.5.2 Calculation of Kinetic Parameters for Second Order Reaction

For second order kinetics, the kinetic reaction rate was determined from the regression analysis of $1/c - 1/c_o$ against heating time, forcing the line through zero. Then the activation energy was determined from the regression analysis of ln k against 1/T. As in the first order case, this method was called the two-step method.

Analogous to the first order one-step method, the equation used was modified for a second order reaction.

From equation (6.6)

$$\frac{1}{c} - \frac{1}{c_o} = kt$$

substituting k by equation (6.7)

$$\frac{1}{c} - \frac{1}{c_o} = Ae^{-Ea/RT}\, t$$

then

$$\ln\left(\frac{1}{c} - \frac{1}{c_o}\right) = \ln A - \frac{Ea}{RT} + \ln t$$

$$\ln\left(\frac{1}{c} - \frac{1}{c_o}\right) - \ln t = \ln A - \frac{Ea}{RT} \qquad (6.10)$$

Plotting $(\ln(1/c - 1/c_o) - \ln t)$ against T gave a straight line of slope and intercept equal to $-Ea/R$ and ln A, respectively.

In the unsteady-state procedure, the computer program was modified for second order kinetics by using:

$$\frac{dc}{dt} = -kc^2$$

so

$$\frac{dc}{c^2} = -kdt$$

$$\int_{c_o}^{c} \frac{dc}{c^2} = -\int_{o}^{t} kdt$$

$$\frac{1}{c} - \frac{1}{c_o} = \int_{o}^{t} kdt$$

As

$$k = k_{Tr} \exp \left(-\frac{Ea}{R} \left(\frac{1}{T} - \frac{1}{Tr}\right)\right)$$

Then

$$\frac{1}{c} - \frac{1}{c_o} = \int_{o}^{t} k_{Tr} \exp \left(- \frac{Ea}{R}\left(\frac{1}{T} - \frac{1}{Tr}\right)\right) dt \quad (6.11)$$

For overall quality retention of the can after time t:

$$\frac{1}{c} - \frac{1}{c_o} = k_{Tr} \int_{o}^{v} \int_{o}^{t} \exp \left(- \frac{Ea}{R}\left(\frac{1}{T} - \frac{1}{Tr}\right)\right) dt\, dv \quad (6.12)$$

Using the graphical integration technique, for small values of Δt, the retained quality for Δv was calculated by

$$\frac{1}{c} - \frac{1}{c_o} = k_{Tr} \exp \left(- \frac{Ea}{R}\left(\frac{1}{T} - \frac{1}{Tr}\right)\right) \Delta t \quad (6.13)$$

$$\frac{1}{c} = k_{Tr} \exp \left(- \frac{Ea}{R}\left(\frac{1}{T} - \frac{1}{Tr}\right)\right) \Delta t + \frac{1}{c_o}$$

Therefore

$$c = \left(\frac{1}{c_o} + k_{Tr} \exp \left(- \frac{Ea}{R}\left(\frac{1}{T} - \frac{1}{Tr}\right)\right) \Delta t\right)^{-1} \quad (6.14)$$

The concentration at the end of the first interval became the initial concentration for the second interval. The calculation was repeated until the end of processing. Then the overall quality retention was calculated by the summation of retained quality of each interation. The computer program in Chapter 5 was modified based on equation (6.14) and is shown in Appendix 6.1.

Then the k_{129^oC} and Ea could be determined from this quality retention calculation program by the trial and error method in section 5.4.

6.5.3 Determination of Kinetic Parameters for Ascorbic Acid

The kinetic reaction rates for ascorbic acid were determined and are shown in Table 6.4. The Arrhenius plot of the natural logarithm of k as a function of absolute temperature is shown in Figure 6.4. The activation energy, frequency factor and k_{129^oC} were determined by both the two-step and the one-step method as shown in Table 6.5 to see whether the methods led to any difference in the estimation of these important parameters.

The activation energies determined by either method were in the same range. The mean activation energy obtained from the two-step method was lower with a higher standard deviation. This difference could be due to the inability to take the deviation of the determined kinetic reaction rate into account in the two-step method while in the one-step method, all deviations would be included as all data were used.

The predicted reaction rates at 129°C obtained from the two-step method and the one-step method were almost identical whereas the frequency factors (A) were different as only a small change in k or Ea could cause a big apparent variation in A. It was considered safe to use the k_{129^oC} only within the studied temperature range, as the extrapolation of the Arrhenius plot beyond this temperature was doubtful.

For the one-step method, the error in the raw data was also determined, a probability plot was constructed of % residual, defined as:

$$\% \text{ residual} = (c_p - c_{obs})/c_p \times 100 \qquad (6.15)$$

where c_p is a predicted concentration
c_{obs} is an observed concentration

The % residual was calculated based on the determined Ea and A from the one-step method shown in Table 6.5. A probability plot (Figure 6.5) as a straight line indicated that all deviations from the line were random and due to experimental uncertainty only. The average residual was 5.99%.

TABLE 6.4 Kinetic Reaction Rate Constants at Various Temperatures for Ascorbic Acid

(Rate for first order kinetics with 95% confidence level)

Temperature °C	k x 10^4 s^{-1}	Correlation Coefficient R^2
110	0.126 ± 0.010	0.990
120	0.216 ± 0.008	0.993
129	0.498 ± 0.054	0.980
139	0.619 ± 0.102	0.953

TABLE 6.5 Activation Energy, Frequency Factor and Kinetic Reaction Rate at 129°C for Ascorbic Acid(1)

	Two-Step Method	One-Step Method
Ea(2), kJ $mole^{-1}$ (kcal $mole^{-1}$)	77 ± 23 (18.2 ± 5.5)	85 ± 10 (20.3 ± 2.3)
A x 10^{-5}, s^{-1}	3.6	42.8
$k_{129°C}$ x 10^4, s^{-1}	0.403	0.418

(1) R^2 for the two-step method was 0.957 and for the one-step method was 1.000.

(2) Activation energy with 95% confidence level.

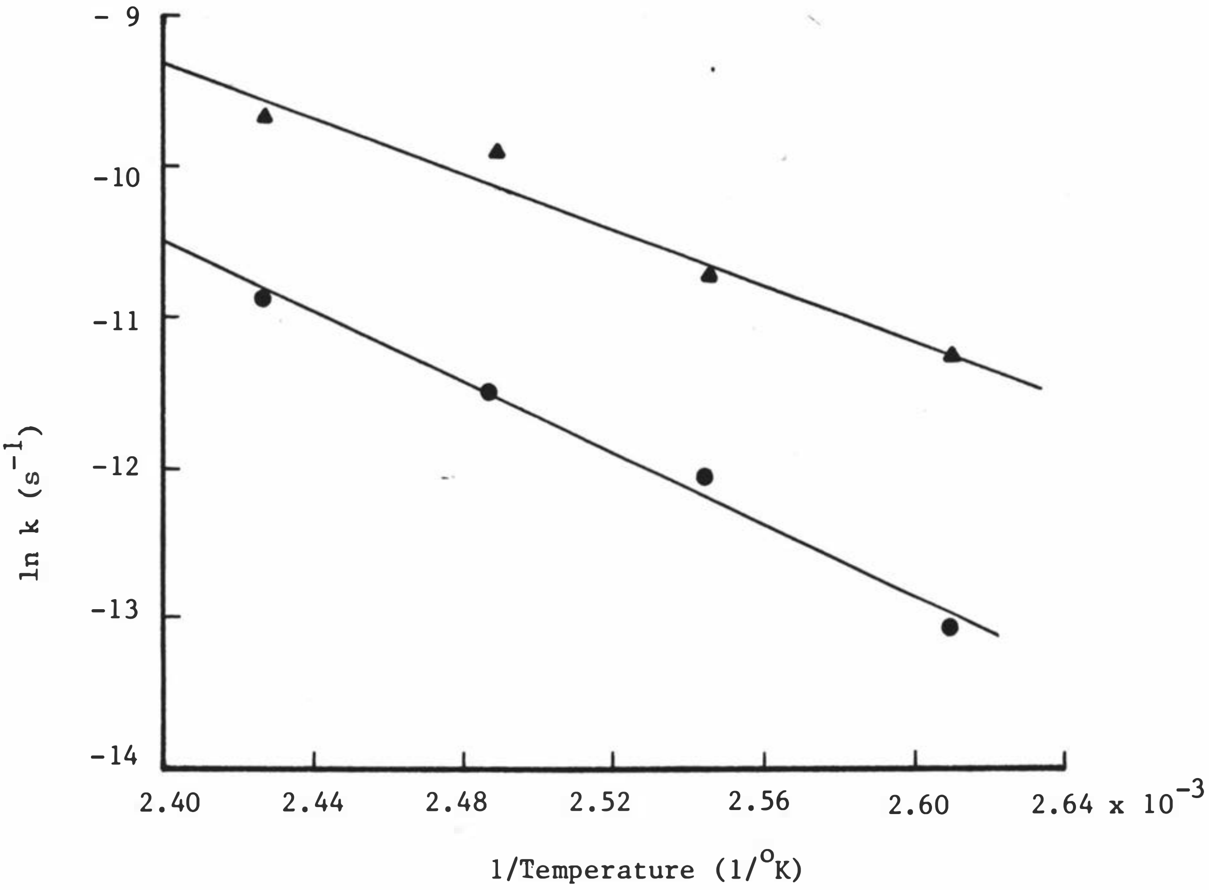


FIG. 6.4 Arrhenius Plot for Degradation of Ascorbic Acid and Riboflavin in Baby Food on Heating

(▲——▲) ascorbic acid

(●——●) riboflavin

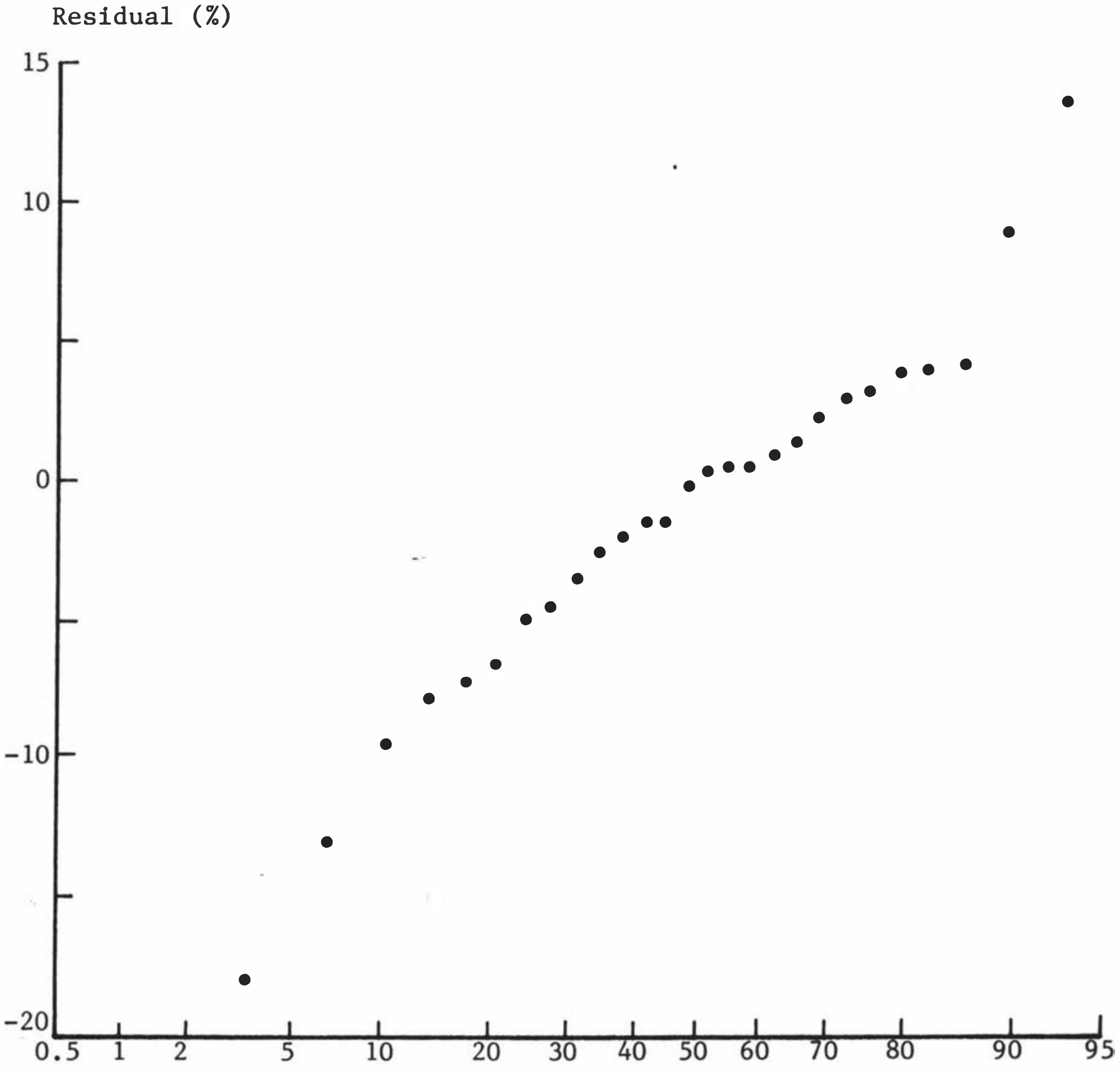


FIG. 6.5 Probability Plot of Calculated % Residual for Ascorbic Acid

As all data were taken into account at once in the one-step method, so all deviations were included. The one-step method should give more accurate results, k_{129^oC} and Ea, and therefore it should be used for determination of kinetic parameters in steady-state procedure.

6.5.4 Determination of Kinetic Parameters for Riboflavin

Assuming that the degradation of riboflavin on heat processing could be described by the first order reaction, the activation energy, frequency factor and k_{129^oC} were determined by both the two-step and the one-step methods. The reaction rate constants at various temperatures were determined by the two-step method and are shown in Table 6.6. The Arrhenius plot of ln k versus 1/T is shown in Figure 6.4. The activation energy, frequency factor and k_{129^oC} obtained from both methods are shown in Table 6.7.

The % residual was also calculated as in section 6.4.3. A probability plot (Figure 6.6) for riboflavin was also a straight line. The average absolute residual was 2.76%.

The k_{129^oC} and the Ea obtained from both methods were slightly different. However, as described in section 6.4.3, the one-step method gave more accurate results and should be used for determination of k_{129^oC} and Ea.

As riboflavin could possibly be better described by second order kinetics, the activation energy, the frequency factor and the k_{129^oC} were also determined using the methods described in section 6.4.2. The kinetic reaction rate constants obtained from the two-step method are shown in Table 6.8. The Arrhenius plot is in Figure 6.7. The activation energy, the frequency factor and the k_{129^oC} determined by both the two-step and the one-step methods are shown in Table 6.9.

TABLE 6.6 Kinetic Reaction Rate Constants at Various Temperatures for Riboflavin

(Rate for first order kinetics with 95% confidence level)

Temperature ^{o}C	$k \times 10^{4}$ s^{-1}	Correlation Coefficient R^2
110	0.021 ± 0.002	0.969
120	0.057 ± 0.006	0.956
129	0.100 ± 0.010	0.940
139	0.189 ± 0.014	0.966

TABLE 6.7 Activation Energy, Frequency Factor and Kinetic Reaction Rate at 129°C for Riboflavin(1)

	Two-Step Method	One-Step Method
Ea(2), kJ $mole^{-1}$ (kcal $mole^{-1}$)	99 ± 15 (23.6 ± 3.6)	105 ± 8 (25.0 ± 1.8)
$A \times 10^{-5}$, s^{-1}	594	1892
$k_{129^oC} \times 10^{4}$, s^{-1}	0.099	0.114

(1) R^2 for the two-step method was 0.989 and for the one-step method 0.999.

(2) Activation energy with 95% confidence level.

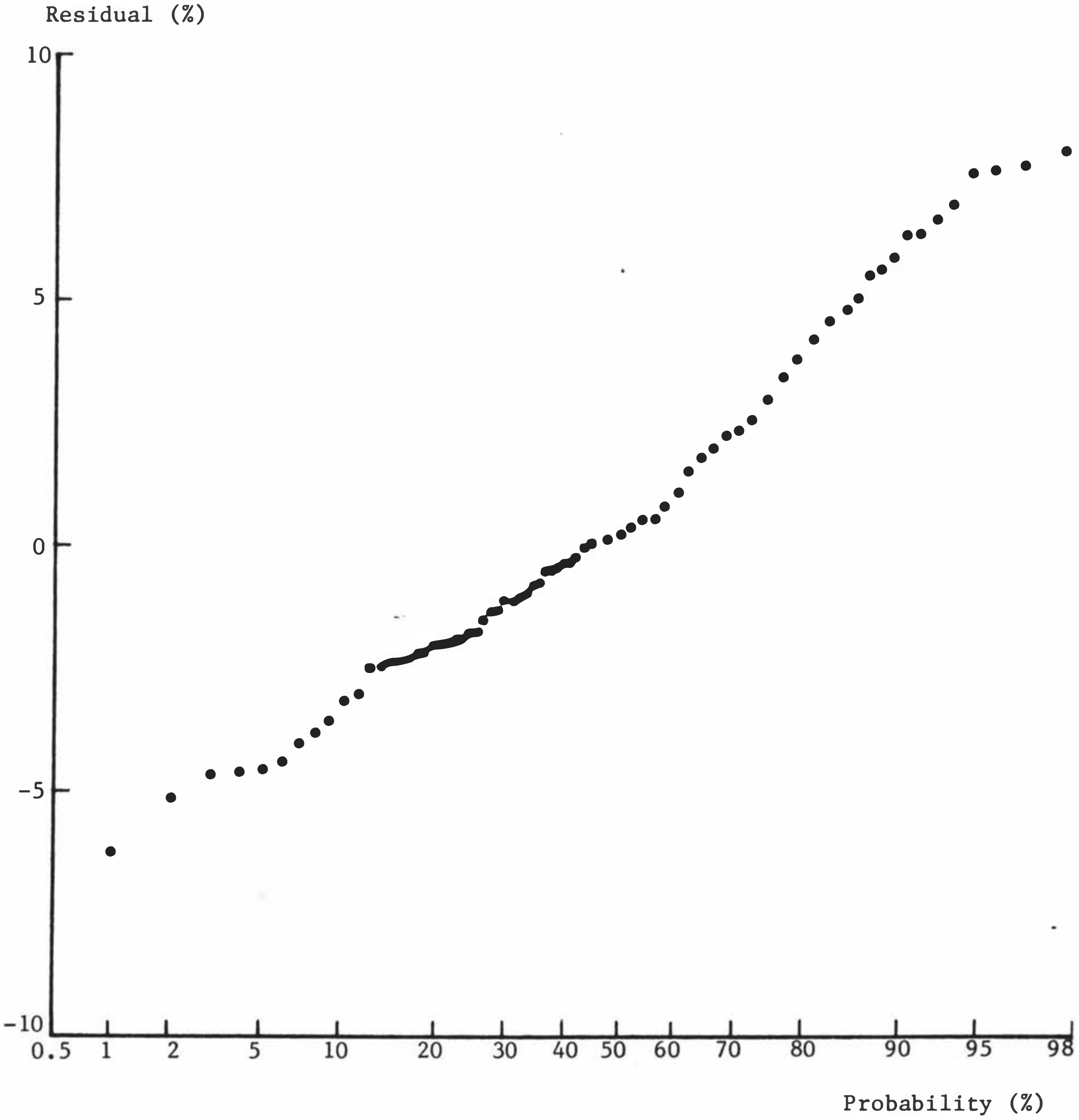


FIG. 6.6 Probability Plot of Calculated % Residual for Riboflavin

TABLE 6.8 Second Order Kinetic Reaction Rate Constants at Various Temperatures for Riboflavin

(Rate constant with 95% confidence level)

Temperature °C	k x 10^4 µg g^{-1} s^{-1}	Correlation Coefficient R^2
110	0.0008 ± 0.0000	0.971
120	0.0023 ± 0.0001	0.966
129	0.0042 ± 0.0002	0.946
139	0.0078 ± 0.0003	0.970

TABLE 6.9 Activation Energy, Frequency Factor, Kinetic Reaction Rate at 129°C for Second Order Kinetics for Riboflavin⁽¹⁾

	Two-Step Method	One-Step Method
Ea⁽²⁾, kJ $mole^{-1}$ (kcal $mole^{-1}$)	100 ± 14 (23.7 ± 3.5)	103 ± 7 (24.5 ± 1.7)
A x 10^{-5}, µg g^{-1} s^{-1}	33	102
k_{129^oC} x 10^4, µg g^{-1} s^{-1}	0.0041	0.0047

(1) R^2 for the two-step method was 0.990 and for the one-step method was 1.000.

(2) Activation energy with 95% confidence level.

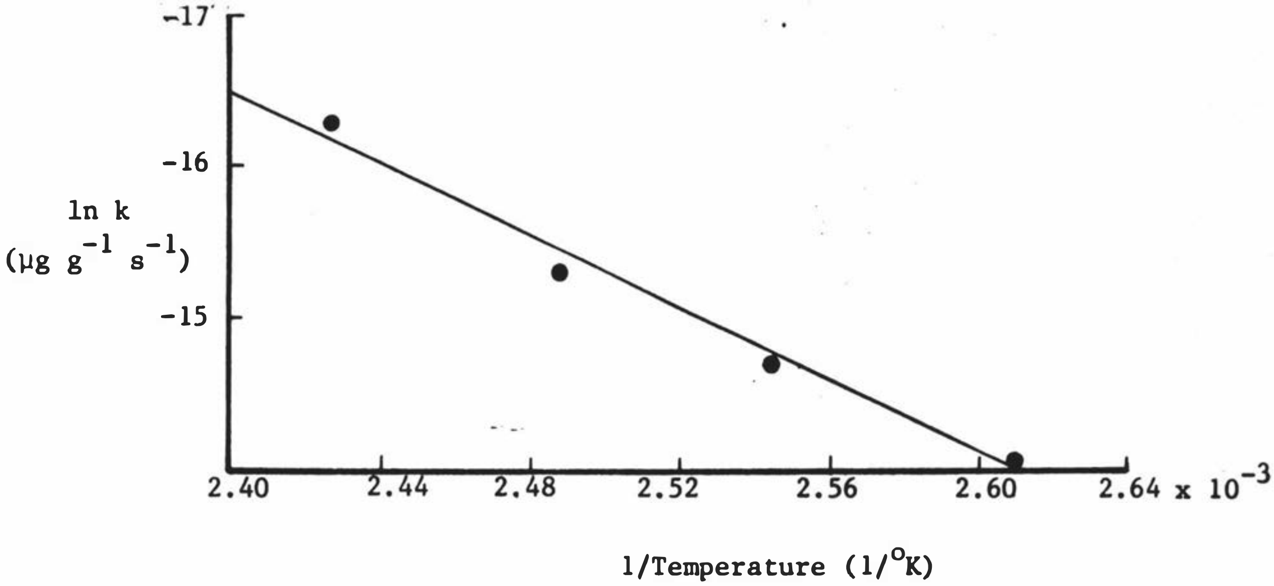


FIG. 6.7 Arrhenius Plot for Degradation of Riboflavin in Baby Food on Heating Described by Second Order Kinetics

The activation energies obtained from assuming first order and second order kinetics were almost the same. So it could be concluded that the activation energy of riboflavin was in the range of 96-113 kJ mole^{-1}. However, the k_{129^oC} was of course different and it was 0.114 x 10^{-4} s^{-1} for first order kinetics and was 0.0047 x 10^{-4} μg g^{-1} s^{-1} for second order kinetics.

6.6 COMPARISON OF KINETIC PARAMETERS DETERMINED BY STEADY-STATE AND UNSTEADY-STATE PROCEDURES

The kinetic parameters determined by the one-step method were compared with the parameters obtained from the unsteady-state procedure (Chapter 5).

6.6.1 Ascorbic Acid

The kinetic reaction rate constant at 129°C and the activation energy of ascorbic acid determined by the steady-state procedure (in tubes) and the unsteady-state procedure (in cans) are tabulated in Table 6.10.

TABLE 6.10 Comparison of Ea and k_{129^oC} for Ascorbic Acid Determined by Steady- and Unsteady-State Procedures

PROCEDURE OBSERVATION	STEADY-STATE (in tubes)	UNSTEADY-STATE (in cans)
Ea, kJ mole^{-1} (kcal mole^{-1})	85 ± 10 (20.3 ± 2.3)	81 (19.2)
k_{129^oC}, s^{-1}	0.418 x 10^{-4}	0.435 x 10^{-4}

The differences in the parameters determined as (absolute difference between procedures/average of these procedures), were 4% for k_{129^oC} and 5% for Ea. The activation energy of 81 kJ $mole^{-1}$ determined by the unsteady-state procedure, actually fell within the 95% confidence limits of that determined by the steady-state procedure. Therefore, it could be concluded that there was no significant difference between these two procedures. Thus, the computer program constructed in Chapter 5 for unsteady-state procedure was feasible and gave a reasonable result when the degradation was described by a first order reaction.

It could be concluded that in this food system, the loss of ascorbic acid on heat processing can be described by a first order reaction with k_{129^oC} 0.41-0.44 x 10^{-2} s^{-1} and Ea 85 $\pm$ 10 kJ $mole^{-1}$.

6.6.2 Riboflavin

Assuming first order kinetics, the activation energy and the k_{129^oC} were compared for unsteady-state and steady-state procedures (Table 6.11).

TABLE 6.11 Comparison of Ea and k_{129^oC} for Riboflavin Determined by Steady-and Unsteady-State Procedures
(assuming first order kinetics)

PROCEDURE OBSERVATION	STEADY-STATE (in tubes)	UNSTEADY-STATE (in cans)
Ea, kJ $mole^{-1}$ (kcal $mole^{-1}$)	105 $\pm$ 8 (25.0 $\pm$ 1.8)	84 (20.0)
k_{129^oC}, s^{-1}	0.114 x 10^{-4}	0.250 x 10^{-4}

The differences were higher than the ones found for ascorbic acid. The k_{129^oC} determined by the steady-state procedure was only 50% of that obtained by the unsteady-state procedure. The activation energy was closer, within about 22%, but was still outside the 95% confidence limit. The difference in the kinetic parameters determined by these two different methods could be caused by the assumption of a first order reaction. Therefore, the computer program for unsteady-state procedures for second order kinetics (Appendix 6.1) was used, and the k_{129^oC} and Ea of riboflavin were redetermined.

Starting at the same k_{129^oC} and Ea as in the steady-state heating, 0.0045×10^{-4} µg g^{-1} s^{-1} and 100.9 kJ $mole^{-1}$, increasing and decreasing the k_{129^oC} and Ea (Table 6.12), indicated that to obtain the minimum average residual a k_{129^oC} of higher than 0.0080×10^{-4} µg g^{-1} s^{-1} and an Ea of less than 92.4 kJ $mole^{-1}$ was necessary. The analysis was, therefore, stopped because these were nearly as far apart as the first order kinetic parameters determined for the unsteady-state and steady-state heating.

Assuming that the steady-state kinetic parameters were the more exact, the absolute residuals were determined for first order and second order kinetics at these values. For the first order kinetics, the absolute residual was determined from equation (5.20) and found to be 0.041 at the k_{129^oC} and Ea of 0.114×10^{-4} s^{-1} and 105 kJ $mole^{-1}$. For the second order kinetics, the absolute residual was 0.028 at the k_{129^oC} and Ea of 0.0045×10^{-4} µg g^{-1} s^{-1} and 101 kJ $mole^{-1}$. So the second order kinetics gave slightly better agreement between unsteady and steady state kinetic parameters.

However, the order of riboflavin degradation on heat processing was still doubtful. As the loss of riboflavin was very small with the maximum of only 15%, the plot of different forms of c and c_o against time, t, would therefore give virtually straight lines thus giving no indication of the exact order of reaction. Another problem was the error of analysis. Because riboflavin degradation was slow, prolonged heating was required and this could cause browning interference in the analysis as can be seen in section 6.3. The rate that the concentration of riboflavin decreased was slower at prolonged heating times. This error could significantly

TABLE 6.12 Average Residuals at Various k_{129^oC} and Ea for Riboflavin in Unsteady-State Heating in Can

$k_{129^oC} \times 10^4$ µg g^{-1} s^{-1}	Ea kJ $mole^{-1}$ (kcal $mole^{-1}$)	AVERAGE RESIDUAL	STANDARD DEVIATION
0.0040	75.6 (18.0)	0.0267	0.0115
	92.4 (22.0)	0.0292	0.0118
	109.2 (16.0)	0.0312	0.0121
0.0045	67.2 (16.0)	0.0224	0.0109
	84.0 (20.0)	0.0255	0.0112
	100.8 (24.0)	0.0280	0.0116
	117.6 (28.0)	0.0301	0.0120
0.0050	75.6	0.0214	0.0106
	92.4	0.0244	0.0110
	109.2	0.0269	0.0114
0.0060	75.6	0.0171	0.0076
	92.4	0.0201	0.0095
	109.2	0.0227	0.0108
0.0070	75.6	0.0127	0.0053
	92.4	0.0163	0.0070
	109.2	0.0192	0.0086
0.0080	92.4	0.0125	0.0052

effect the determination of k and Ea.

Therefore, it could be concluded that the effect of heat on riboflavin in the baby food was nutritionally not very significant under normal processing conditions as the loss of riboflavin was small. The exact order of destruction of riboflavin on heat processing could not be determined. Thus, the simplest form, zero order reaction kinetics, could have been used but this was not chosen as zero order is unlikely to be in fact correct. Also as the change, on heat processing, of food qualities and vitamins were mostly described by first order kinetics, and as the quality retention calculation program based on first order kinetics was available, it was sufficiently accurate for present purpose to estimate the final concentration of riboflavin after processing of baby food using first order kinetics. The high difference in the k_{121^oC} and Ea obtained from steady-state compared with the unsteady-state procedure was also found in Lenz (1977) for chlorophyll in spinach puree, where k_{121^oC} of 0.014 ± 0.004 and 0.029 ± 0.008 min^{-1} and the Ea of 80 and 97 kJ $mole^{-1}$ were reported for the steady-state and unsteady-state heating, respectively. Therefore it was concluded that the k_{129^oC} and Ea of $0.114-0.250 \times 10^{-4}$ s^{-1} and 84-105 kJ $mole^{-1}$ could safely be used for riboflavin assuming the first order kinetics.

6.7 CONCLUSION

Using the same food model, beef and mixed vegetables baby food, the kinetic reaction rate at 129°C and the activation energy of ascorbic acid and riboflavin were determined by a steady-state procedure where foods were heated in small glass vials in a thermostatically controlled oil bath in which instantaneous heating and cooling could be assumed. It was found that the degradation on heat processing of ascorbic acid could be best described by a first order reaction. The kinetic reaction rate at 129°C and the activation energy were 0.418×10^{-4} s^{-1} and 85 ± 10 kJ $mole^{-1}$. These were in a close agreement with the results from the unsteady-state procedure. Therefore, it was concluded that the computer program constructed in Chapter 5 was feasible and could give a reasonable result where the degradation could be described by a first order reaction.

However, for riboflavin, the determination of the kinetic parameters was difficult. The correlation coefficients (R^2) obtained from regression of various forms of initial and final concentration on heating time were higher than 0.94 but they were not significantly different. Marked differences between the k_{129^oC} and Ea for the unsteady-state and steady-state heating when determined for first order and second order kinetics were also found. For the steady-state heating, the k_{129^oC} and Ea determined for first order kinetics were 0.114×10^{-4} s^{-1} and 105 ± 8 kJ $mole^{-1}$ and for second order kinetics were 0.0047×10^{-4} $\mu g\ g^{-1}\ s^{-1}$ and 103 ± 7 kJ $mole^{-1}$. The k_{129^oC} were half as much and the Ea about 20 kJ $mole^{-1}$ more compared with the unsteady-state heating. These differences may have been caused by the very small loss of riboflavin in these experiments which made it difficult to calculate accurate kinetic parameters or may have been due to variations in other conditions in the cans and the tubes.

7. DISCUSSION

The two methods developed for studying the kinetics of changes in ascorbic acid, riboflavin, colour and viscosity during heat processing of a canned baby food were an unsteady-state procedure of heating in a can and a steady-state procedure of heating in a small tube . In using these methods, there are several points to consider.

7.1 TEMPERATURE PREDICTION IN THE CAN

Using the unsteady-state procedure, accurate temperature distribution prediction in the can is necessary. Analytical solutions and numerical finite difference methods gave nearly identical results and either can be used to predict temperatures. Generally, finite difference methods should be used because of the shorter computing time but where there is a need for form fitting because of an unusual temperature history in the can, the analytical solution is easier to manipulate.

In general, both analytical solutions and numerical finite difference methods gave a very good fit for most of the experimental temperatures. There was a consistent irregularity in the early stages of cooling and therefore temperature prediction was carried out by using the analytical solution for fitting the actual temperatures in the can. The predicted temperatures from the modified analytical program were compared with the experimental temperatures. The residual mean was found to vary from 0.1°C to 0.7°C with the standard deviation varying from 0.9°C to 1.7°C for overall process. These were considered sufficiently accurate as they were in the range found by Lenz (1977) as the biological variability of physical constants.

Prediction of the temperature in the early cooling stage could have been done by numerical finite difference method as the computing cost would be cheaper but there was no available instrument for measuring C and λ. Besides further investigations were needed to fully explain the phenomenon of the irregularity in the cooling curve.

7.2 USE OF STEADY-STATE KINETICS DATA TO PREDICT QUALITY CHANGES IN UNSTEADY-STATE HEAT PROCESSING

From the temperature distribution prediction, the quality retention can be determined if the kinetic data from steady-state determination are available. Knowing the order of the reaction kinetics, the kinetic reaction rate and the activation energy, quality retention can be calculated by numerical integration based on the predicted temperatures. If the calculated and the experimental quality retentions are similar, then the kinetic parameters can be assumed to be true for the unsteady-state heating conditions. This was certainly true for ascorbic acid, where k_{129^oC} and Ea, from the unsteady-state heating were 0.435×10^{-4} s^{-1} and 81 kJ $mole^{-1}$ and from steady-state heating were 0.418×10^{-4} s^{-1} and 85 ± 10 kJ $mole^{-1}$.

However, great care should be taken in assuming the steady-state kinetic paramcters are true in unsteady-state heat processing. As was seen in the riboflavin determination, there can be inaccuracies caused by low destruction rates and the assay method used. There can also be disagreement due to some changes in conditions between the two methods of heating.

Therefore, there should always be experimental determination of the quality loss in unsteady-state heat processing to confirm the predicted loss - two temperatures and two processing times are enough to confirm this for the temperature range and food composition studied.

7.3 KINETIC ANALYSIS USING UNSTEADY-STATE HEATING PROCEDURE

Assuming the order of reaction kinetics, the quality retention can be determined where standard k and Ea are unknown. The ranges of standard k and Ea have to be roughly estimated either from any data available on that property, or the data available on a similar property, and they have to be carefully chosen to cover the possible ranges of the actual standard k and Ea of that quality. Using an orthogonal composite design method to determine the empirical relationships of standard k, Ea and residual (difference in predicted and experimental retained quality), the standard k and Ea giving the lowest residual can be determined.

The experimental quality loss should be determined from using at least 2 processing temperatures and 3 processing times. More experimental runs can be carried out to get higher accuracy.

The order of reaction kinetics is usually first order, however the deviation from first order kinetics can also be accommodated in this procedure then the parameters can be determined using the same method of calculation.

If it is possible, the accuracy of the temperature prediction should be confirmed by studying of the known kinetics quality changes, for example, in this study, ascorbic acid determination confirmed the accuracy of temperature prediction and therefore gave a basis for the use of temperature prediction to determine the k_{129^oC} and Ea of the colour and viscosity by orthogonal composite design method

Where more than one quality was required, the estimation of parameters should start with the one with the most available information. Then, the rough ranges of k and Ea for other qualities could be estimated using the equivalent processing time method.

7.4 KINETIC PARAMETERS FOR ASCORBIC ACID, RIBOFLAVIN, COLOUR AND VISCOSITY IN HEAT PROCESSING OF BABY FOOD

For ascorbic acid, it was found that the degradation could be described by first order kinetics and the kinetic reaction rate at 129°C and the activation energy were 0.418×10^{-4} s^{-1} and 85 ± 10 kJ $mole^{-1}$ which were 4-5% different from those found in the unsteady-state procedure - 0.435×10^{-4} s^{-1} and 81 kJ $mole^{-1}$.

This activation energy was almost the same as found for anaerobic decomposition at pH 6.0 of ascorbic acid calculated from results of Huelin (1953) and Lin and Agalleco (1979). A higher activation energy of 172 kJ $mole^{-1}$ was reported by Lathrop and Leung (1980) for peas in can. This marked difference may be due to the environmental conditions such as moisture, pH and food product composition as well as the determination method. The kinetic reaction rate at 129°C of $0.418 \times 10^{-4}\ s^{-1}$ was also found by Garrett (1956) in liquid-multivitamin. This is also in an agreement with the kinetic reaction rate at 129°C of $0.263 \times 10^{-4} s^{-1}$ calculated from Lamb et al (1951) for canned tomato juice and tomato paste. Both higher and lower kinetic reaction rates were also reported. These variations were, again, due to the difference in environment as well as the method involved.

The activation energies of riboflavin thermodegradation were 105 ± 8 kJ $mole^{-1}$ with 95% confidence for steady-state heating procedure and 84 kJ $mole^{-1}$ for unsteady-state heating procedure. These were insignificantly different from the 97 kJ $mole^{-1}$ reported by Gillespy (1962). They were also fairly close to 78 kJ $mole^{-1}$ found for milk packed in gold-pigmented BMP (Singh et al, 1975). The kinetic reaction rates at 129°C, of $0.11 \times 10^{-4}\ s^{-1}$ (steady-state heating procedure) and of 0.25 $\times 10^{-4}\ s^{-1}$ (unsteady-state heating procedure) were also found to be comparable to the rates for canned green lima bean, whole kernel corn (Guerrant et al, 1945) and canned luncheon pork (Greenwood et al, 1944) when extrapolated to 129°C.

The reaction involved in colour change of baby food, consisting of beef, peas, potatoes, carrots, yeast extracts and flour, could possibly be mainly the non-enzymatic browning reaction. Chlorophyll destruction could be another minor reaction involved. The activation energy of 122 kJ $mole^{-1}$ found for colour change was comparable to the activation energies found for non-enzymatic browning reaction of liquid foods i.e. 87-113 kJ $mole^{-1}$ for apple juice (Hermann, 1970); 113 kJ $mole^{-1}$ for milk (Burton, 1963); 118-166 kJ $mole^{-1}$ for apple juice model system (Drilleau and Priouet, 1971). This was found to be higher than the activation energies reported for chlorophyll destruction (Table 2.5) with one exception of 135 kJ $mole^{-1}$ found for frozen Brussels sprouts during storage (Tijskens et al, 1979). The rate of reaction at 129°C of $1.2 \times 10^{-4}\ s^{-1}$ was much slower than the rate reported for milk by Burton (1963) and about half of the rate reported for apple juice by Hermann (1970). This could possibly be explained as the effect of food composition, pH, oxygen concentration as well as the method used in following the change of the colour. As there are at least 3 mechanisms that could possibly explain the development of brown colour, so the kinetic studies should be conducted for different food systems and should be applied for only similar food products in which the environmental factors such as composition, pH, oxygen concentration are almost the same. However, it could be concluded that the colour change was mainly the non-enzymatic browning reaction, the reaction rate constant at 129°C and the activation energy were $1.2 \times 10^{-4}\ s^{-1}$ and 122 kJ $mole^{-1}$.

For viscosity, there is little kinetic parameter information. The activation energy of 151 kJ $mole^{-1}$ for baby food is in a close agreement with the activation energies of 130, 103, 150 kJ $mole^{-1}$ reported for consistency change during heating in thin cans at 110-134°C of fish pudding, liver paste and vanilla sauce, respectively (Ohlsson, 1980).

7.5 APPLICATION TO PROCESSING

As foods are generally composite materials whose constituents change with processing, so these procedures for determining kinetic parameters and using them to follow process effects could be applied to optimisation of the heating process. Generally, there are several quality changes occurring together in heat processing and if the kinetic parameters can be determined in a specific food system, then the process can be studied to find the heating conditions which will give satisfactory microbiological safety together with acceptable nutritional and eating qualities. The relative importance of the constituents or properties would have to be related on some common basis and from this an optimum process or at least some preferred process could be sought. Once the equations are set up for the different parameters, the different heating systems can be compared very quickly.

8. CONCLUSIONS

To establish the kinetic parameters for changes of food during processing, the steady-state heating procedure should be used wherever possible as the analysis is simpler and gives more exact results. Also, the order of reaction kinetics can be directly determined. However, some food qualities require large amount of sample for analysis, e.g. colour, viscosity, flavour and the unsteady-state heating procedure must be used. The order of reaction, activation energy and the standard k can only be determined indirectly by using a systematic trial and error method.

In using kinetic data determined from steady-state studies to predict quality changes in food during unsteady-state heat processing, it is important to confirm the predicted changes with the experimental changes at at least two different times and temperatures.

The computer method, developed to predict temperatures at different points in the can at different times of heating to calculate the quality change, accurately determined the destruction of ascorbic acid in heat processing during can sterilization but did not so accurately predict riboflavin destruction. This was possibly due to the very small loss of riboflavin during can sterilization.

The computer method can be used to determine the unknown kinetic parameters by a systematic trial and error method but it is important that the method is first examined for accuracy in the particular food system by using a quality change with known kinetic parameters. After determining the accuracy of the method using the ascorbic acid destruction, it was possible to determine the Ea and k_{129^oC} for viscosity and colour.

It was concluded in this food system for the temperature ranges of 60-139^{o}C, the kinetic reaction rate at 129^{o}C and the activation energy were 0.42-0.44 x 10^{-4} s^{-1} and 77-85 kJ $mole^{-1}$, 0.11-0.25 x 10^{-4} s^{-1} and 84-105 kJ $mole^{-1}$, 1.20 x 10^{-4} s^{-1} and 122 kJ $mole^{-1}$ and 1.65 x 10^{-4} s^{-1} and 151 kJ $mole^{-1}$ for ascorbic acid, riboflavin, colour and viscosity respectively.

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APPENDIX 3.1 Analysis of Ascorbic Acid and Riboflavin

(a) Ascorbic Acid

Sample	Concentration mg g^{-1} x 10^{-2}			% Accuracy of duplication*
	1	2	3	
Control (1)	24.71(5)	25.47(7)	24.28(7)	1.8
Heated (1)	23.04(0)	22.06(5)	22.59(2)	1.5
Control (2)	23.58(0)	23.39(8)	22.91(9)	1.1
Heated (2)	21.12(0)	20.70(9)	21.03(7)	0.8
Control (3)	25.04(8)	24.92(8)	24.79(0)	0.3
Heated (3)	22.62(9)	22.43(8)	22.10(9)	0.8
			Average	1.1(5)

(b) Riboflavin

Sample	Concentration µg g^{-1}				% Accuracy of duplication*
	1	2	3	4	
Control (1)	26.22(0)	26.36(3)	26.10(0)	26.16(4)	0.4
Heated (1)	24.36(5)	26.14(0)	25.28(0)	24.81(5)	1.6
Control (2)	26.44(2)	25.77(6)	25.90(3)	26.49(5)	1.2
Heated (2)	24.32(4)	24.10(8)	25.00(8)	24.42(1)	1.1
Control (3)	25.66(9)	26.12(2)	26.13(4)	25.85(1)	0.7
Heated (3)	24.02(6)	24.00(7)	24.86(1)	24.07(3)	1.3
				Average	1.1(5)

* calculated as the mean of the % difference, defined as

$$\% \text{ difference} = \left|\frac{\text{observed concentration} - \text{mean concentration}}{\text{mean concentration}}\right|$$

APPENDIX 3.2 Analytical Method

(a) Ascorbic Acid

Instrument

Spectronic 20 spectrophotometer (Bausch & Lomb)

Reagents

Stock ascorbic acid solution:

Prepare 0.1% solution of ascorbic acid in 0.4% oxalic acid solution.

Working standards:

Take 20 ml of stock ascorbic acid solution and make up to 100 ml with 0.4% oxalic acid solution. Take 25, 20, 15, 10, 5 ml from the prepared solution and make up each to 100 ml with 0.4% oxalic acid solution (WS).

Stock dye solution:

Dissolve ca 200 mg of 2,6-Dichlorophenol indo phenol in 150 ml hot water containing 42 mg sodium bicarbonate, cool, dilute to 200 ml with distilled water. This solution will be stable for 5 weeks at 3°C.

Standard dye solution:

Take 12 ml of stock dye solution and make up to 1 litre with distilled water.

Standard Curve

To four absorptiometer tubes add the following

DW - 10 ml distilled water

No.1 - 1 ml 0.4% oxalic acid

S - 1 ml WS No.1 + 9 ml water

No.2 - 1 ml WS No.1

Adjust the Spectronic 20 to zero absorbance, using DW and a green filter of 520 nm. To tube No.1 add 9 ml of standard dye solution, mix and record the reading (L1) exactly 15 seconds after adding the dye. Then adjust the instrument to zero with tube S in the Spectronic 20.

To tube No.2, add 9 ml dye, mix and read after 15 seconds (L2). Record L1 and L2 for each working standard and construct the standard curve with concentrations of ascorbic acid as abcissae and (L1-L2) for each working standard as ordinates.

Method

Macerate 8-10 g of thawed sample with 70 ml 0.4% oxalic acid solution, dilute to exactly 100 ml in volumetric flask with 0.4% oxalic acid and then filter through No.4 Whatman filter paper. Obtain L1 as above. To tube S add 1 ml filtrate + 9 ml water and adjust the instrument to zero. Then to tube No.2 add 1 ml filtrate + 9 ml dye and record L2 after 15 seconds. Calculate (L1-L2) and obtain the concentration from the standard curve.

Remarks

(1) Use only distilled water from glass still.

(2) At least duplicate readings of L1 and triplicate readings of L2 are required. Average of L1 and L2 are used.

(3) In steady-state procedure where small sample size was obtained, 0.8-1.0 g sample was used and diluted to 10 ml. No.540 Whatman filter paper was used instead of No.4 because darker samples were obtained as the heating times used were longer than in unsteady-state procedure.

(b) Riboflavin

Instrument

Turner Fluorometer Model 111.

Primary filter of 110-816 (2A) plus 110-813(47B) where 2A is placed nearest to the lamp.

Secondary filter of 110-818 (2A-12).

Reagents

Riboflavin stock solution (100 µg ml^{-1}):

Dissolve 50 mg Riboflavin Reference Standard, previously dried and stored in dark in dessicator, in 0.02 M acetic acid to make 500 ml. Store under toluene at ca 10°C.

Riboflavin intermediate solution (10 µg ml^{-1}):

Dilute 10 ml stock solution to 100 ml with 0.02 M acetic acid. Store under toluene at ca 10°C.

Riboflavin working solution (1 µg ml^{-1});

Dilute 10 ml intermediate solution to 100 ml with distilled water. Prepare fresh for each assay.

4.0% $KMnO_4$ solution:

Dissolve 4.0 g of $KMnO_4$ in distilled water to make 100 ml. Prepare fresh weekly.

3.0% H_2O_2 solution:

Prepare fresh at the time of use.

Sodium Hydrosulfite:

High purity and stored to avoid undue exposure to light and air.

Method

Transfer a thawed sample of approximately 4 g[1] to a 125 ml erlenmeyer flask, add about 75 ml 0.1 M HCl. Agitate vigorously and wash down sides of flask with 0.1 M HCl.

Heat mixture in autoclave at 121-123°C 30 min and cool. Adjust, with vigorous agitation, to pH 6.0-6.5 with 1 M NaOH solution; then immediately add 1 M HCl to pH about 4.5.

Dilute mixture to exactly 100 ml in volumetric flask with distilled water. Centrifuge and then filter through ash-free filter paper (Whatman filter paper No.41).

Take 25 ml[2] filtrate and check for dissolved protein by adding dropwise, first 1 M HCl, and if no precipitation forms, then, with vigorous agitation, 1 M NaOH to pH 6.8, dilute solution to exactly 100 ml with distilled water in volumetric flask. If further precipitation occur, continue as in AOAC. Dilute 5 ml of this solution to exactly 100 ml with distilled water[3].

To each of ≥ 4 tubes, add 10 ml sample solution. To each of ≥ 2 tubes add 1 ml standard working solution and mix and to each of ≥ 2 remaining tubes, add 1 ml distilled water and mix.

To each tube, add 1 ml glacial acetic acid and mix; add, with mixing, 0.5 ml 4.0% $KMnO_4$ solution. Stand for exactly 2 min; then to each tube add, with mixing, 0.5 ml 3.0% H_2O_2 solution; permanganate colour must be destroyed within 10 s. Shake vigorously until excess O is expelled.

Measure fluorescence of sample solution containing 1 ml added standard riboflavin working solution as X and of the sample solution containing 1 ml added water as B. Add, with mixing, 20 mg powder $Na_2S_2O_4$ to the sample solution containing added water, measure fluorescence within 5 s as C.

Calculation of concentration ($\mu g\ g^{-1}$)[4]

$$= \frac{B-C}{X-B} \times 0.1 \times \frac{800}{W}$$

where W is sample weight (g)

Remarks (for riboflavin analysis of samples from steady-state procedure)

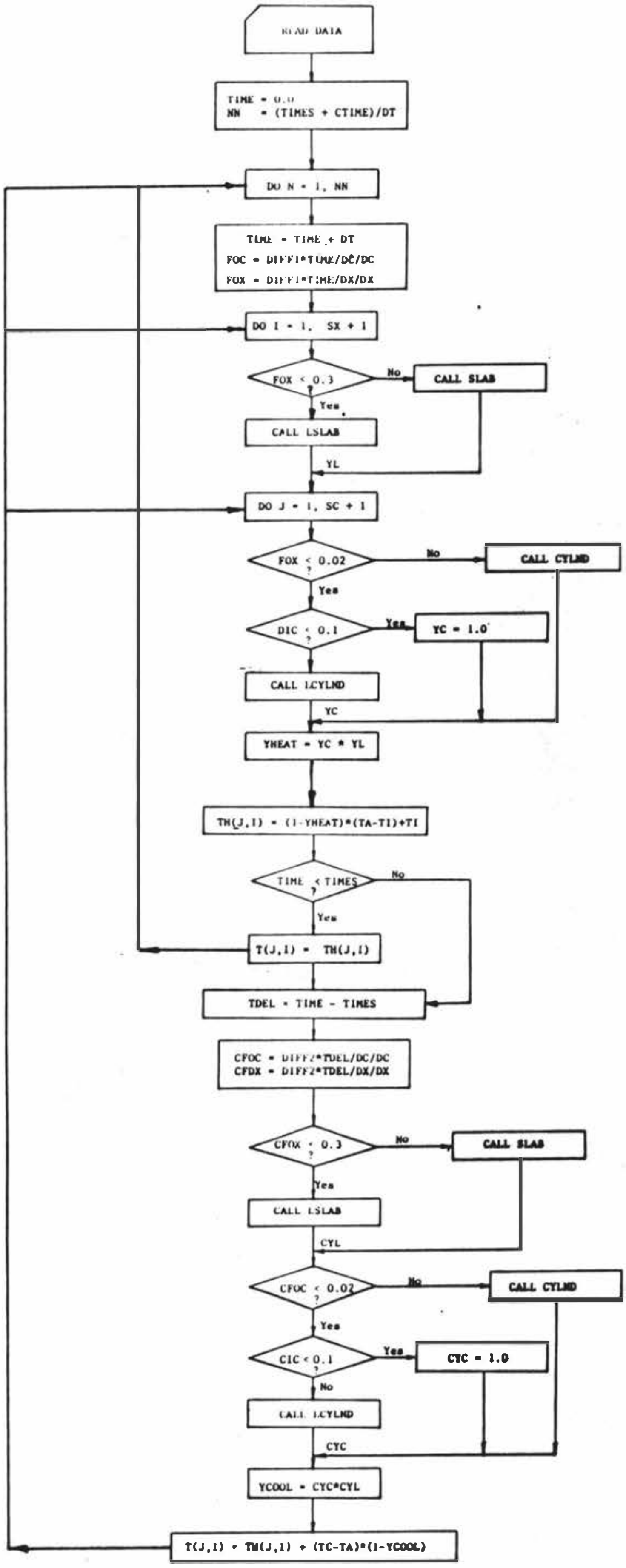
(1) use 0.8 g
(2) take 50-75 ml
(3) omit this step
(4) concentration ($\mu g\ g^{-1}$) $= \frac{B-C}{X-B} \times 0.1 \times \frac{200}{W}$

APPENDIX 3.3 x, y and Y of Control and Heated Samples

Sample	x	y	Y
Control	0.40	0.40	23.60
Heated, $F^{10}_{121.1}$ = 6.25	0.43	0.42	21.60
Control	0.40	0.40	23.30
Heated, $F^{10}_{121.1}$ = 9.47	0.43	0.42	20.20
Control	0.40	0.40	22.98
Heated, $F^{10}_{121.1}$ = 13.47	0.43	0.42	19.50
Control	0.40	0.40	23.27
Heated, $F^{10}_{121.1}$ = 16.62	0.43	0.42	18.85
Control	0.40	0.40	24.50
Heated, $F^{10}_{121.1}$ = 22.86	0.43	0.42	18.70

APPENDIX 4.1 Analytical Solution Computer Program

(a) Flow Chart of the Program



(b) Computer Program

```
      DIMENSION T(50,50),TH(50,50),B(10),XJIB(10),BRA(10),XJOB(10)
      COMMON XJ0(200),ARG(200)
      DATA ARG/0.0,0.1,0.2,0.3,0.4,0.5,0.6,0.7,0.8,0.9,1.0,
     * 1.1,1.2,1.3,1.4,1.5,1.6,1.7,1.8,1.9,2.0,
     * 2.1,2.2,2.3,2.4,2.5,2.6,2.7,2.8,2.9,3.0,3.1,3.2,3.3,3.4,3.5,
     * 3.6,3.7,3.8,3.9,4.0,4.1,4.2,4.3,4.4,4.5,4.6,4.7,4.8,4.9,5.0,
     * 5.1,5.2,5.3,5.4,5.5,5.6,5.7,5.8,5.9,6.0,6.1,6.2,6.3,6.4,6.5,
     * 6.6,6.7,6.8,6.9,7.0,7.1,7.2,7.3,7.4,7.5,7.6,7.7,7.8,7.9,8.0,
     * 8.1,8.2,8.3,8.4,8.5,8.6,8.7,8.8,8.9,9.0,9.1,9.2,9.3,9.4,9.5,
     * 9.6,9.7,9.8,9.9,10.0,10.1,10.2,10.3,10.4,10.5,10.6,10.7,10.8,
     *10.9,11.0,11.1,11.2,11.3,11.4,11.5,11.6,11.7,11.8,11.9,12.0,
     *  12.1,12.2,12.3,12.4,12.5,12.6,12.7,12.8,12.9,13.0
     * ,13.1,13.2,13.3,13.4,13.5,13.6,13.7,13.8,13.9,14.0,14.1,14.2,
     * 14.3,14.4,14.5,14.6,14.7,14.8,14.9,0.0,0.0,0.0,0.0,0.0/
      DATA XJ0/1.0,0.9975,0.9900,0.9776,0.9604,0.9385,0.9120,
     * 0.8812,0.8463,0.8075,0.7652,0.7196,0.6711,0.6201,0.5669,
     * 0.5118,0.4554,0.3980,0.3400,0.2818,0.2239,0.1666,0.1104,
     *  0.0555,0.0025,-0.0484,-0.0968,-0.1424,-0.1850,-0.2243,
     * -0.2601,-0.2921,-0.3202,-0.3443,-0.3643,-0.3801,
     * -0.3918,-0.3992,-0.4026,-0.4018,-0.3971,-0.3887,
     * -0.3766,-0.3610,-0.3423,-0.3205,-0.2916,-0.2693,-0.2404,
     * -0.2097,-0.1776,-0.1443,-0.1103,-0.0758,-0.0412,-0.0068,
     * 0.0270,0.0599,0.0917,0.1220,0.1506,0.1773,0.2017,0.2238,
     * 0.2433,0.2601,0.2740,0.2851,0.2931,0.2981,0.3001,0.2991,
     * 0.2951,0.2882,0.2786,0.2663,0.2516,0.2346,0.2154,0.1944,
     * 0.1717,0.1475,0.1222,0.0960,0.0692,0.0419,0.0146,
     * -0.0125,-0.0392,-0.0653,-0.0903,-0.1142,-0.1367,-0.1577,
     * -0.1768,-0.1939,-0.2090,-0.2218,-0.2323,-0.2403,-0.2459,
     * -0.2490,-0.2496,-0.2477,-0.2434,-0.2366,-0.2276,-0.2164,
     * -0.2032,-0.1881,-0.1712,-0.1528,-0.1330,-0.1121,-0.0902
     * ,-0.0677,-0.0446,-0.0213,0.0020,0.0250,0.0477,0.0697,
     * 0.0908,0.1108,0.1296,0.1469,0.1626,0.1766,0.1887,0.1988,
     * 0.2,0.2129,0.2167,0.2183,0.2177,0.2150,0.2101,0.2032,
     * 0.1943,0.1836,0.1711,0.1570,0.1414,0.1245,0.1065,0.0875,
     * 0.0679,0.0476,0.0271,0.0064,1.0,1.0,1.0,1.0,1.0/
      DATA B/2.4048,5.5201,8.6537,11.7915,14.9309,18.0711,0.,0.,0./
      DATA XJIB/0.5191,-0.3403,0.2715,-0.2325,0.2066,-0.1890,0.,0.,0./
      READ(5,/)DC,DX,DIFF1,DIFF2,DT,SC,SX,TI,TA,TC,TIMES,CTIME
      WRITE(6,30)DIFF1,DIFF2,TI,TA,TC
      WRITE(6,39)DC,2.0*DX,1/SC,1/SX
   30 FORMAT(1H0,"  THERMAL DIFFUSIVITY IN HEATING PHASE(MM/S)=",
     *  F12.10,//,"  THERMAL DIFFUSIVITY IN COOLING PHASE(MM/S)=",
     *  F12.10,//,"  INITIAL TEMPERATURE(C)=",F12.2,//
     *  "   RETORT TEMPERATURE(C)=",F12.2,//
     *  "     COOLING TEMPERATURE(C)=",F12.2,//)
```

```
 39  FORMAT("    CAN RADIUS(M)=",F12.5,/
 *    "    CAN HEIGHT(M)=",F12.5,/
 *    "    SIZE OF DIMENSIONLESS SPACE INCREMENT IN R DIRECTION=",
 *    F12.5,/
 *    "  SIZE OF DIMENSIONLESS SPACE INCREMENT IN X DIRECTION=",
 *    F12.5,///
 *    "    TEMPERATURE DISTRIBUTION IN A CAN"///)
     TIME=0
     NN=(TIMES+CTIME)/DT
     DO 42 N=1,NN
     TIME=TIME+DT
     FOC=DIFF1*TIME/DC/DC
     FOX=DIFF1*TIME/DX/DX

     DO 58 I=1,SX+1
     DIX=FLOAT(I-1)/SX
     IF(FOX.LT.0.03)GO TO 110
     CALL SLAB(FOX,YL,DIX)
    GO TO 80
110   XL=DIX*DX
        CALL LSLAB(FOX,YL,DX,XL)
 80   DO 59 J=1,SC+1
     DIC=FLOAT(J-1)/SC
     IF(FOC.LT.0.02)GO TO 120
     DO 49 JJ=1,6
 49   BRA(JJ)=B(JJ)*DIC
     CALL CYLND(FOC,YC,B,BRA,XJOB,XJIB)
     GO TO 90
120   IF(DIC.LT.0.1)GO TO 100
     R=DC*DIC
     CALL LCYLND(FOC,YC,DC,R)
     GO TO 90
 100   YC=1.0
 90   YHEAT=YC*YL
     TH(J,I)=(1-YHEAT)*(TA-TI)+TI
     IF(TIME.LE.TIMES)GO TO 200
     TDEL=TIME-TIMES
     CFOC=DIFF2*TDEL/DC/DC
     CFOX=DIFF2*TDEL/DX/DX
     CIX=DIX
     IF(CFOX.LT.0.03)GO TO 145
     CALL SLAB(CFOX,CYL,CIX)
     GO TO 155
145   CXL=CIX*DX
     CALL LSLAB(CFOX,CYL,DX,CXL)
155   CIC=DIC
     IF(CFOC.LT.0.02)GO TO 165
```

```
      DO 55 JJ=1,6
   55  BRA(JJ)=B(JJ)*CIC
      CALL CYLND(CFOC,CYC,B,BRA,XJOB,XJIB)
      GO TO 175
  165  IF(CIC.LT.0.1)GO TO 185
       CR=DC*CIC
      CALL LCYLND(CFOC,CYC,DC,CR)
      GO TO 175
  185 CYC=1.0
  175 YCOOL=CYC*CYL
      T(J,I)=TH(J,I)+(TC-TA)*(1-YCOOL)
      GO TO 58
  200 T(J,I)=TH(J,I)
   58 CONTINUE
      WRITE(6,59)TIME
   59 FORMAT(//"    TIME(S)=",F12.2,//
    * "      X DIRECTION ACROSS, R DIRECTION DOWN"//)
      DO 60 J=1,SC+1
   60 WRITE(6,79)(T(J,I),I=1,SX+1)
   79 FORMAT(12F10.2)
   42 CONTINUE
      STOP
      END
      SUBROUTINE CYLND(FO,YC,B,BRA,XJOB,XJIB)
      DIMENSION B(10),XJIB(10),BRA(10),XJOB(10)
      COMMON XJO(200),ARG(200)
      DO 1 I=1,6
      IF(BRA(I).GT.14.89)GO TU 3
      DO 2 J=1,152
      IF(BRA(I)-ARG(J))5,4,2
    2 CONTINUE
    4 XJOB(I)=XJO(J)
      GO TO 1
    5 IF(J.GT.1)J=J-1
      XJOB(I)=XJO(J)+(XJO(J+1)-XJO(J))/(ARG(J+1)-ARG(J))*
    * (BRA(I)-ARG(J))
      GO TO 1
    3 XJOB(I)=(0.7979/BRA(I))**0.5*(COS(BRA(I)-0.7854)+0.125/
    * BRA(I)*SIN(BRA(I)-C.7854))
    1 CONTINUE
      YC=0
      DO 6 I=1,6
    6 YC=YC+2.0*XJOB(I)/B(I)/XJIB(I)*EXP(-B(I)**2*FO)
      RETURN
      END
```

```
      SUBROUTINE SLAB(FO,YL,D)
      YL=1.2732395*(COS(1.57143*D)*EXP(-FO*2.467401)+
     * (-1)/3.0*COS(3.0*1.57143*D)*EXP(-9.0*FO*2.467401)+
     * (+1)/5.0*COS(5.0*1.57143*D)*EXP(-25.0*FO*2.467401)+
     * (-1)/7.0*COS(7.0*1.57143*D)*EXP(-49.0*FO*2.467401)+
     * (+1)/9.0*COS(9.0*1.57143*D)*EXP(-81.0*FO*2.467401)+
     * (-1)/11.0*COS(11.0*1.57143*D)*EXP(-121.0*FO*2.467401))
      RETURN
      END
      SUBROUTINE LCYLND(FO,YC,DC,R)
      X=(DC-R)/2.0/(FO*DC**2.0)**0.5
      A=ERFN(X)
      E1=0.56428958*EXP(-X*X)-X*A
      X2=X+X
      E2=0.25*(A-X2*E1)
      YC=1-((DC/R)**0.5*A+(DC-R)*(FO*DC**3.0)**0.5/4/
     * DC/R**1.5*E1+(9*DC**2.0-7.0*R**2.0-2.0*DC*R)/
     * (32.0*DC**1.5*R**2.5)*FO*DC**2.0*E2)
      RETURN
      END
      SUBROUTINE LSLAB(FO,YL,DX,XL)
      YL=1.0
      XFO=(FO*DX**2.0)**0.5
      DO 102 I=1,3
      N=I-1
       Y1=((2*N+1)*DX-XL)/2.0/XFO
       Y2=((2*N+1)*DX+XL)/2.0/XFO
  102  YL=YL-((-1)**N*(ERFN(Y1)+ERFN(Y2)))
       RETURN
       END
       FUNCTION ERFN(X)
       DATA P,A1,A2,A3,A4,A5/0.3275911,0.25482959,-0.28449674,
      * 1.42141374,-1.45315203,1.06140543/
       IF(X.GT.0.0)GO TO 13
       X=(-1)*X
   13  T1=1.0/(1+P*X)
       T2=T1*T1
       T3=T2*T1
       T4=T3*T1
       T5=T4*T1
       ERFN=EXP(-X*X)*(A1*T1+A2*T2+A3*T3+A4*T4+A5*T5)
       RETURN
       END
```

```
      DIMENSION T(50,50),TI(50,50)
       REAL K
      READ(5,/)DR,DX,DIFF1,DIFF2,DELTA,NN,MM,TIN,TAH,TAC,TIMEH
     *,TIMEC,FREQ
      WRITE(6,1)DIFF1,DIFF2,TIN,TAH,TAC
    1 FORMAT(1H0,"  THERMAL DIFFUSIVITY IN HEATING PHASE(MM/S)=",
     *F12.10,//
     *"  THERMAL DIFFUSIVITY IN COOLING PHASE(MM/S)=",F12.10,//
     *"  INITIAL TEMPERATURE(C)=",F12.2,//
     *" RETORT TEMPERATURE(C)=",F12.2,//
     *"  COOLING TEMPERATURE(C)=",F12.2,//)
      DELX=DX/FLOAT(MM-1)
      DELR=DR/FLOAT(NN-1)
      WRITE(6,2)DR,DX*2,DELR,DELX
    2 FORMAT("   CAN RADIUS(M)=",F12.5,//
     *"    CAN HEIGHT(M)=",F12.5,//
     *"    SIZE OF DIMENSIONLESS SPACE INCREMENT IN R DIRECTION=",
     *F12.5,//
     *"    SIZE OF DIMENSIONLESS SPACE INCREMENT IN X DIRECTION=",
     *F12.5,////
     *"     TEMPERATURE DISTRIBUTION IN A CAN"///)
      PR=FREQ/DELTA
      TIME =0.0
      DO 10 M=1,MM-1
      DO 10 N=1,NN-1
   10 TI(M,N)=TIN
      DO 20 M=1,MM
      TI(M,NN)=TAH
   20 T(M,NN)=TAH
      DO 30 N=1,NN
      TI(MM,N)=TAH
   30 T(MM,N)=TAH
      LL=0.0
      CHANGE=TIMEH/DELTA
      DO 40 I=1,CHANGE
      DO 50 N=2,NN-1
      DO 50 M=2,MM-1
   50 T(M,N)=(DIFF1*((TI(M+1,N)-2*TI(M,N)+TI(M-1,N))/(DELX**2.0))+
     *DIFF1*((TI(M,N+1)-2*TI(M,N)+TI(M,N-1))/DELR**2.0)+
     *DIFF1/FLOAT(N-1)*((TI(M,N+1)-TI(M,N-1))/(2*DELR**2.0)))*DELTA+
     *TI(M,N)
      DO 60 N=2,NN-1
   60 T(1,N)=(DIFF1*((2*TI(2,N)-2*TI(1,N))/DELX**2.0)+
     *DIFF1*((TI(1,N+1)-2*TI(1,N)+TI(1,N-1))/DELR**2.0)+
     *DIFF1/FLOAT(N-1)*((TI(1,N+1)-TI(1,N-1))/(2*DELR**2.0)))*DELTA+
     *TI(1,N)
```

```
      DO70 M=2,MM-1
   70 T(M,1)=(DIFF1*((TI(M+1,1)-2*TI(M,1)+TI(M-1,1))/DELX**2.0)+2.0*
     *DIFF1*((2*TI(M,2)-2*TI(M,1))/DELR**2.0))*DELTA+TI(M,1)
      T(1,1)=(DIFF1*((2*TI(2,1)-2*TI(1,1))/DELX**2.0)+2.0*
     *DIFF1*((2*TI(1,2)-2*TI(1,1))/DELR**2.0))*DELTA+TI(1,1)
      DO 80 N=1,NN-1
      DO 80 M=1,MM-1
   80 TI(M,N)=T(M,N)
      TIME=TIME+DELTA
      LL=LL+1
      IF(LL.LT.PR)GO TO 40
      LL=0

      WRITE(6,3)TIME
    3 FORMAT(//"   HEATING TIME(S)=",F12.2,//
     *"     X DIRECTION ACROSS, R DIRECTION DOWN"//)
      DO 90 N=1,NN
   90 WRITE(6,4)(TI(M,N),M=1,MM)
    4 FORMAT(12F10.2)
   40 CONTINUE
      TIME=0.0
      LL=0.0
      CHANGE=TIMEC/DELTA
      DO 5 M=1,MM
      TI(M,NN)=TAC
    5 T(M,NN)=TAC
      DO 15 N=1,NN
      TI(MM,N)=TAC
   15 T(MM,N)=TAC
      DO 140 I=1,CHANGE
      DO 150 N=2,NN-1
      DO 150 M=2,MM-1
  150  T(M,N)=(DIFF2*((TI(M+1,N)-2*TI(M,N)+TI(M-1,N))/(DELX**2.0))+
     * DIFF2*((TI(M,N+1)-2*TI(M,N)+TI(M,N-1))/DELR**2.0)+
     * DIFF2/FLOAT(N-1)*((TI(M,N+1)-TI(M,N-1))/(2*DELR**2.0)))*DELTA+
     * TI(M,N)
      DO 160 N=2,NN-1
  160  T(1,N)=(DIFF2*((2*TI(2,N)-2*TI(1,N))/DELX**2.0)+
     * DIFF2*((TI(1,N+1)-2*TI(1,N)+TI(1,N-1))/DELR**2.0)+
     * DIFF2/FLOAT(N-1)*((TI(1,N+1)-TI(1,N-1))/(2*DELR**2.0)))*DELTA+
     * TI(1,N)
      DO 170 M=2,MM-1
  170  T(M,1)=(DIFF2*((TI(M+1,1)-2*TI(M,1)+TI(M-1,1))/DELX**2.0)+2.0*
     * DIFF2*((2*TI(M,2)-2*TI(M,1))/DELR**2.0))*DELTA+TI(M,1)
      T(1,1)=(DIFF2*((2*TI(2,1)-2*TI(1,1))/DELX**2.0)+2.0*
```

```
     *   DIFF2*((2*TI(1,2)-2*TI(1,1))/DELR**2.0))*DELTA+TI(1,1)
         DO 180 N=1,NN-1
         DO 180 M=1,MM-1
 180      TI(M,N)=T(M,N)
         TIME=TIME+DELTA
         LL=LL+1
         IF(LL.LT.PR)GO TO 140
         LL=0
         WRITE(6,13)TIME
 13       FORMAT(//"   COOLING TIME(S)=",F12.2,//
     *   "     X DIRECTION ACROSS, R DIRECTION DOWN"//)
         DO 190 N=1,NN
 190      WRITE(6,4)(TI(M,N),M=1,MM)
 140     CONTINUE
         STOP
         END
```

APPENDIX 4.3 Thermal Diffusivity Determination Results

Run No.	Retort (^oC) Temperature	Thermal Diffusivity x 10^7 m^2s^{-1}	Mean Thermal Diffusivity x 10^7 m^2s^{-1}	Standard Deviation x 10^7 m^2s^{-1}
7	120.2	1.5491	1.5429	0.0196
3	119.5	1.5511		
4	119.6	1.5090		
9	120.0	1.5459		
2	119.8	1.5593		
6	129.1	1.5305	1.5277	0.0318
1	128.7	1.4916		
8	128.6	1.5694		
5	129.2	1.5452		
10	129.1	1.5016		
		TOTAL MEAN m^2s^{-1}	1.5353×10^{-7}	
		STANDARD DEVIATION m^2s^{-1}	0.0261×10^{-7}	

Test of Significant Difference Between Means

$\bar{x}_1 = 1.5429$ $\quad s_1 = 0.0196$ $\quad n_1 = 5$

$\bar{x}_2 = 1.5277$ $\quad s_2 = 0.0318$ $\quad n_2 = 5$

$$s = \sqrt{\frac{4(0.0196)^2 + 4(0.0318)^2}{8}}$$

$$= 0.02639317$$

$$S.E = 0.02639317 \sqrt{\frac{1}{5} + \frac{1}{5}}$$

$$= 0.01169$$

$$t = \frac{1.5429 - 1.5277}{0.01169}$$

$$= 0.9102$$

Therefore, there is no significant difference betweeen these two means.

APPENDIX 4.4 Distribution of Residuals for Determining Accuracy of the Analytical Solution for Calculating Temperatures

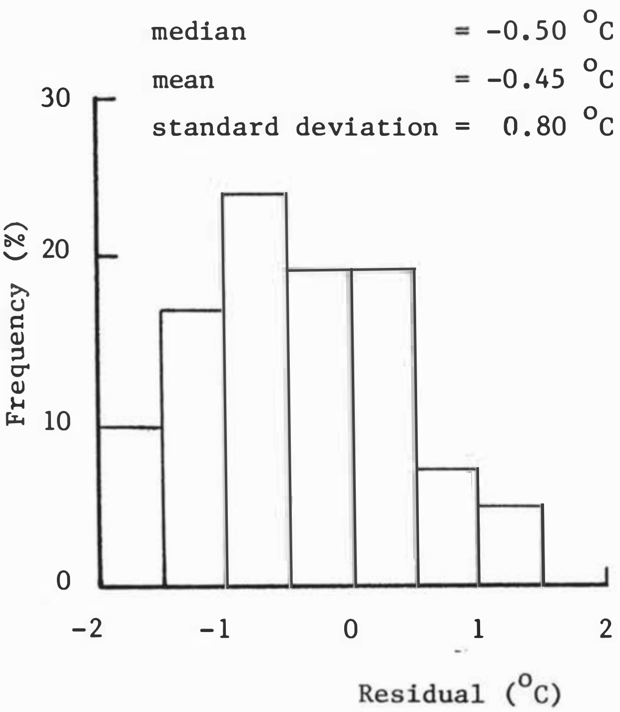
(a) In the Heating Phase

Run no.6

median = -0.50 °C

mean = -0.45 °C

standard deviation = 0.80 °C

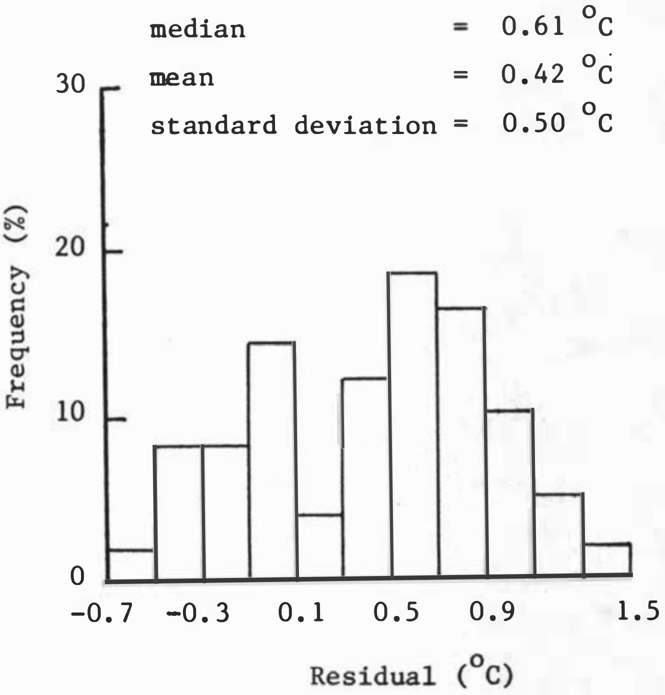


Run no.8

median = 0.61 °C

mean = 0.42 °C

standard deviation = 0.50 °C

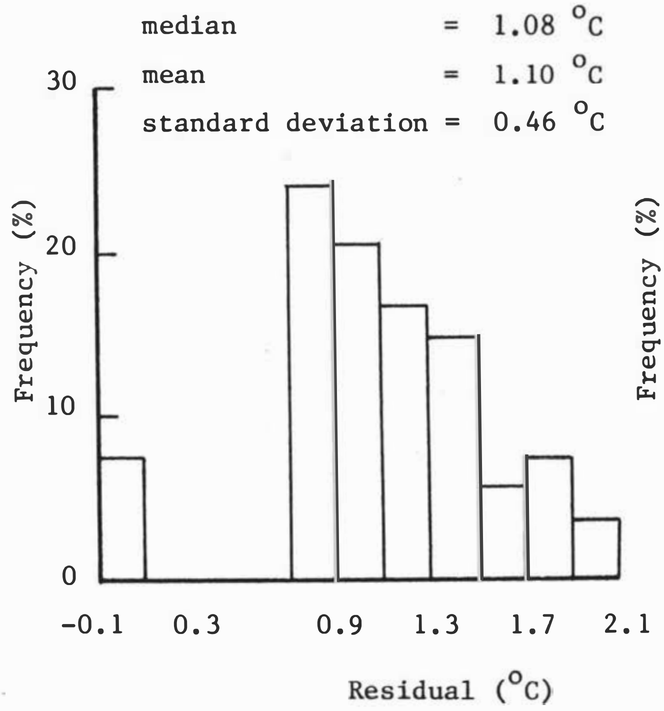


Run no.7

median = 1.08 °C

mean = 1.10 °C

standard deviation = 0.46 °C

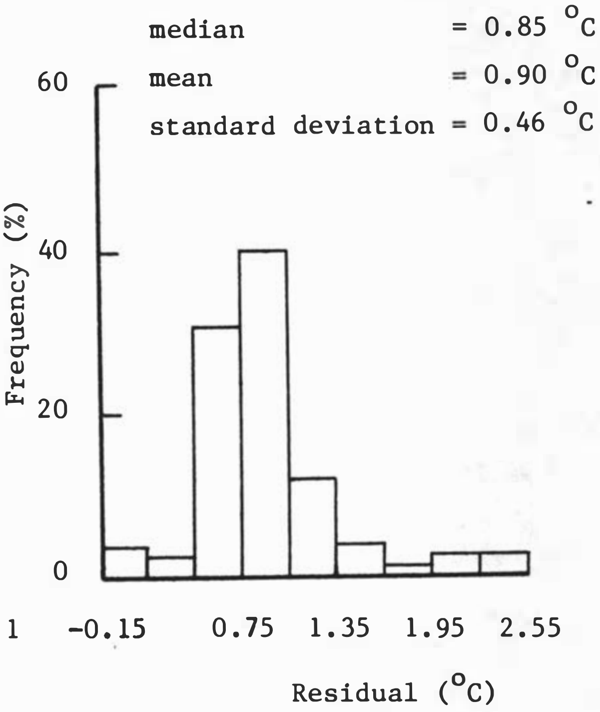


Run no.9

median = 0.85 °C

mean = 0.90 °C

standard deviation = 0.46 °C



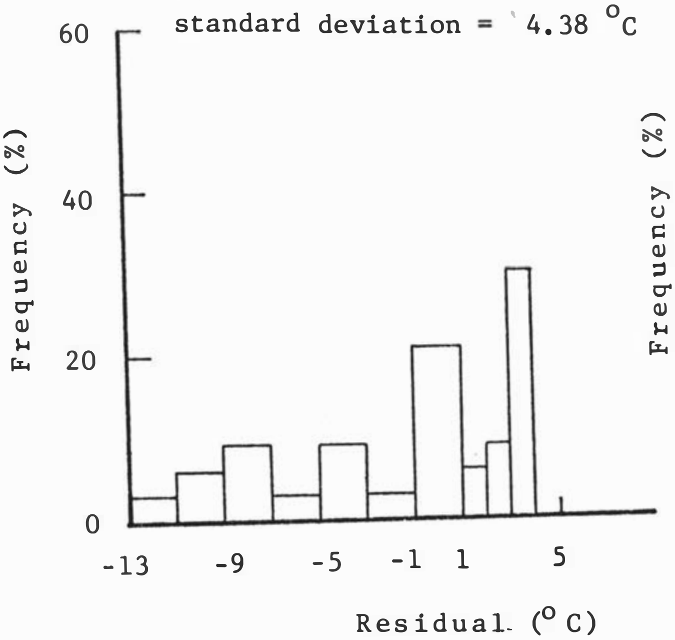
(b) In the Cooling Phase

Run no.6

median = -0.57 °C

mean = -3.00 °C

standard deviation = 4.38 °C

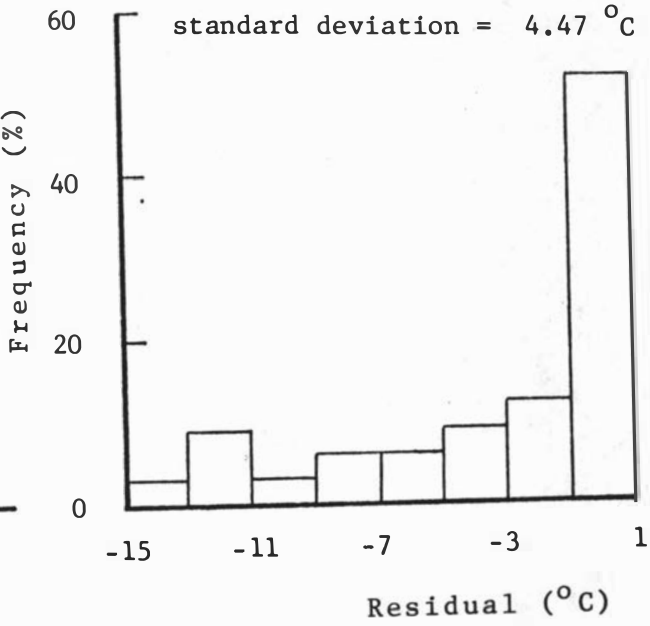


Run no.8

median = -0.94 °C

mean = -3.27 °C

standard deviation = 4.47 °C

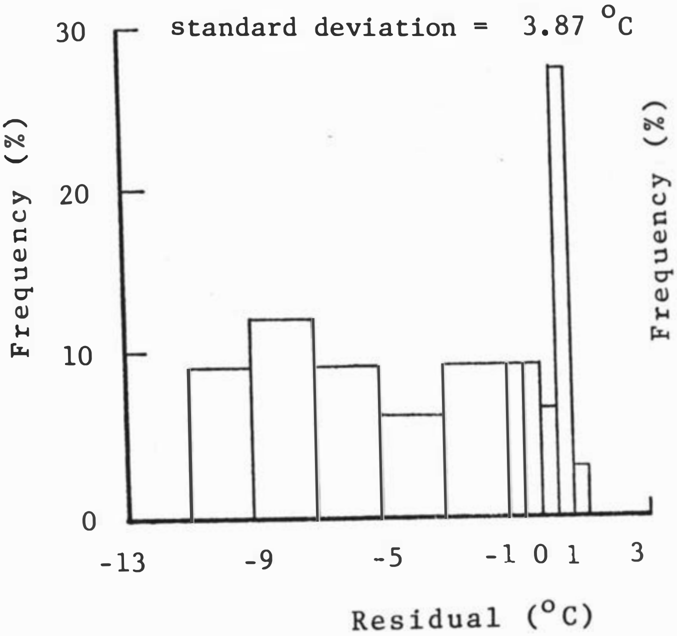


Run no.7

median = -0.82 °C

mean = -2.68 °C

standard deviation = 3.87 °C

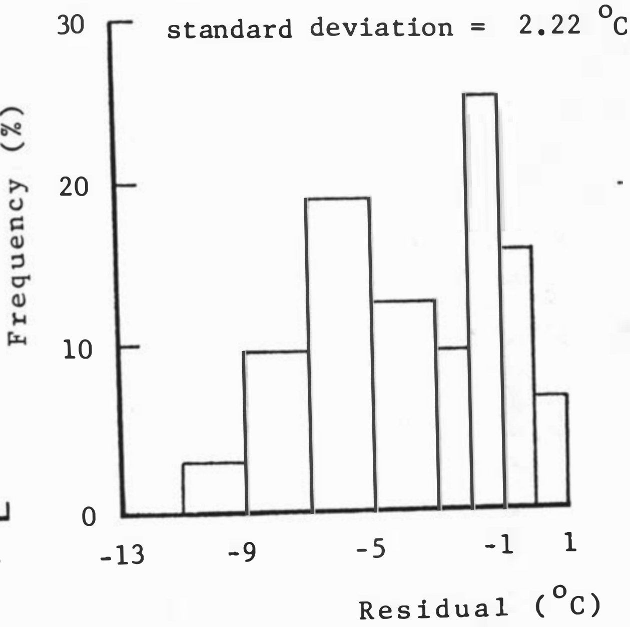


Run no.9

median = -2.64 °C

mean = -3.30 °C

standard deviation = 2.22 °C



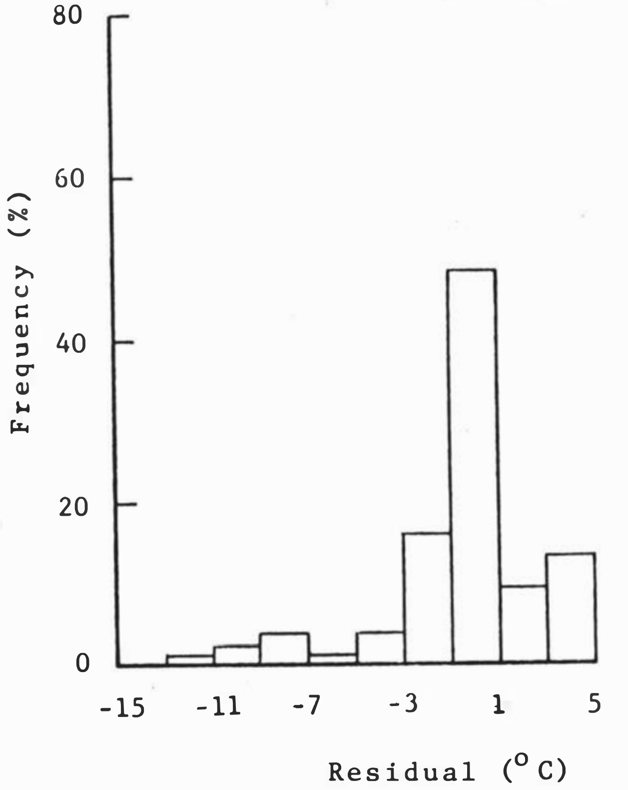
(c) In the Overall Process

Run no.6

median = -0.14 ^{o}C

mean = -0.59 ^{o}C

standard deviation = 3.35 ^{o}C

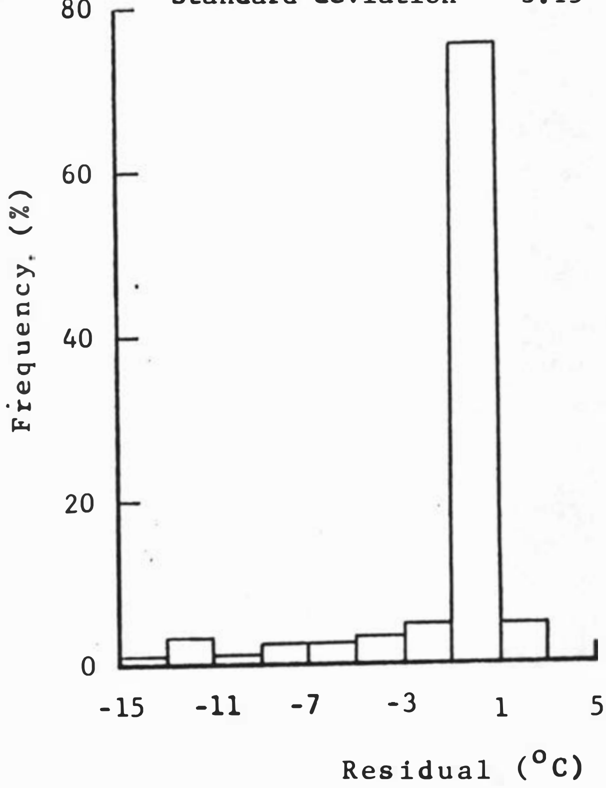


Run no.8

median = -0.33 ^{o}C

mean = -1.22 ^{o}C

standard deviation = 3.15 ^{o}C

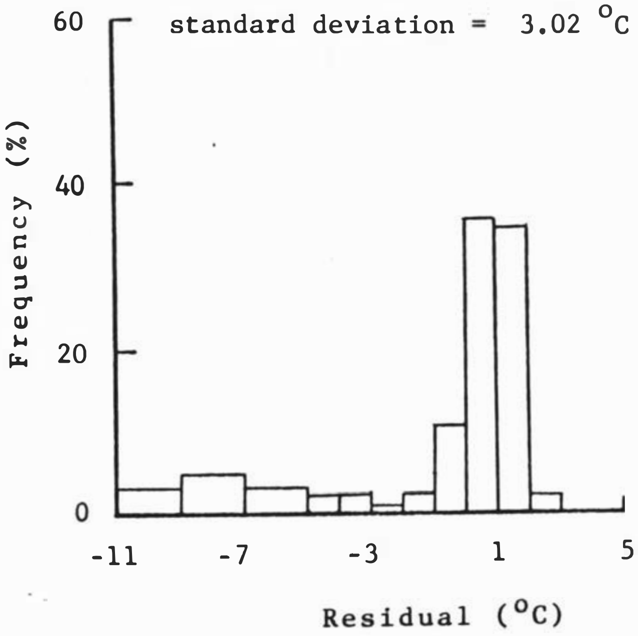


Run no.7

median = 1.26 ^{o}C

mean = -0.37 ^{o}C

standard deviation = 3.02 ^{o}C

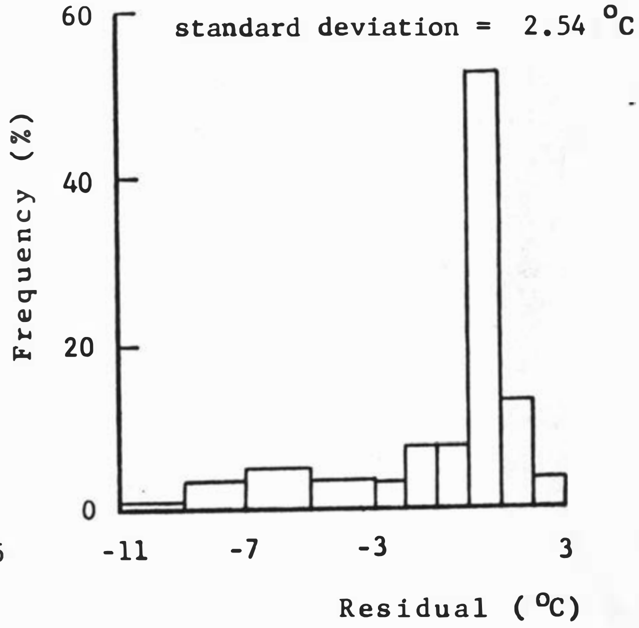


Run no.9

median = -0.11 ^{o}C

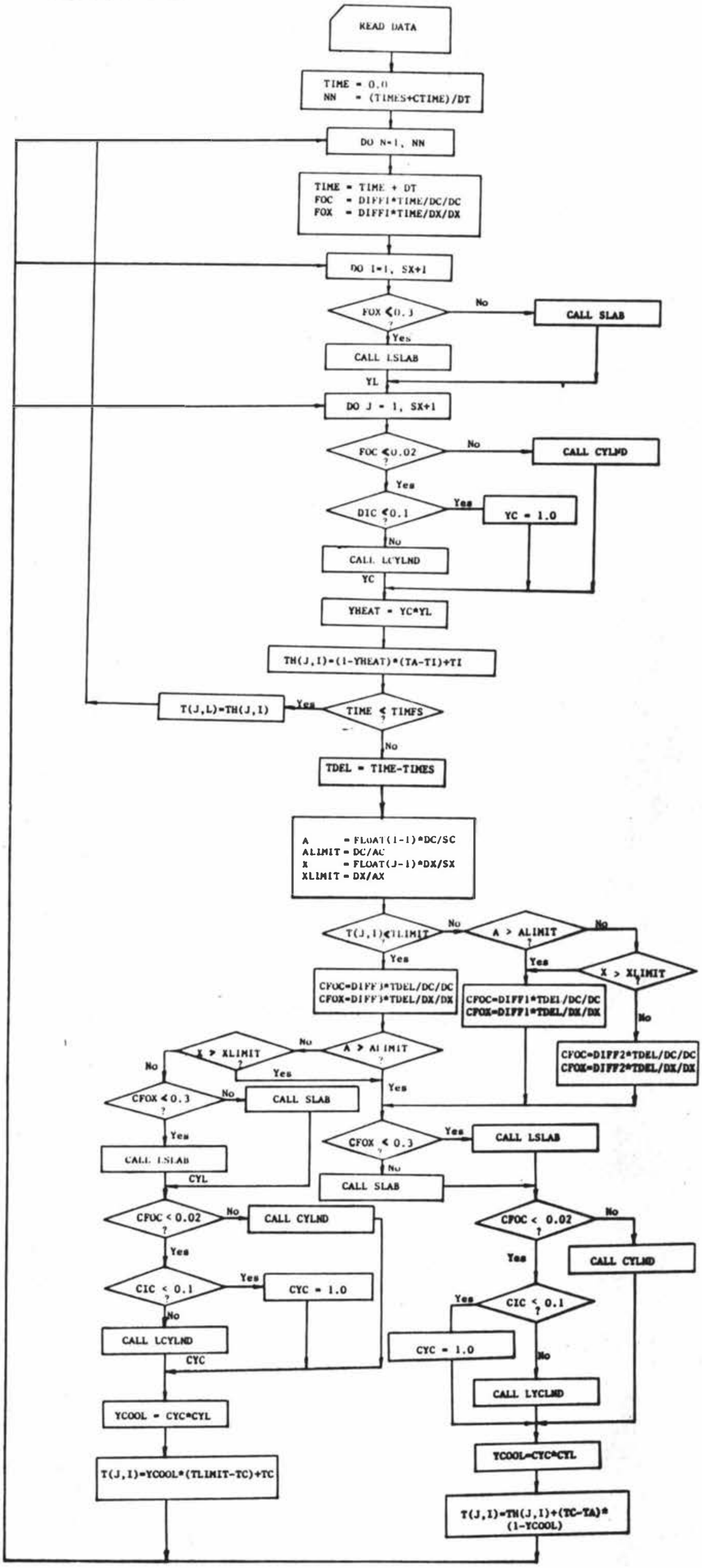
mean = -0.49 ^{o}C

standard deviation = 2.54 ^{o}C



APPENDIX 4.5 Modified Analytical Solution Program

(a) Flow Chart



(b) Computer Program

```
      DIMENSION T(50,50),TH(50,50),B(10),XJIB(10),BRA(10),XJOB(10)
      COMMON XJO(200),ARG(200)
      DATA ARG/0.0,0.1,0.2,0.3,0.4,0.5,0.6,0.7,0.8,0.9,1.0,
     * 1.1,1.2,1.3,1.4,1.5,1.6,1.7,1.8,1.9,2.0,
     * 2.1,2.2,2.3,2.4,2.5,2.6,2.7,2.8,2.9,3.0,3.1,3.2,3.3,3.4,3.5,
     * 3.6,3.7,3.8,3.9,4.0,4.1,4.2,4.3,4.4,4.5,4.6,4.7,4.8,4.9,5.0,
     * 5.1,5.2,5.3,5.4,5.5,5.6,5.7,5.8,5.9,6.0,6.1,6.2,6.3,6.4,6.5,
     * 6.6,6.7,6.8,6.9,7.0,7.1,7.2,7.3,7.4,7.5,7.6,7.7,7.8,7.9,8.0,
     * 8.1,8.2,8.3,8.4,8.5,8.6,8.7,8.8,8.9,9.0,9.1,9.2,9.3,9.4,9.5,
     * 9.6,9.7,9.8,9.9,10.0,10.1,10.2,10.3,10.4,10.5,10.6,10.7,10.8,
    *10.9,11.0,11.1,11.2,11.3,11.4,11.5,11.6,11.7,11.8,11.9,12.0,
     *   12.1,12.2,12.3,12.4,12.5,12.6,12.7,12.8,12.9,13.0
     * ,13.1,13.2,13.3,13.4,13.5,13.6,13.7,13.8,13.9,14.0,14.1,14.2,
     * 14.3,14.4,14.5,14.6,14.7,14.8,14.9,0.0,0.0,0.0,0.0,0.0/
      DATA XJO/1.0,0.9975,0.9900,0.9776,0.9604,0.9385,0.9120,
     * 0.8812,0.8463,0.8075,0.7652,0.7196,0.6711,0.6201,0.5669,
     * 0.5118,0.4554,0.3980,0.3400,0.2818,0.2239,0.1666,0.1104,
     * 0.0555,0.0025,-0.0484,-0.0968,-0.1424,-0.1850,-0.2243,
     * -0.2601,-0.2921,-0.3202,-0.3443,-0.3643,-0.3801,
     * -0.3918,-0.3992,-0.4026,-0.4018,-0.3971,-0.3887,
     * -0.3766,-0.3610,-0.3423,-0.3205,-0.2916,-0.2693,-0.2404,
     * -0.2097,-0.1776,-0.1443,-0.1103,-0.0758,-0.0412,-0.0068,
     * 0.0270,0.0599,0.0917,0.1220,0.1506,0.1773,0.2017,0.2238,
     * 0.2433,0.2601,0.2740,0.2851,0.2931,0.2981,0.3001,0.2991,
     * 0.2951,0.2882,0.2786,0.2663,0.2516,0.2346,0.2154,0.1944,
     * 0.1717,0.1475,0.1222,0.0960,0.0692,0.0419,0.0146,
     * -0.0125,-0.0392,-0.0653,-0.0903,-0.1142,-0.1367,-0.1577,
     * -0.1768,-0.1939,-0.2090,-0.2218,-0.2323,-0.2403,-0.2459,
     * -0.2490,-0.2496,-0.2477,-0.2434,-0.2366,-0.2276,-0.2164,
     * -0.2032,-0.1881,-0.1712,-0.1528,-0.1330,-0.1121,-0.0902
     * ,-0.0677,-0.0446,-0.0213,0.0020,0.0250,0.0477,0.0697,
     * 0.0908,0.1108,0.1296,0.1469,0.1626,0.1766,0.1887,0.1988,
     * 0.2,0.2129,0.2167,0.2183,0.2177,0.2150,0.2101,0.2032,
     * 0.1943,0.1836,0.1711,0.1570,0.1414,0.1245,0.1065,0.0875,
     * 0.0679,0.0476,0.0271,0.0064,1.0,1.0,1.0,1.0,1.0/
      DATA B/2.4048,5.5201,8.6537,11.7915,14.9309,18.0711,0.,0.,0./
      DATA XJIB/0.5191,-0.3403,0.2715,-0.2325,0.2066,-0.1890,0.,0.,0./
      READ(5,/)DC,DX,DIFF1,DIFF2,DIFF3,DT,SC,SX,TI,TA,TC,TIMES,
     * CTIME,TLIMIT,AX,AC
      WRITE(6,30)DIFF1,DIFF2,DIFF3,TI,TA,TC
      WRITE(6,39)DC,2.0*DX,1/SC,1/SX
```

```
   30 FORMAT(1H0," THERMAL DIFFUSIVITY IN HEATING PHASE(MM/S)=",
     * F12.10,//," THERMAL DIFFUSIVITY IN COOLING(START) (MM/S)=",
     * F12.10,//," THERMAL DIFFUSIVITY IN LATER COOLING(MM/S)=",
     * F12.10,//,"  INITIAL TEMPERATURE(C)=",F12.2,//
     * "   RETORT TEMPERATURE(C)=",F12.2,//
     * "     COOLING TEMPERATURE(C)=",F12.2,//)
   39 FORMAT("    CAN RADIUS(M)=",F12.5,/
     * "     CAN HEIGHT(M)=",F12.5,/
     * "     SIZE OF DIMENSIONLESS SPACE INCREMENT IN R DIRECTION=",
     * F12.5,/
     * "   SIZE OF DIMENSIONLESS SPACE INCREMENT IN X DIRECTION=",
     * F12.5,///
     * "     TEMPERATURE DISTRIBUTION IN A CAN"////)
      TIME=0
      NN=(TIMES+CTIME)/DT
      DO 42 N=1,NN
      TIME=TIME+DT

      FOC=DIFF1*TIME/DC/DC
      FOX=DIFF1*TIME/DX/DX
      DO 58 I=1,SX+1
      DIX=FLOAT(I-1)/SX
      IF(FOX.LT.0.03)GO TO 110
      CALL SLAB(FOX,YL,DIX)
     GO TO 80
  110  XL=DIX*DX
        CALL LSLAB(FOX,YL,DX,XL)
   80  DO 58 J=1,SC+1
      DIC=FLOAT(J-1)/SC
      IF(FOC.LT.0.02)GO TO 120
      DO 49 JJ=1,6
   49  BRA(JJ)=B(JJ)*DIC
      CALL CYLND(FOC,YC,B,BRA,XJOB,XJIB)
      GO TO 90
  120  IF(DIC.LT.0.1)GO TO 100
      R=DC*DIC
      CALL LCYLND(FOC,YC,DC,R)
      GO TO 90
   100  YC=1.0
   90  YHEAT=YC*YL
      TH(J,I)=(1-YHEAT)*(TA-TI)+TI
      IF(TIME.LE.TIMES)GO TO 200
      TDEL=TIME-TIMES
       A=FLOAT(I-1)*DX/SX
       ALIMIT=DX/AX
       X=FLOAT(J-1)*DC/SC
       XLIMIT=DC/AC
```

```
      IF(T(J,I).LT.TLIMIT)GO TO 800
      IF(A.GT.ALIMIT)GO TO 300
      IF(X.GT.XLIMIT)GO TO 300
      CFOC=DIFF2*TDEL/DC/DC
      CFOX=DIFF2*TDEL/DX/DX
      GO TO 400
  800  CFOC=DIFF3*TDEL/DC/DC
       CFOX=DIFF3*TDEL/DX/DX
      IF(A.GT.ALIMIT)GO TO 400
      IF(X.GT.XLIMIT)GO TO 400
       GO TO 500
  300 CFOC=DIFF1*TDEL/DC/DC
      CFOX=DIFF1*TDEL/DX/DX
  400 CIX=DIX
      IF(CFOX.LT.0.03)GO TO 145
      CALL SLAB(CFOX,CYL,CIX)
      GO TO 155
  145  CXL=CIX*DX
      CALL LSLAB(CFOX,CYL,DX,CXL)
  155  CIC=DIC
      IF(CFOC.LT.0.02)GO TO 165
      DO 55 JJ=1,6
   55  BRA(JJ)=B(JJ)*CIC
      CALL CYLND(CFOC,CYC,B,BRA,XJOB,XJIB)
      GO TO 175
  165  IF(CIC.LT.0.1)GO TO 185
       CR=DC*CIC
      CALL LCYLND(CFOC,CYC,DC,CR)
      GO TO 175
  185 CYC=1.0
  175 YCOOL=CYC*CYL
      T(J,I)=TH(J,I)+(TC-TA)*(1-YCOOL)
      GO TO 58
  500 CIX=DIX
      IF(CFOX.LT.0.03)GO TO 245
      CALL SLAB(CFOX,CYL,CIX)
      GO TO 255
  245  CXL=CIX*DX
      CALL LSLAB(CFOX,CYL,DX,CXL)
  255  CIC=DIC
      IF(CFOC.LT.0.02)GO TO 265
      DO 355 JJ=1,6
  355  BRA(JJ)=B(JJ)*CIC
      CALL CYLND(CFOC,CYC,B,BRA,XJOB,XJIB)
      GO TO 275
```

```
  265  IF(CIC.LT.0.1)GO TO 285
         CR=DC*CIC
        CALL LCYLND(CFOC,CYC,DC,CR)
        GO TO 275
  285    CYC=1.0
  275  YCOOL=CYC*CYL
         T(J,I)=YCOOL*(TLIMIT-TC)+TC
        GO TO 58
  200  T(J,I)=TH(J,I)
   58  CONTINUE
       WRITE(6,59)TIME
   59  FORMAT(//"     TIME(S)=",F12.2,//
     * "      X DIRECTION ACROSS, R DIRECTION DOWN"//)
       DO 60 J=1,SC+1
   60  WRITE(6,79)(T(J,I),I=1,SX+1)
   79  FORMAT(12F10.2)
   42  CONTINUE
       STOP
       END
       SUBROUTINE CYLND(FO,YC,B,BRA,XJOB,XJIB)
       DIMENSION B(10),XJIB(10),BRA(10),XJOB(10)
       COMMON XJO(200),ARG(200)
       DO 1 I=1,6
       IF(BRA(I).GT.14.89)GO TO 3
       DO 2 J=1,152
       IF(BRA(I)-ARG(J))5,4,2
    2  CONTINUE
    4  XJOB(I)=XJO(J)
       GO TO 1
    5  IF(J.GT.1)J=J-1
       XJOB(I)=XJO(J)+(XJO(J+1)-XJO(J))/(ARG(J+1)-ARG(J))*
     * (BRA(I)-ARG(J))
       GO TO 1
    3  XJOB(I)=(0.7979/BRA(I))**0.5*(COS(BRA(I)-0.7854)+0.125/
     * BRA(I)*SIN(BRA(I)-0.7854))
    1  CONTINUE
       YC=0
       DO 6 I=1,6
    6  YC=YC+2.0*XJOB(I)/B(I)/XJIB(I)*EXP(-B(I)**2*FO)
       RETURN
       END
       SUBROUTINE SLAB(FO,YL,D)
       YL=1.2732395*(COS(1.57143*D)*EXP(-FO*2.467401)+
     * (-1)/3.0*COS(3.0*1.57143*D)*EXP(-9.0*FO*2.467401)+
     * (+1)/5.0*COS(5.0*1.57143*D)*EXP(-25.0*FO*2.467401)+
     * (-1)/7.0*COS(7.0*1.57143*D)*EXP(-49.0*FO*2.467401)+
     * (+1)/9.0*COS(9.0*1.57143*D)*EXP(-81.0*FO*2.467401)+
     * (-1)/11.0*COS(11.0*1.57143*D)*EXP(-121.0*FO*2.467401))
```

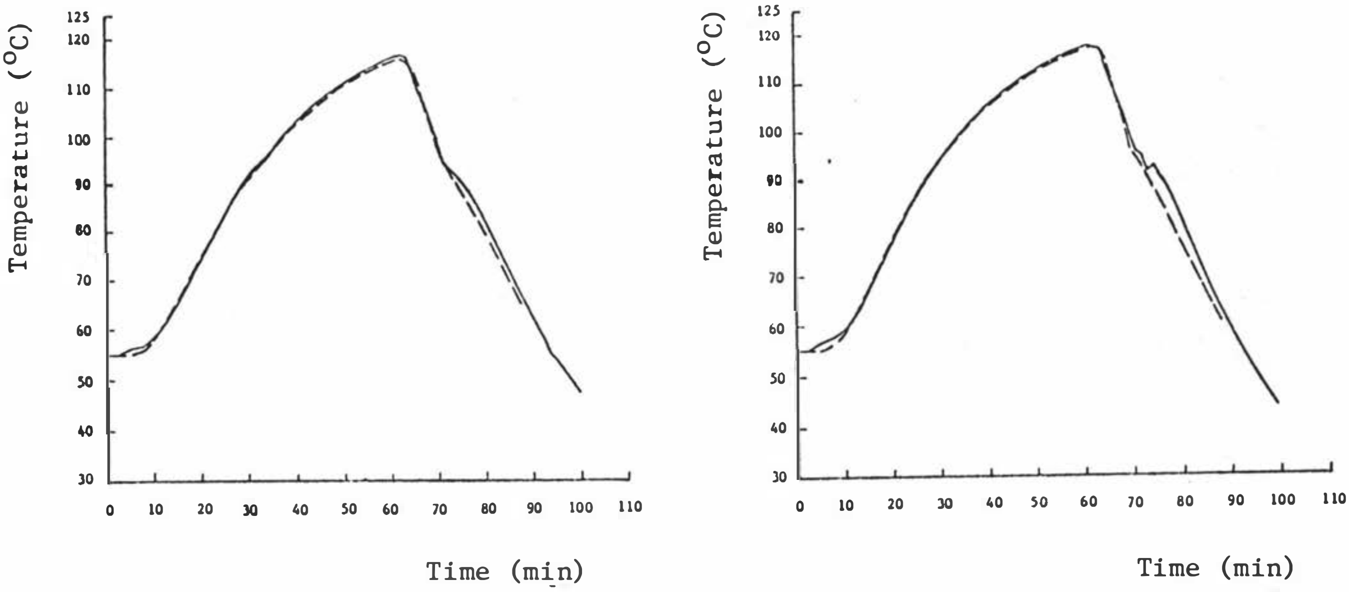
```
      RETURN
      END
      SUBROUTINE LCYLND(FO,YC,DC,R)
      X=(DC-R)/2.0/(FO*DC**2.0)**0.5
      A=ERFN(X)
      E1=0.56428958*EXP(-X*X)-X*A
      X2=X+X
      E2=0.25*(A-X2*E1)
      YC=1-((DC/R)**0.5*A+(DC-R)*(FO*DC**3.0)**0.5/4/
     * DC/R**1.5*E1+(9*DC**2.0-7.0*R**2.0-2.0*DC*R)/
     * (32.0*DC**1.5*R**2.5)*FO*DC**2.0*E2)
      RETURN
      END
      SUBROUTINE LSLAB(FO,YL,DX,XL)
      YL=1.0
      XFO=(FO*DX**2.0)**0.5
      DO 102 I=1,3
      N=I-1
       Y1=((2*N+1)*DX-XL)/2.0/XFO
       Y2=((2*N+1)*DX+XL)/2.0/XFO
  102  YL=YL-((-1)**N*(ERFN(Y1)+ERFN(Y2)))
       RETURN
       END
       FUNCTION ERFN(X)
       DATA P,A1,A2,A3,A4,A5/0.3275911,0.25482959,-0.28449674,
      * 1.42141374,-1.45315203,1.061405437/
       IF(X.GT.0.0)GO TO 13
       X=(-1)*X
   13  T1=1.0/(1+P*X)
       T2=T1*T1
       T3=T2*T1
       T4=T3*T1
       T5=T4*T1
       ERFN=EXP(-X*X)*(A1*T1+A2*T2+A3*T3+A4*T4+A5*T5)
       RETURN
       END
```

APPENDIX 4.6 Comparison of Experimental Temperatures and Predicted Temperatures from the Modified Analytical Solution Program

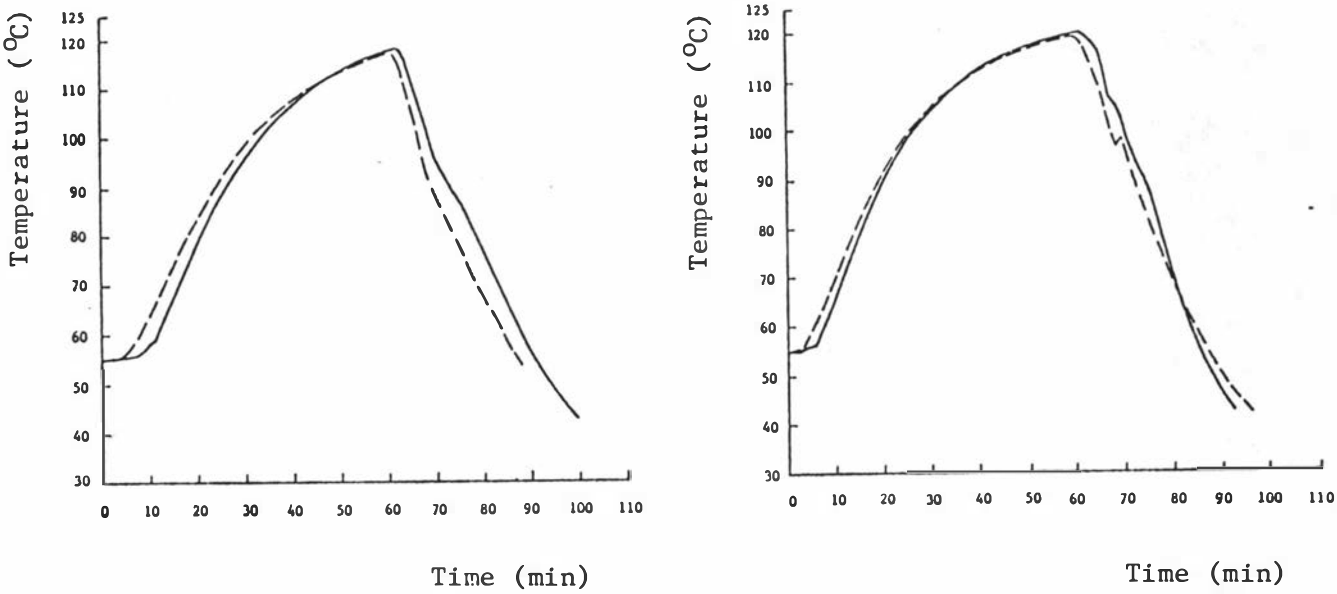
(————) experimental temperatures

(—— ——) predicted temperatures

(a) Run no.8 (retort temperature was 129°C)

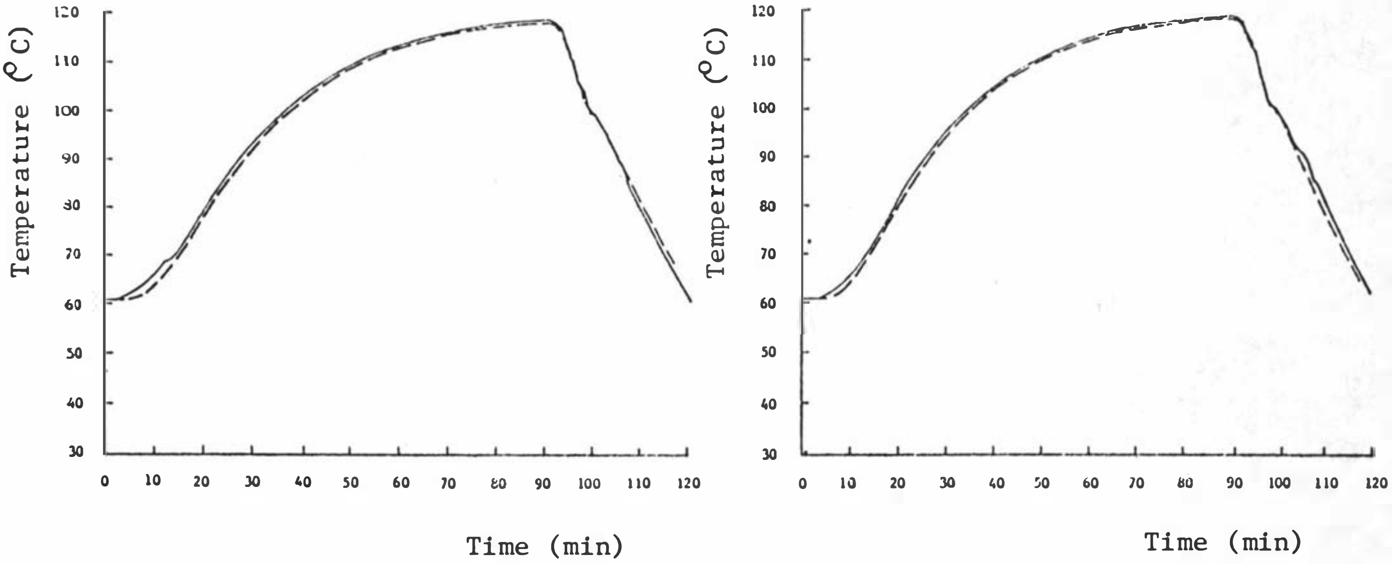


(a) at r/a = 0.0 , x/h = 0.0 (b) at r/a = 0.0 , x/h = 1/3



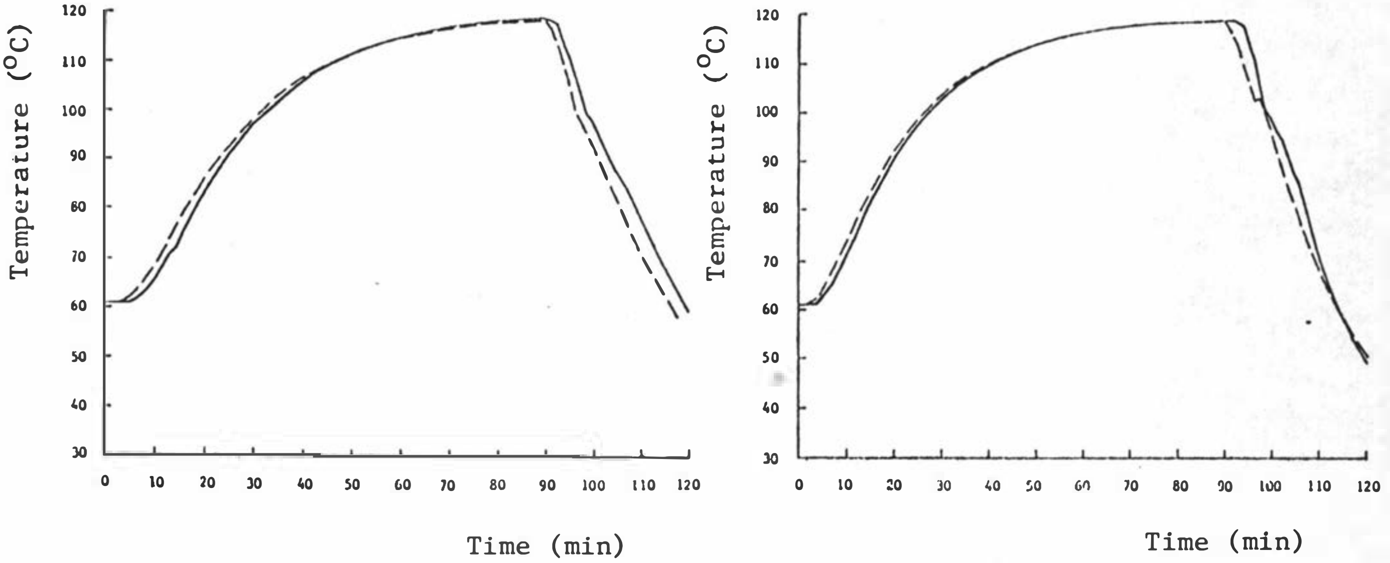
(c) at r/a = 1/3 , x/h = 1/3 (d) at r/a = 0.0 , x/h = 2/3

(b) Run no.9 (retort temperature was 120°C)



(a) at r/a = 0.0 , x/h = 0.0

(b) at r/a = 0.0 , x/h = 1/3



(c) at r/a = 1/3 , x/h = 1/3

(d) at r/a = 0.0 , x/h = 2/3

APPENDIX 4.7 Method of Quality Retention Calculation for Micro-Organisms and Ascorbic Acid

For Micro-Organisms

For generally basis, $z = 10^{o}C$,
assuming temperature range studied was $50^{o}C - 130^{o}C$:

$$Ea = \frac{2.303\ R(T_1 - T_2)}{z} \times \frac{9}{5}$$

$$= \frac{2.303 \times 0.0083 \times (50+273) \times (130+273)}{10}$$

$$= 250 \text{ kJ mole}^{-1}$$

From Lund (1977); $D_{121.1^{o}C}$ was found in the range of 0.48-1.40 min, and 0.15 min

$$D_{121.1^{o}C} \text{ average} = 0.68 \text{ min}$$

$$\text{from } k = \frac{2.303}{D}$$

$$k_{121.1^{o}C} = \frac{2.303}{0.68}$$

$$= 3.3868 \text{ min}^{-1}$$

$$\ln S = \ln k_1 + Ea/RT_1$$

$$\ln S = \ln 3.3868 + 250/(0.0083 \times (121.1 + 273))$$

$$= 77.8407$$

$$S = 6.3943 \times 10^{33} \text{ min}^{-1}$$

From

$$\ln No/N = s \int_o^t e^{-Ea/RT}\, dt$$

for the time interval Δt;

$$\ln No/N = S\ e^{-Ea/RT}\ \Delta t$$

where T was the average temperature over t, Δt.

So No/N could be calculated from the temperature data, N calculated at the end of Δt became No for the next Δt. The calculation was repeated to obtain the final concentration at the end of processing time.

Then, $F_{121.1}^{10}$ could be determined from:

$$\ln No/N = 6.3943 \times 10^{33} \times e^{-(\frac{250}{0.0083} \times 394.1)}$$

Substitute, final No/N from the calculation, the equivalent time, t, at 121.1°C can be determined.

For Ascorbic Acid

From Chittaporn (1977),

$$Ea = 84.2 \text{ kJ mole}^{-1}$$

$$k = 840 \times 10^{-3} \text{ h}^{-1} \text{ at } 129^{o}C$$

$$= 14 \times 10^{-3} \text{ min}^{-1} \text{ at } 129^{o}C$$

$$\ln S = \ln (14 \times 10^{-3}) + \frac{84.2}{0.0083 \times 402}$$

$$= 3.6632 \times 10^{9} \text{ min}^{-1}$$

Calculation could be done same as for micro-organisms.

APPENDIX 4.8 An Example of Lethality Calculation

(a) Predicted Temperatures and Lethality Calculation at the Centre Point for Run no.6

PREDICTED TEMPERATURE°C	AVERAGE TEMPERATURE°C	MICROBIOLOGY		ASCORBIC ACID	
		$e^{-Ea/RT}$	No/N	$e^{-Ea/RT}$	No/n
61.0					
61.0	61.00			1.8101-14	1.0001
61.0	60.99			1.8101	1.0001
60.99	61.02			1.8135	1.0001
61.05	61.15			1.8369	1.0001
61.26	61.50			1.8978	1.0001
61.74	62.14			2.0168	1.0001
62.55	62.12			2.2099	1.0001
63.69	64.40			2.4911	1.0001
65.12	65.95			2.8747	1.0001
66.79	67.72			3.3787	1.0001
68.65	69.65	5.3394-39	1.0000	4.0237	1.0002
70.65	71.69	9.0064	1.0001	4.8316	1.0002
72.74	73.81	1.5366-38	1.0001	5.8250	1.0003
74.88	75.97	2.6340	1.0002	7.0342	1.0003
77.06	78.14	4.5018	1.0003	8.4857	1.0004
79.23	80.30	7.6158	1.0006	1.0200-13	1.0004
87.38	82.44	1.2725-37	1.0010	1.2208	1.0005
83.50	84.54	2.0959	1.0016	1.4537	1.0006
85.58	86.59	3.3922	1.0026	1.7205	1.0008
87.60	88.58	5.3913	1.0041	2.0234	1.0009
89.57	90.51	8.3995	1.0065	2.3631	1.0010
91.46	92.38	1.2835-36	1.0099	2.7412	1.0012
93.30	94.18	1.9246	1.0149	3.1588	1.0014
95.06	95.90	2.8271	1.0219	3.6139	1.0016
96.75	99.56	4.0749	1.0318	4.1071	1.0018
98.37	99.14	5.7656	1.0452	4.6376	1.0020
99.92	100.66	8.0203	1.0635	5.2055	1.0023
101.41	102.12	1.0973-35	1.0878	5.8091	1.0026
102.83	103.50	1.4754	1.1199	6.4435	1.0028
104.18	104.82	1.9526	1.1616	7.1074	1.0031
105.47	106.08	2.5440	1.2156	7.7971	1.0034
106.69	107.27	1.2576	1.2840	8.5110	1.0037
107.86	108.41	4.1429	1.3742	9.2482	1.0041
108.97	109.50	5.1960	1.4899	1.0004-12	1.0044
110.03	110.53	6.4108	1.6354	1.0775	1.0047
111.03	111.51	7.8353	1.8243	1.5590	1.0051
111.99	112.44	9.4700	2.0691	1.2352	1.0054
112.89	113.32	1.132-34	2.3836	1.3148	1.0058
113.75	114.16	1.3412	2.7986	1.3952	1.0062
114.57	114.95	1.5737	3.3452	1.4754	1.0065
115.34	115.70	1.8287	4.0682	1.5551	1.0069
116.07	116.42	2.1111	5.0525	1.6352	1.0072
116.78	117.03	2.3833	6.2261	1.7061	1.0075
117.29	117.21	2.4675	6.6416	1.7270	1.0076
117.13	116.52	2.1536	5.2200	1.6467	1.0073
115.92	114.77	1.5163	3.2011	1.4564	1.0064
113.62	112.03	8.712-35	1.9513	1.1996	1.0053
110.44	108.53	4.2429	1.3848	9.3257-13	1.0041
106.62	104.50	1.8247	1.1503	6.9409	1.0031
102.39	101.52	9.6556-36	1.0769	5.5549	1.0024
100.66	99.82	6.6852	1.0526	4.8842	1.0021
98.99	98.06	4.5478	1.0355	4.2681	1.0019
97.13	96.12	2.9652	1.0230	3.6747	1.0016
95.11	94.04	1.8652	1.0144	3.1243	1.0014
92.97	91.86	1.1409	1.0088	2.6305	1.0012
90.75	89.61	6.8346-37	1.0053	2.1986	1.0010
88.48	87.32	4.0259	1.0031	1.8269	1.0008
86.17	85.01	2.3444	1.0018	1.5119	1.0007
83.86	82.70	1.3557	1.0010	1.2481	1.0005
81.55	80.41	7.8116-38	1.0006	1.0291	1.0005
79.27	78.14	4.5018	1.0003	8.4857-14	1.0004
77.02	75.91	2.5983	1.0002	7.0007	1.0003
74.81	73.73	1.5061	1.0001	5.7842	1.0003
72.65	71.59	8.7803-39	1.0001	4.7888	1.0002
70.54					
Final concentration		2.3946×10^{-8} No		0.8664 No	
Calculate $F^{10}_{121.1}$ (min)		5.1813		17.3510	

(b) Calculated Final Concentration and $F^{10}_{121.1}$

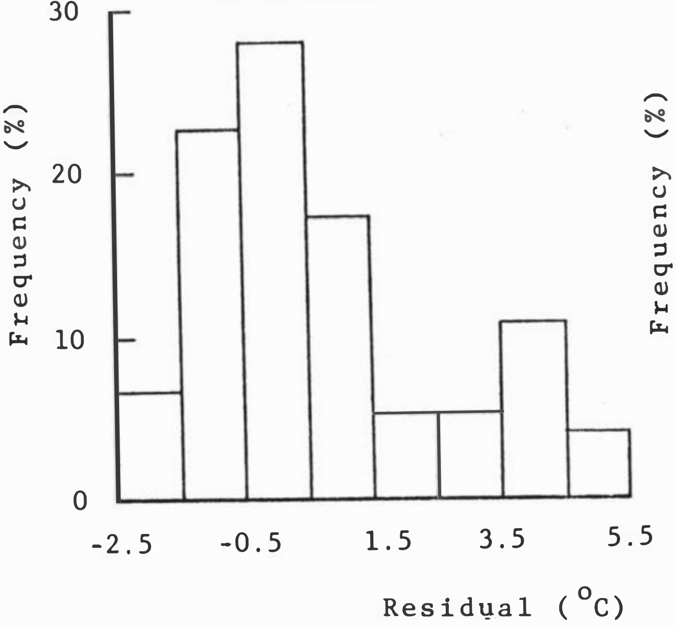
Details	Based on Experimental temperature data	Based on Predicted temperature data	% Difference
run no.6; at centre point			
final microbiological concentration x 10^{9}	8.7214 No	2.3946 No	-
final ascorbic acid concentration	0.8609 No	0.8664 No	0.6
$F^{10}_{121.1}$ (microbiology), min	5.4795	5.1813	5.4
$F^{10}_{121.1}$ (ascorbic acid), min	18.1210	17.3510	4.3
run no.6; r=0.0, x=1.8 cm			
final microbiological concentration x 10^{11}	3.7258 No	5.6827 No	-
final ascorbic acid concentration	0.8478 No	0.8522 No	0.5
$F^{10}_{121.1}$ (microbiology), min	7.0904	6.9653	1.8
$F^{10}_{121.1}$ (ascorbic acid), min	19.9710	19.3440	3.1
run no.7; at centre point			
final microbiological concentration x 10^{8}	3.1369 No	1.5574 No	-
final ascorbic acid concentration	0.8391 No	0.8444 No	0.6
$F^{10}_{121.1}$ (microbiology), min	5.1016	4.6284	9.3
$F^{10}_{121.1}$ (ascorbic acid), min	21.2242	20.4651	3.6
run no.7; at r=0.0, x=1.8 cm			
final microbiological concentration x 10^{10}	7.4204 No	7.8255 No	-
final ascorbic acid concentration	0.8279 No	0.8349 No	0.8
$F^{10}_{121.1}$ (microbiology), min	6.2071	5.5115	11.2
$F^{10}_{121.1}$ (ascorbic acid), min	22.8505	21.8386	4.4

APPENDIX 4.9 Distribution of Residuals for Determining the Accuracy of the Modified Analytical Solution Program for Calculating Tempertures

(a) In the Overall Process

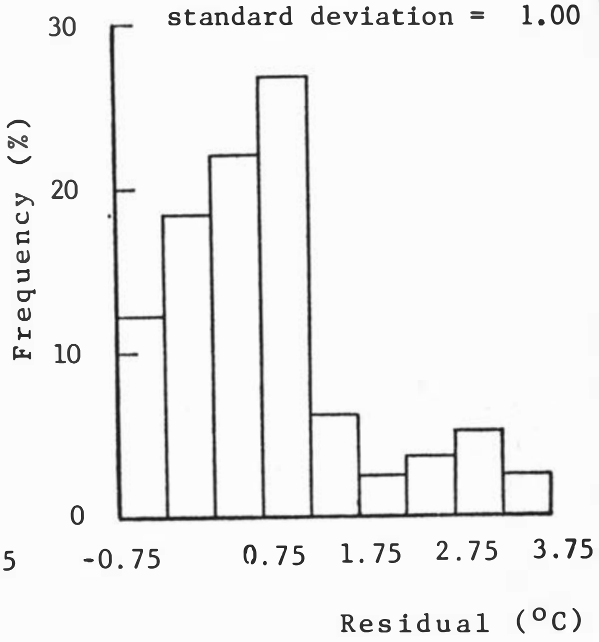
Run no.6

median = 0.24 °C
mean = 0.71 °C
standard deviation = 1.90 °C



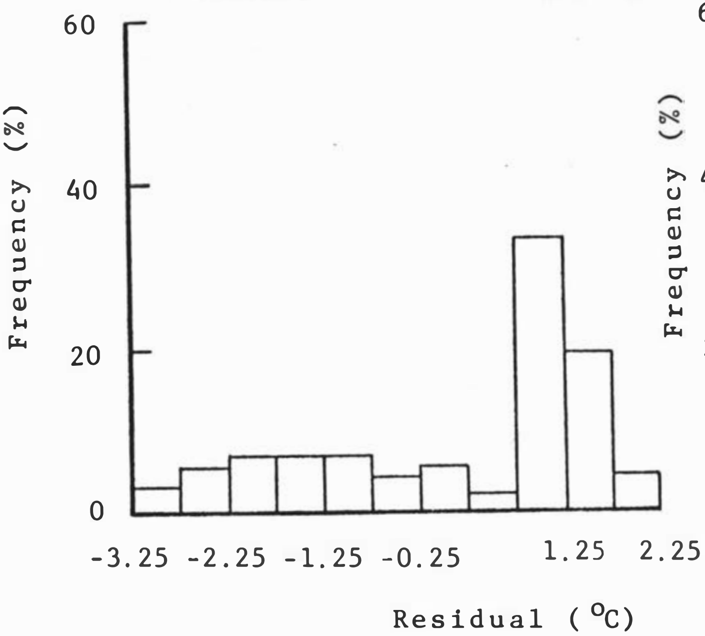
Run no.8

median = 0.67 °C
mean = 0.76 °C
standard deviation = 1.00 °C



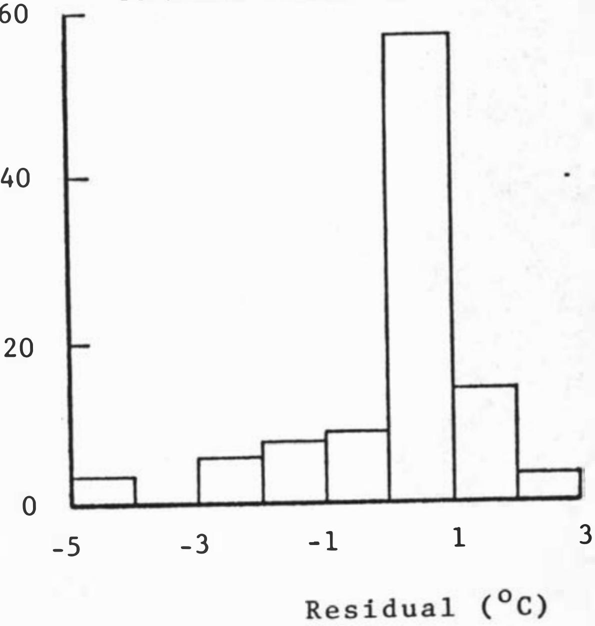
Run no.7

median = 0.85 °C
mean = 0.15 °C
standard deviation = 1.47 °C

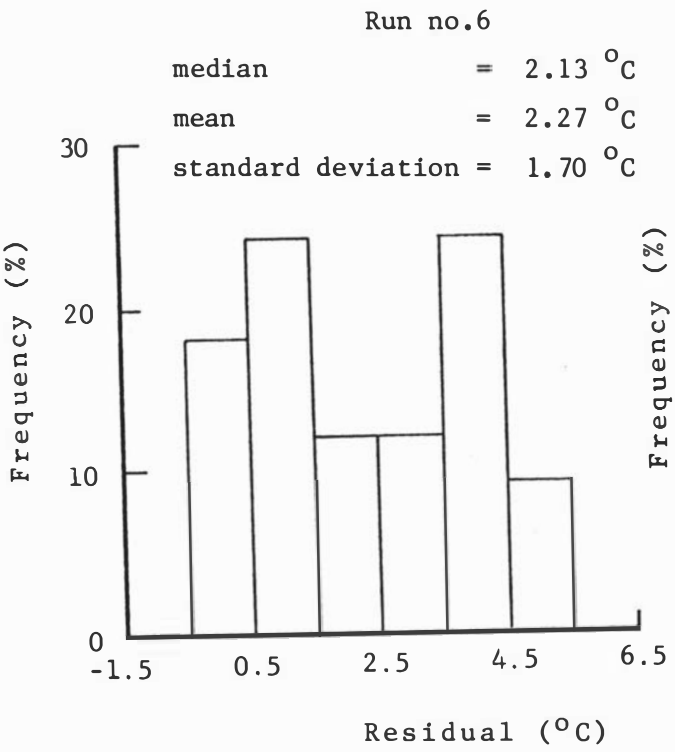


Run no.9

median = 0.43 °C
mean = 0.13 °C
standard deviation = 1.41 °C



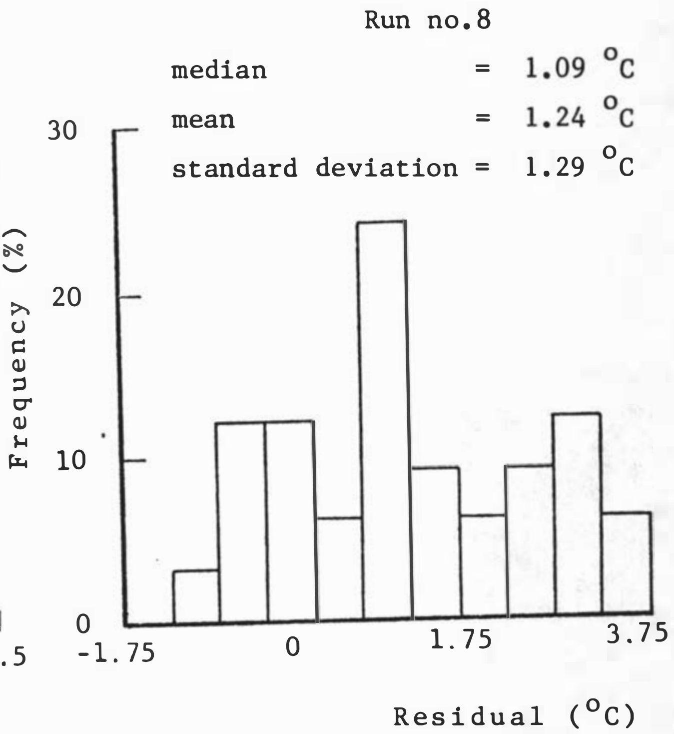
(b) In the Cooling Phase


Run no.6

median = 2.13 °C

mean = 2.27 °C

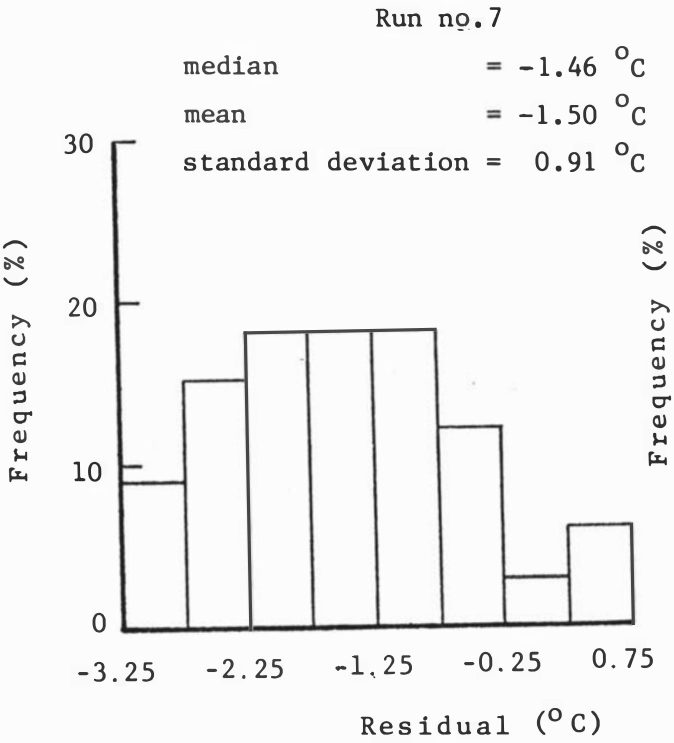
standard deviation = 1.70 °C


Run no.8

median = 1.09 °C

mean = 1.24 °C

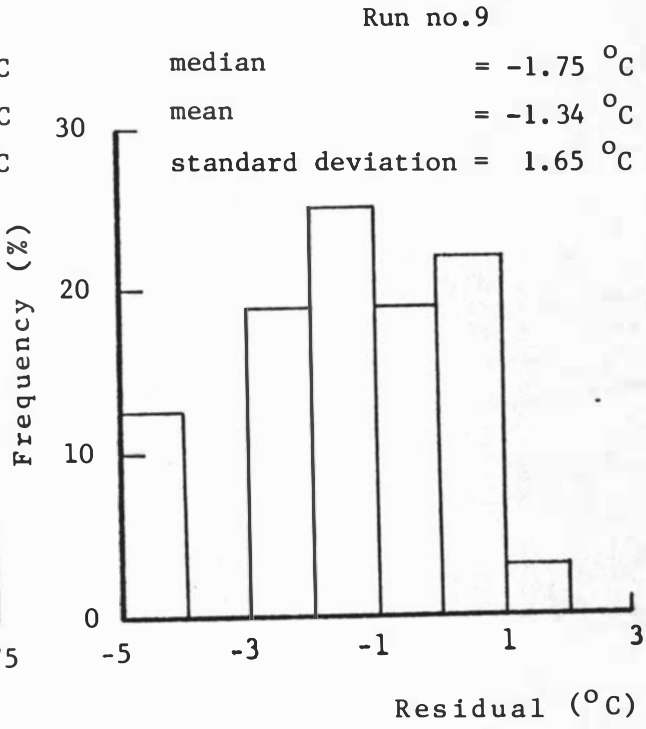
standard deviation = 1.29 °C


Run no.7

median = -1.46 °C

mean = -1.50 °C

standard deviation = 0.91 °C


Run no.9

median = -1.75 °C

mean = -1.34 °C

standard deviation = 1.65 °C

APPENDIX 5.1 Analytical Results

(a) Ascorbic Acid

Run No.	Sample	CONCENTRATION x 10^{2} mg g^{-1}			Mean Concentration x 10^{2} mg g^{-1}	Standard Deviation x 10^{2} mg g^{-1}
		1	2	3		
120°C						
7	control	25.00(6)	24.46(7)	24.04(2)	24.50(8)	0.48(8)
	heated	23.23(9)	21.80(4)	22.34(8)	22.46(7)	0.72(0)
4	control	26.48(2)	25.66(2)	26.28(0)	26.14(1)	0.43(8)
	heated	23.72(4)	23.97(5)	23.79(4)	23.83(8)	0.13(6)
9	control	25.84(2)	25.95(4)	26.05(2)	25.95(9)	0.11(5)
	heated	23.54(7)	23.64(6)	23.65(9)	23.60(9)	0.06(2)
2	control	23.89(7)	24.48(9)	24.11(3)	24.16(9)	0.30(9)
	heated	21.00(1)	22.16(9)	21.95(4)	21.71(5)	0.62(8)
129°C						
6	control	25.32(0)	25.75(2)	25.47(6)	25.68(9)	0.30(0)
	heated	23.89(9)	24.53(7)	23.88(0)	24.10(0)	0.37(1)
1	control	23.61(7)	23.97(1)	24.09(8)	23.89(8)	0.25(1)
	heated	22.46(1)	21.53(7)	21.54(3)	21.84(4)	0.53(4)
8	control	25.45(2)	25.26(2)	25.16(7)	25.29(1)	0.15(0)
	heated	23.20(8)	23.41(9)	22.79(7)	23.04(4)	0.33(4)
5	control	24.71(5)	25.47(6)	24.28(8)	24.82(7)	0.60(3)
	heated	23.04(0)	22.06(5)	22.59(2)	22.56(2)	0.49(3)
10	control	23.58(0)	23.39(9)	22.91(0)	23.29(3)	0.35(5)
	heated	21.12(1)	20.70(0)	21.03(7)	20.95(9)	0.22(1)

(b) Riboflavin

Run No.	Sample	CONCENTRATION μg g^{-1}				Mean Concentration	Standard Deviation
		1	2	3	4	μg g^{-1}	μg g^{-1}
120°C							
7	control	25.16(1)	25.92(5)	25.14(8)	25.42(0)	25.41(9)	0.36(1)
	heated	25.09(0)	25.47(3)	23.98(0)	24.05(9)	24.65(8)	0.75(9)
4	control	25.95(5)	25.35(6)	25.37(8)	25.34(6)	25.59(0)	0.34(0)
	heated	24.63(6)	24.89(0)	23.27(2)	24.61(1)	24.35(0)	0.73(0)
9	control	26.07(2)	26.03(6)	26.26(7)	25.87(8)	26.06(6)	0.16(0)
	heated	24.78(9)	24.81(0)	24.27(2)	24.17(2)	24.64(2)	0.25(1)
2	control	25.66(9)	25.12(2)	26.13(4)	25.85(1)	25.94(2)	0.23(9)
	heated	24.02(6)	24.00(7)	24.86(1)	24.07(3)	24.24(7)	0.42(7)
129°C							
6	control	25.59(3)	25.78(2)	24.99(3)	24.76(9)	25.28(2)	0.48(4)
	heated	25.14(9)	25.04(1)	24.25(9)	24.52(7)	24.74(7)	0.42(4)
1	control	25.54(4)	25.87(5)	-	-	25.70(4)	0.19(5)
	heated	25.40(5)	24.17(8)	24.32(2)	-	24.63(8)	0.63(0)
8	control	25.88(3)	25.52(5)	26.49(0)	23.70(9)	25.40(7)	1.20(1)
	heated	24.13(2)	24.25(4)	23.65(1)	24.21(3)	24.06(3)	0.28(9)
5	control	26.22(0)	26.36(4)	26.10(7)	26.16(4)	26.21(1)	0.38(3)
	heated	24.36(5)	24.14(0)	25.28(0)	24.81(5)	24.65(5)	0.51(6)
10	control	26.44(2)	25.77(6)	25.90(3)	26.49(1)	26.15(1)	0.37(0)
	heated	24.32(4)	24.10(8)	25.00(8)	24.42(1)	24.46(0)	0.38(3)

(c) Colour

The colour of both control and heated samples were duplicate measured. The instrumental readings of X, Y and Z were transferred to x, y and Y by:

$$x = X/(X + Y + Z)$$
$$y = Y/(X + Y + Z)$$

The x and y of both control and heated samples of each processing run are shown below:

Run No.	x		y		c/c_o	
	Control c_o	Heated c	Control c_o	Heated c	x	y
129°C						
6	0.44	0.45	0.44	0.44	1.02	1.00
1	0.44	0.45	0.44	0.44	1.02	1.00
8	0.44	0.44	0.44	0.44	1.02	1.00
5	0.44	0.45	0.44	0.44	1.02	1.00
10	0.43	0.44	0.44	0.44	1.02	1.00
120°C						
7	0.44	0.45	0.44	0.44	1.02	1.00
4	0.44	0.45	0.44	0.43	1.02	1.00
9	0.44	0.45	0.44	0.44	1.02	1.00
2	0.44	0.45	0.44	0.44	1.02	1.00

As can be seen from above figures, c/c_o of both x and y were constant. The c/c_o of x was about 1.02 and of y was 1.00. Therefore it could be concluded that only Y can be used to describe the change of colour of baby food caused by heat in this study and the readings, Y, are shown in the following table.

Run No.	Sample	Reading, Y		Mean, Y
		1	2	
$120^{o}C$				
7	control	30.4	30.2	30.3
	heated	26.9	26.9	26.9
4	control	31.2	30.7	30.9
	heated	27.2	26.6	26.9
9	control	30.1	30.1	30.1
	heated	25.1	25.1	25.1
2	control	30.6	30.7	30.6
	heated	24.2	24.0	24.1
$129^{o}C$				
6	control	30.8	30.2	30.5
	heated	26.2	26.0	26.1
1	control	30.3	30.3	30.3
	heated	25.3	25.6	25.4
8	control	30.4	30.4	30.4
	heated	24.9	24.9	24.9
5	control	30.1	30.3	30.2
	heated	23.2	23.8	23.5
10	control	30.9	30.9	30.9
	heated	23.7	24.0	23.8

(d) Viscosity

Run no.	Sample	Reading of Viscosity				Mean Reading	Standard Deviation
		1	2	3	4		
120°C							
7	control	64.2	67.0	67.0	68.6	66.7	1.8
	heated	60.1	60.6	59.6	-	60.1	0.5
4	control	63.9	63.0	62.5	61.4	62.7	1.0
	heated	53.3	55.4	56.1	54.8	54.9	1.2
9	control	60.3	60.4	59.4	-	60.0	0.6
	heated	49.6	49.7	49.6	-	49.6	0.1
2	control	66.0	65.5	64.2	-	65.2	0.9
	heated	49.1	48.9	51.7	50.8	50.1	1.4
129°C							
6	control	72.0	68.0	70.3	-	70.1	2.0
	heated	56.8	56.3	57.9	-	57.0	0.8
1	control	71.5	73.5	72.4	72.2	72.4	0.8
	heated	57.5	57.3	57.0	-	57.3	0.3
8	control	66.8	69.4	66.1	-	67.4	1.7
	heated	51.2	52.8	53.3	-	52.4	1.1
5	control	64.4	63.2	65.3	-	64.3	1.1
	heated	49.5	49.2	47.6	-	48.8	1.0
10	control	76.5	75.6	74.8	-	75.6	0.9
	heated	56.0	55.3	55.5	-	55.6	0.4

APPENDIX 5.2 Quality Retention Calculation Program Based on First Order Kinetics

```
      SUPT=1
            DIMENSION T(15,15),TH(15,15),B(10),XJIB(10),BRA(10),XJOB(10),
          *  C(15,15,40),TAVE(20,20),AVET(20,20),V(15,15),TAVER(20,20),
          *   FNEA(20,20,40),RK(40),EA(40),RETEN(40),RATIO(40)
            COMMON XJO(200),ARG(200)
            DATA ARG/0.0,0.1,0.2,0.3,0.4,0.5,0.6,0.7,0.8,0.9,1.0,
          * 1.1,1.2,1.3,1.4,1.5,1.6,1.7,1.8,1.9,2.0,
          * 2.1,2.2,2.3,2.4,2.5,2.6,2.7,2.8,2.9,3.0,3.1,3.2,3.3,3.4,3.5,
          * 3.6,3.7,3.8,3.9,4.0,4.1,4.2,4.3,4.4,4.5,4.6,4.7,4.8,4.9,5.0,
          * 5.1,5.2,5.3,5.4,5.5,5.6,5.7,5.8,5.9,6.0,6.1,6.2,6.3,6.4,6.5,
          * 6.6,6.7,6.8,6.9,7.0,7.1,7.2,7.3,7.4,7.5,7.6,7.7,7.8,7.9,8.0,
          * 8.1,8.2,8.3,8.4,8.5,8.6,8.7,8.8,8.9,9.0,9.1,9.2,9.3,9.4,9.5,
          * 9.6,9.7,9.8,9.9,10.0,10.1,10.2,10.3,10.4,10.5,10.6,10.7,10.8,
         * 10.9,11.0,11.1,11.2,11.3,11.4,11.5,11.6,11.7,11.8,11.9,12.0,
          *  12.1,12.2,12.3,12.4,12.5,12.6,12.7,12.8,12.9,13.0
          * ,13.1,13.2,13.3,13.4,13.5,13.6,13.7,13.8,13.9,14.0,14.1,14.2,
          * 14.3,14.4,14.5,14.6,14.7,14.8,14.9,0.0,0.0,0.0,0.0,0.0/
            DATA XJO/1.0,0.9975,0.9900,0.9776,0.9604,0.9385,0.9120,
          * 0.8812,0.8463,0.8075,0.7652,0.7196,0.6711,0.6201,0.5669,
         * 0.5118,0.4554,0.3980,0.3400,0.2818,0.2239,0.1666,0.1104,
         *   0.0555,0.0025,-0.0484,-0.0968,-0.1424,-0.1850,-0.2243,
         *  -0.2601,-0.2921,-0.3202,-0.3443,-0.3643,-0.3801,
          *  -0.3915,-0.3992,-0.4026,-0.4018,-0.3971,-0.3887,
          *  -0.3766,-0.3610,-0.3423,-0.3205,-0.2916,-0.2693,-0.2404,
          *  -0.2097,-0.1776,-0.1443,-0.1103,-0.0758,-0.0412,-0.0068,
          *  0.0270,0.0599,0.0917,0.1220,0.1506,0.1773,0.2017,0.2238,
          *  0.2433,0.2601,0.2740,0.2851,0.2931,0.2981,0.3001,0.2991,
          *  0.2951,0.2882,0.2786,0.2663,0.2516,0.2346,0.2154,0.1944,
          *  0.1717,0.1475,0.1222,0.0960,0.0692,0.0419,0.0146,
          *  -0.0125,-0.0392,-0.0653,-0.0903,-0.1142,-0.1367,-0.1577,
          *  -0.1768,-0.1939,-0.2090,-0.2218,-0.2323,-0.2403,-0.2459,
          *  -0.2490,-0.2496,-0.2477,-0.2434,-0.2366,-0.2276,-0.2164,
          *  -0.2032,-0.1881,-0.1712,-0.1528,-0.1330,-0.1121,-0.0902
          *  ,-0.0677,-0.0446,-0.0213,0.0020,0.0250,0.0477,0.0697,
          *  0.0905,0.1108,0.1296,0.1469,0.1626,0.1766,0.1887,0.1988,
          *  0.2,0.2129,0.2167,0.2183,0.2177,0.2150,0.2101,0.2032,
          *  0.1943,0.1836,0.1711,0.1570,0.1414,0.1245,0.1065,0.0875,
          *  0.0679,0.0476,0.0271,0.0064,1.0,1.0,1.0,1.0,1.0/
             DATA B/2.4048,5.5201,8.6537,11.7915,14.9309,18.0711,0.,0.,0./
             DATA XJIB/0.5191,-0.3403,0.2715,-0.2325,0.2066,-0.1890,0.,0.,0./
             READ(5,7)DC,DX,DIFF1,DIFF2,DIFF3,DT,SC,SX,TI,TA,TC,TIMES,
          *  CTIME,TLIMIT,AX,AC,CI,TREF,NLEVEL
         9  READ(5,7)(RK(NL),EA(NL),NL=1,NLEVEL)
                    WRITE(6,7)(RK(NL),EA(NL),NL=1,NLEVEL)
             WRITE(6,30)DIFF1,DIFF2,DIFF3,TI,TA,TC
             WRITE(6,39)DC,2.0*DX,1/SC,1/SX
```

```
   30 FORMAT(1H0,"  THERMAL DIFFUSIVITY IN HEATING PHASE(MM/S)=",
     *  F12.10,//," THERMAL DIFFUSIVITY IN COOLING(START) (MM/S)=",
     *  F12.10,//," THERMAL DIFFUSIVITY IN LATER COOLING(MM/S)=",
     *  F12.10,//,"  INITIAL TEMPERATURE(C)=",F12.2,//
     *  "  RETORT TEMPERATURE(C)=",F12.2,//
     *  "    COOLING TEMPERATURE(C)=",F12.2,//)
   39 FORMAT("    CAN RADIUS(M)=",F12.5,/
     *  "    CAN HEIGHT(M)=",F12.5,/
     *  "    SIZE OF DIMENSIONLESS SPACE INCREMENT IN R DIRECTION=",
     *  F12.5,/
     *  "   SIZE OF DIMENSIONLESS SPACE INCREMENT IN X DIRECTION=",
     *  F12.5,///)
          CU=CI/(DC*DC*DX*2*22.0/7.0)
         DO 102 NL=1,NLEVEL
        DO 102 II=1,SX
        DO 102 JJ=1,SC
         AVET(JJ,II)=TI
  102   C(JJ,II,NL)=CU
          WRITE(6,/)CU
      TIME=0
      NN=(TIMES+CTIME)/DT
      DO 42 N=1,NN
      TIME=TIME+DT
      FOC=DIFF1*TIME/DC/DC
      FOX=DIFF1*TIME/DX/DX
      DO 58 I=1,SX+1
      DIX=FLOAT(I-1)/SX
      IF(FOX.LT.0.03)GO TO 110
      CALL SLAB(FOX,YL,DIX)
     GO TO 80
  110  XL=DIX*DX
        CALL LSLAB(FOX,YL,DX,XL)
   80  DO 58 J=1,SC+1
      DIC=FLOAT(J-1)/SC
      IF(FOC.LT.0.02)GO TO 120
      DO 49 JJ=1,6
   49  BRA(JJ)=B(JJ)*DIC
      CALL CYLND(FOC,YC,B,BRA,XJ0B,XJIB)
      GO TO 90
  120  IF(DIC.LT.0.1)GO TO 100
      R=DC*DIC
      CALL LCYLND(FOC,YC,DC,R)
      GO TO 90
  100  YC=1.0
   90  YHEAT=YC*YL
```

```
          TH(J,I)=(1-YHEAT)*(TA-TI)+TI
          IF(TIME.LE.TIMES)GO TO 200
          TDEL=TIME-TIMES
           A=FLOAT(I-1)*DX/SX
           ALIMIT=DX/AX
           X=FLOAT(J-1)*DC/SC
           XLIMIT=DC/AC
           IF(T(J,I).LT.TLIMIT)GO TO 800
           IF(A.GT.ALIMIT)GO TO 300
           IF(X.GT.XLIMIT)GO TO 300
           CFOC=DIFF2*TDEL/DC/DC
           CFOX=DIFF2*TDEL/DX/DX
           GO TO 400
      800   CFOC=DIFF3*TDEL/DC/DC
            CFOX=DIFF3*TDEL/DX/DX
           IF(A.GT.ALIMIT)GO TO 400
           IF(X.GT.XLIMIT)GO TO 400
            GO TO 500
    300   CFOC=DIFF1*TDEL/DC/DC
          CFOX=DIFF1*TDEL/DX/DX
    400   CIX=DIX
          IF(CFOX.LT.0.03)GO TO 145
          CALL SLAB(CFOX,CYL,CIX)
          GO TO 155
      145  CXL=CIX*DX
          CALL LSLAB(CFOX,CYL,DX,CXL)
      155  CIC=DIC
          IF(CFOC.LT.0.02)GO TO 165
          DO 55 JJ=1,6
       55  BRA(JJ)=B(JJ)*CIC
          CALL CYLND(CFOC,CYC,B,BRA,XJOB,XJIB)
          GO TO 175
      165  IF(CIC.LT.0.1)GO TO 185
           CR=DC*CIC
          CALL LCYLND(CFOC,CYC,DC,CR)
          GO TO 175
     185  CYC=1.0
    175  YCOOL=CYC*CYL
         T(J,I)=TH(J,I)+(TC-TA)*(1-YCOOL)
         GO TO 58
 500  CIX=DIX
          IF(CFOX.LT.0.03)GO TO 245
          CALL SLAB(CFOX,CYL,CIX)
          GO TO 255
      245  CXL=CIX*DX
          CALL LSLAB(CFOX,CYL,DX,CXL)
      255  CIC=DIC
          IF(CFOC.LT.0.02)GO TO 265
```

```
          DO 355 JJ=1,6
    355    BRA(JJ)=B(JJ)*CIC
          CALL CYLND(CFOC,CYC,B,BRA,XJOB,XJIB)
          GO TO 275
    265    IF(CIC.LT.0.1)GO TO 265
           CR=DC*CIC
          CALL LCYLND(CFOC,CYC,DC,CR)
          GO TO 275
    285    CYC=1.0
    275  YCOOL=CYC*CYL
           T(J,I)=YCOOL*(TLIMIT-TC)+TC
          GO TO 58
    200  T(J,I)=TH(J,I)
     58  CONTINUE
           DO 42 NL=1,NLEVEL
            DO 42 I=1,SX
            DO 42 J=1,SC
            TAVE(J,I)=(T(J,I)+T(J,I+1)+T(J+1,I)+T(J+1,I+1))/4
             TAVER(J,I)=(TAVE(J,I)+AVET(J,I))/2+273
           FNEA(J,I,NL)=EXP(-EA(NL)*((1.0/TAVER(J,I))-(1/TREF))/0,0083)
            C(J,I,NL)=C(J,I,NL)*EXP(-RK(NL)*DT*FNEA(J,I,NL))
          AVET(J,I)=TAVE(J,I)
     42  CONTINUE
         DO 108 I=1,SX
         DO 108 J=1,SC
         R1=(J-1)*DC/SC
         R2=J*DC/SC
    108    V(J,I)=(22.0*(R2**2.0-R1**2.0)*DX)/(7.0*2.0*SX)
           DO 308 NL=1,NLEVEL
            SUM=0.0
            DO 208 I=1,SX
            DO 208 J=1,SC
         SUM=SUM+C(J,I,NL)*V(J,I)
     208    CONTINUE
       RETEN(NL)=SUM*4
    308    RATIO(NL)=RETEN(NL)/CI
         WRITE(6,202)TIMES,CTIME
    202  FORMAT("   HEATING TIME(SEC)=",F12.1,//
      *  "   COOLING TIME(SEC)=",F12.1,//)
            WRITE(6,22)(RETEN(NL),RATIO(NL),RK(NL),EA(NL),NL=1,NLEVEL)
     22   FORMAT("    RETENTION CONCENTRATION=",F12.5,//
      *   "        RATIO OF C/CO=",F9.7,//
      *   "        REACTION RATE(1/SEC)=",E12.5,//
      *   "        ACTIVATION ENERGY(CAL/MOLE)=",E12.5,//)
         STOP
         END
```

```
      SUBROUTINE CYLND(FO,YC,B,BRA,XJOB,XJIB)
      DIMENSION B(10),XJIB(10),BRA(10),XJOB(10)
      COMMON XJO(200),ARG(200)
      DO 1 I=1,6
      IF(BRA(I).GT.14.89)GO TO 3
      DO 2 J=1,152
      IF(BRA(I)-ARG(J))5,4,2
    2 CONTINUE
    4 XJOB(I)=XJO(J)
      GO TO 1
    5 IF(J.GT.1)J=J-1
      XJOB(I)=XJO(J)+(XJO(J+1)-XJO(J))/(ARG(J+1)-ARG(J))*
     * (BRA(I)-ARG(J))
      GO TO 1
    3 XJOB(I)=(0.7979/BRA(I))**0.5*(COS(BRA(I)-0.7854)+0.125/
     * BRA(I)*SIN(BRA(I)-0.7854))
    1 CONTINUE
      YC=0
      DO 6 I=1,6
    6 YC=YC+2.0*XJOB(I)/B(I)/XJIB(I)*EXP(-B(I)**2*FO)
      RETURN
      END
      SUBROUTINE SLAB(FO,YL,D)
      YL=1.2732395*(COS(1.57143*D)*EXP(-FO*2.467401)+
     * (-1)/3.0*COS(3.0*1.57143*D)*EXP(-9.0*FO*2.467401)+
     * (+1)/5.0*COS(5.0*1.57143*D)*EXP(-25.0*FO*2.467401)+
     * (-1)/7.0*COS(7.0*1.57143*D)*EXP(-49.0*FO*2.467401)+
     * (+1)/9.0*COS(9.0*1.57143*D)*EXP(-81.0*FO*2.467401)+
     * (-1)/11.0*COS(11.0*1.57143*D)*EXP(-121.0*FO*2.467401))
      RETURN
      END
      SUBROUTINE LCYLND(FO,YC,DC,R)
      X=(DC-R)/2.0/(FO*DC**2.0)**0.5
      A=ERFN(X)
      E1=0.56428958*EXP(-X*X)-X*A
      X2=X*X
      E2=0.25*(A-X2*E1)
      YC=1-((DC/R)**0.5*A+(DC-R)*(FO*DC**3.0)**0.5/4/
     * DC/R**1.5*E1+(9*DC**2.0-7.0*R**2.0-2.0*DC*R)/
     * (32.0*DC**1.5*R**2.5)*FO*DC**2.0*E2)
      RETURN
      END
```

```
      SUBROUTINE LSLAB(FU,YL,DX,XL)
      YL=1.0
      XFU=(FU*DX**2.0)**0.5
      DO 102 I=1,3
      N=I-1
       Y1=((2*N+1)*DX-XL)/2.0/XFU
       Y2=((2*N+1)*DX+XL)/2.0/XFU
  102  YL=YL-((-1)**N*(ERFN( Y1 )+ERFN(Y2)))
       RETURN
       END
       FUNCTION ERFN(X)
       DATA P,A1,A2,A3,A4,A5/0.3275911,0.25482959,-0.28449674,
     * 1.42141374,-1.45315203,1.06140543/
       IF(X.GT.0.0)GO TO 13
       X=(-1)*X
   13  T1=1.0/(1+P*X)
       T2=T1*T1
       T3=T2*T1
       T4=T3*T1
       T5=T4*T1
       ERFN=EXP(-X*X)*(A1*T1+A2*T2+A3*T3+A4*T4+A5*T5)
       RETURN
       END
```

APPENDIX 5.3 An Example of the Kinetic Parameters Calculation

(a) Calculated (c/c_o) at each k_{129^oC} and Ea Level

Temperature ^oC	k_{129^oC} / Ea Run no.	0.3352×10^{-4} 93	0.3352×10^{-4} 73	0.4878×10^{-4} 93	0.4878×10^{-4} 73	0.4115×10^{-4} 83	0.4115×10^{-4} 103	0.4115×10^{-4} 63	0.2589×10^{-4} 83	0.5641×10^{-4} 83	Experimental c/c_o
129	6	0.94988	0.94369	0.92803	0.91922	0.93540	0.94192	0.92656	0.95879	0.91266	0.93884
	1	0.94072	0.93389	0.91505	0.90538	0.92394	0.93119	0.91432	0.95137	0.89738	0.91440
	8	0.93851	0.93157	0.91193	0.90103	0.92031	0.92857	0.91049	0.94960	0.89254	0.91116
	5	0.92861	0.92177	0.89798	0.88834	0.90930	0.91657	0.89973	0.94185	0.87796	0.90916
	10	0.92703	0.92019	0.89576	0.88612	0.90739	0.91467	0.89783	0.94061	0.87545	0.89939
120	7	0.95886	0.94861	0.94074	0.92615	0.94398	0.95480	0.92949	0.96435	0.92407	0.91667
	4	0.94109	0.92754	0.91547	0.89636	0.92052	0.93498	0.90180	0.94921	0.89274	0.91150
	9	0.93644	0.92269	0.90890	0.88955	0.91477	0.92951	0.89589	0.94547	0.88510	0.90942
	2	0.92334	0.90754	0.89046	0.86838	0.89778	0.91479	0.87637	0.93438	0.86265	0.89839

(b) Calculated Absolute Residuals

Temperature ^oC	k_{129^oC} / Ea Run no.	0.3352×10^{-4} 93	0.3352×10^{-4} 73	0.4878×10^{-4} 93	0.4878×10^{-4} 73	0.4115×10^{-4} 83	0.4115×10^{-4} 103	0.4115×10^{-4} 63	0.2589×10^{-4} 83	0.5641×10^{-4} 83
129	6	0.01144	0.00525	0.01041	0.01922	0.00304	0.00348	0.01188	0.02035	0.02578
	1	0.02632	0.01949	0.00065	0.00902	0.00954	0.01679	0.00008	0.03697	0.01702
	8	0.02735	0.02041	0.00077	0.01013	0.00915	0.01741	0.00067	0.03844	0.01862
	5	0.01945	0.01261	0.01118	0.02082	0.00014	0.00741	0.00943	0.03269	0.03120
	10	0.02764	0.02080	0.00363	0.01327	0.00800	0.01528	0.00156	0.04122	0.02394
Average absolute residuals		0.02244	0.01571	0.00533	0.01449	0.00597	0.01207	0.00472	0.03393	0.02331
Standard deviation		0.00700	0.00673	0.00514	0.00531	0.00417	0.00626	0.00551	0.00820	0.00571
120	7	0.04219	0.03194	0.02407	0.00948	0.02731	0.03813	0.01282	0.04768	0.00740
	4	0.02959	0.01604	0.00397	0.01514	0.00902	0.02348	0.00970	0.03771	0.01876
	9	0.02702	0.01327	0.00052	0.01988	0.00535	0.02009	0.01353	0.03605	0.02432
	2	0.02495	0.00915	0.00793	0.03001	0.00061	0.01640	0.02202	0.03599	0.03574
Average absolute residuals		0.03093	0.01760	0.00912	0.01863	0.01057	0.02453	0.01452	0.03936	0.02156
Standard deviation		0.00774	0.00997	0.01040	0.00870	0.01170	0.00952	0.00527	0.00561	0.01180
Overall average absolute residuals		0.02621	0.01655	0.00701	0.01633	0.00802	0.01761	0.00908	0.03634	0.02253
Standard deviation		0.00819	0.00781	0.00761	0.00687	0.00811	0.00983	0.00732	0.00732	0.00832

(c) Multiple Regression Analysis

(c).1 Using average absolute residual at each processing temperature:

regression of residuals (Q) to X1, X2, $X1^2$, $X2^2$, X1X2:

Variable	Coefficient	t-ratio
-	0.00985	4.11
X1	-0.00400	-4.31
X2	0.00151	1.62
$X1^2$	0.00502	5.59
$X2^2$	0.00113	1.25
X1X2	-0.00484	-3.01

R^2 = 85.1%, degree of freedom = 12.

As $X2^2$ was lower than 80% significance, therefore, the regression was repeated using only X1, X2, $X1^2$, X1X2:

Variable	Coefficient	t-ratio
-	0.01225	8.34
X1	-0.00400	-4.22
X2	0.00151	1.59
$X1^2$	0.00435	5.92
X1X2	-0.00484	-2.95

R^2 = 83.1%, degree of freedom = 13.0.

(c).2 Using individual residuals:

regression of residuals (Q) to X1, X2, $X1^2$, $X2^2$, X1X2:

Variable	Coefficient	t-ratio
-	0.00964	4.87
X1	-0.00392	-5.11
X2	0.00145	1.89
$X1^2$	0.00505	6.80
$X2^2$	0.00103	1.38
X1X2	-0.00475	-3.57

R^2 = 57.2%, degree of freedom = 75.

As $X2^2$ was lower than 80% significance, therefore, the regression was repeated using only X1, X2, $X1^2$, X1X2:

Variable	Coefficient	t-ratio
-	0.01183	9.90
X1	-0.00392	-5.08
X2	0.00145	1.88
$X1^2$	0.00444	7.42
X1X2	-0.00475	-3.55

R^2 = 56.1%, degree of freedom = 76.

(d) Decoding the Regression Equation and Minimization of Residual

From equation:

$$Q = |0.01225 - 0.00400X1 + 0.00151X2 + 0.00435X1^2 - 0.00484X1X2|$$

substitute X1 by $\dfrac{k_{129^oC} - 0.4115 \times 10^{-4}}{0.763 \times 10^{-5}}$ and

X2 by $\dfrac{Ea - 83}{10}$

giving

$$Q = |-0.0651 - 1.4904x10^{-3}\ k_{129^oC} + 2.699x10^{-3}\ Ea + 7.4652x10^{7}\ k_{129^oC}$$

$$-62.0238\ k_{129^oC}\ Ea|$$

Minimization of Q was done by:

$$\frac{dQ}{dk_{129^oC}} = -1.4904x10^{3} + 14.9304x10^{7}\ k_{129^oC} - 62.0238\ Ea = 0$$

$$\frac{dQ}{dEa} = 2.6995x10^{-3} - 62.0238\ k_{129^oC} = 0$$

$$k_{129^oC} = 0.4352x10^{-4}\ s^{-1}$$

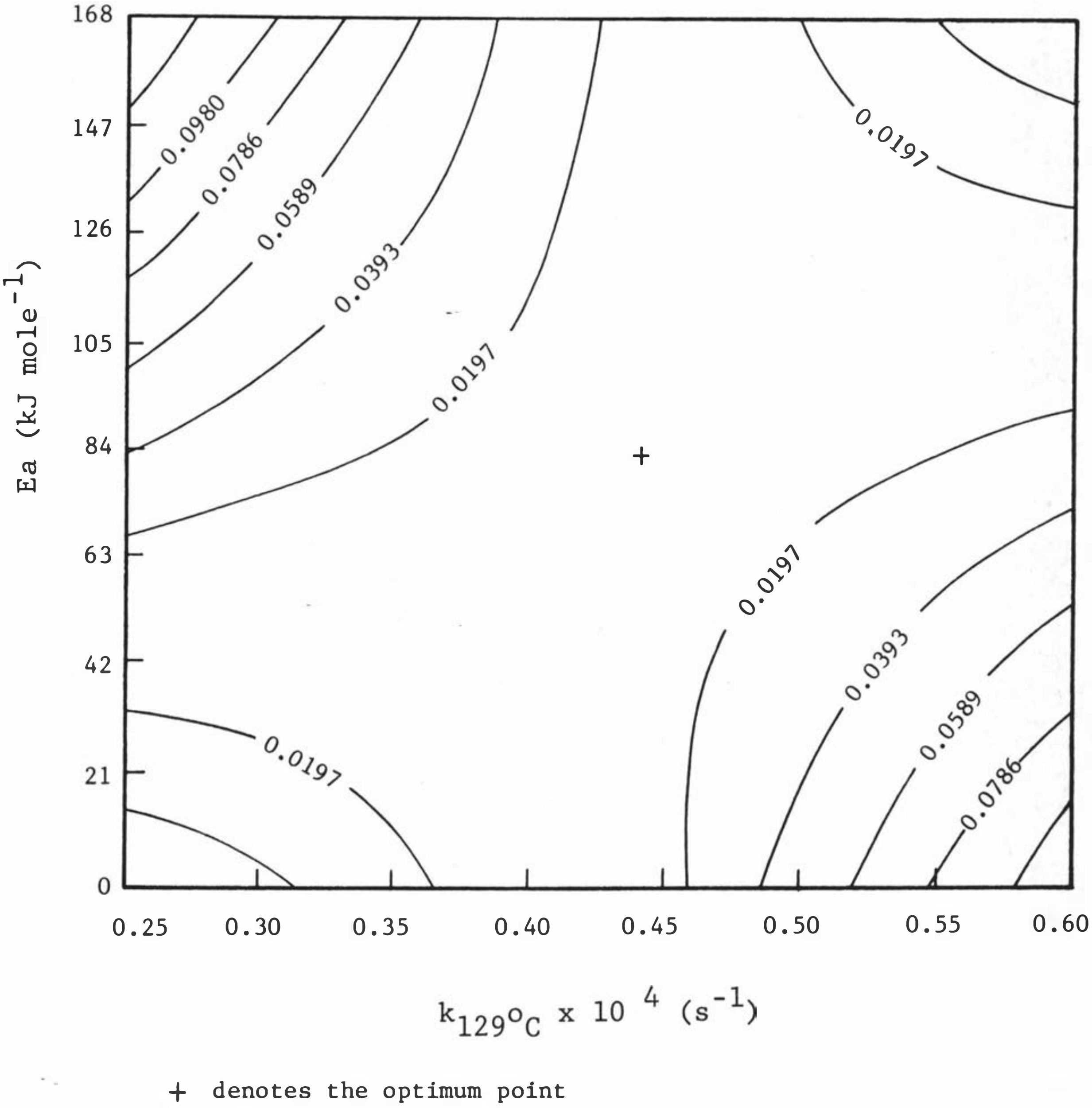
$$Ea = 80.7\ kJ\ mole^{-1}$$

(e) Contour Plot Program

```
      READ (5,/)XHI,XLO,YHI,YLO
       69 FORMAT(4F6.2)
       WRITE(6,1)XHI,XLO,YHI,YLO
      1 FORMAT(T10,' X= ',2G12.5/T10,' Y= ',2G12.5)
      CALL CONT(XHI,XLO,YHI,YLO)
      END
      FUNCTION FCT(X1,X2)
       FCT=ABS(-0.0651-1490*X1+2.6995E-3*X2+7.4652E7*X1*X1-62.0238*X1*X2)
      RETURN
      END
      SUBROUTINE CONT(XHI,XLO,YHI,YLO)
      DIMENSION Z(41,41),IPT(41)
      DX=(XHI-XLO)/40.
      DY=(YHI-YLO)/40.
      ZMAX=-1.E+20
      ZMIN=1.E+20
      Y=YHI+DY
      DO 1 I=1,41
      Y=Y-DY
      X=XLO-DX
      DO 2 J=1,41
      X=X+DX
      Z(I,J)=FCT(X,Y)
      IF(Z(I,J).LT.ZMIN) GO TO 3
      IF(Z(I,J).GT.ZMAX) GO TO 4
      GO TO 2
      3 ZMIN=Z(I,J)
      XMIN=X
      YMIN=Y
      IMIN=I
      JMIN=J
      00 GO TO 2
      4 ZMAX=Z(I,J)
      XMAX=X
      YMAX=Y
      IMAX=I
      JMAX=J
      GO TO 2
      2 CONTINUE
      1 CONTINUE
      C* SCALE THE Z VALUES
      DO 21 I=1,41
      DO 21 J=1,41
      Z(I,J)=((Z(I,J)-ZMIN)/(ZMAX-ZMIN))*10.
      21 CONTINUE
      ZZ=ZMIN+(FLOAT(I-1))*(ZMAX-ZMIN)/10.
```

```
      ZZ1=ZZ+(ZMAX-ZMIN)/10.
      WRITE(6,121)
      121 FORMAT ('1',T10,'X2 VALUES')
      DO 122 K=1,41
      Y=YHI-(FLOAT(K-1))*DY
      DO 382 IAN=1,41
       382 IPT(IAN)=Z(K,IAN)
      WRITE(6,124)Y,(IPT(L),L=1,41)
       124 FORMAT(T15,G12.5,T30,41(I1,1X))
       122 CONTINUE
      C* LABEL X1 AXIS
      DXX=(XHI-XLO)/5.
      XX2=XLO+DXX
      XX3=XX2+DXX
      XX4=XX3+DXX
      XX5=XX4+DXX
      WRITE(6,1127)
       1127 FORMAT(T30,'I',5(15X,'I'))
      WRITE(6,127)XLO,XX2,XX3,XX4,XX5,XHI
       127 FORMAT(T25,G12.5,5(4X,G12.5))
      WRITE(6,998)
       998 FORMAT(T50,'X1 VALUES')
      C* NOW DO THE KEY
      WRITE(6,128)
       128 FORMAT('1',//T20,'KEY TO CONTOURS')
      DO 150 I=1,10
      ZZ=ZMIN+(FLOAT(I-1))*(ZMAX-ZMIN)/10.
      ZZ1=ZZ+(ZMAX-ZMIN)/10.
      KK=I-1
      WRITE(6,129)KK,ZZ,ZZ1
       129 FORMAT(T10,'FOR SYMBOL',I3,'Y IS BETWEEN',G12.5,'AND',G12.5)
       150 CONTINUE
      WRITE(6,151)XMAX,YMAX
       151 FORMAT(/T20,'MAX VAL IS AT',/T30,'X1=',G12.5/T30,'X2=',G12.5/)
      WRITE(6,152)ZMAX
       152 FORMAT(T30,'AND IT IS',G12.5)
      RETURN
      END
```

(f) Contour Plot Based on Decoded Equation Shown in (d)



+ denotes the optimum point

APPENDIX 5.4 Estimation of k_{129^oC} for the Design for Ascorbic Acid

From equation (5.4), the final concentration at the end of a small time interval, Δt, was:

$$c_1 = c_o \text{ fn } (k_{129^oC}, \text{Ea}, T)$$

where $\text{fn}(k_{129^oC}, \text{Ea}, T)$ is $\exp(-k_{129^oC} \exp(-\frac{Ea}{R}(\frac{1}{T} - \frac{1}{402}))\ \Delta t)$

Tr is 129°C or 402°K

If T is constant, fn $(k_{129^oC}, \text{Ea}, T)$ will be constant as well. So at the end of the second Δt, the final concentration will be:

$$c_2 = c_1 \text{ fn } (k_{129^oC}, \text{Ea}, T)$$

$$= c_o (\text{fn}(k_{129^oC}, \text{Ea}, T))^2$$

Therefore, at the end of the nth Δt, the final concentration will be:

$$c_n = c_o (\text{fn}(k_{129^oC}, \text{Ea}, T)^n$$

For run no.6, assuming the average temperature was 110°C or 383°K over the processing time of 2952 + 2400 seconds, k could be calculated from the measured initial and final concentration of ascorbic acid of 25.68×10^{-2} and 24.10×10^{-2} mg g^{-1} using Δt of 72 seconds and assuming that Ea was 84.2 kJ mole^{-1} (Chittaporn, 1977).

As

$$n\Delta t = 2952 + 2400$$

$$n = \frac{2952 + 2400}{72}$$

$$\simeq 74$$

So

$$\text{fn}\ (k_{129^{o}C},\ 84.2,\ 383)^{74} = \frac{24.10 \times 10^{-2}}{25.68 \times 10^{-2}}$$

$$\text{fn}\ (k_{129^{o}C},\ 84.2,\ 383) = 0.999196$$

$$\exp(-k_{129^{o}C}\ \exp\ (\frac{84.2}{0.0083}(\frac{1}{383} - \frac{1}{402}))\ \times 72) = 0.999196$$

$$k_{129^{o}C} = 0.4115 \times 10^{-4}\ s^{-1}$$

APPENDIX 5.5 Determination of k_{129^oC} and Ea for Riboflavin, Colour Y, and Viscosity Using Equivalent Processing Time

(a) Riboflavin

The equivalent processing time at specified temperatures can be calculated if the kinetic reaction rate at that temperature is known by:

$$\ln \frac{c}{c_o} = -k_r t_r$$

$$t_r = -\frac{1}{k_r} (\ln \frac{c}{c_o})$$

where t_r is an equivalent processing time at reference temperature, r.

Knowing that the k_{129^oC} of ascorbic acid was 0.435×10^{-4} s^{-1}, the equivalent processing time at 129°C, t_{129^oC}, could be calculated from the experimental of c/c_o of ascorbic acid.

Run no.	$(c/c_o)_{exp}$, ascorbic acid	t_{129^oC}, min
6	0.93844	24.3
1	0.91440	34.3
8	0.91116	35.6
5	0.90916	36.5
10	0.89939	40.6

As t_{129^oC} for ascorbic acid and riboflavin should be the same, c/c_o for riboflavin corresponding to t_{129^oC} was calculated:

Run no.	t_{129^oC}, min	$(c/c_o)_{exp}$, riboflavin
6	24.3	0.97844
1	34.3	0.95813
8	35.6	0.94745
5	36.5	0.94025
10	40.6	0.93537

Regression of ln c/c_o with t_{129^oC} resulted in k_{129^oC} of 0.2459 x 10^{-4} s^{-1} with 99.9% significance and 0.973 correlation coefficient.

As the Ea of ascorbic acid was 81 kJ $mole^{-1}$, the k_{120^oC} could be calculated from:

$$k = k_{Tr} \exp \left(- \frac{Ea\ (Tr - T)}{RTTr}\right)$$

$$k_{120} = 0.435 \times 10^{-4} \exp \left(\frac{-81(129-120)}{0.0083(129+273)(120+273)}\right)$$

$$= 0.2495 \times 10^{-4}\ s^{-1}$$

The equivalent processing time at 120°C was again calculated based on the experimental c/c_o resulted from 120°C processing temperature experiments. These calculated equivalent processing times were corresponded to experimental c/c_o of riboflavin resulted from 120°C processing temperature experiments as shown below.

Run no.	t_{120^oC}, min	$(c/c_o)_{exp}$, riboflavin
7	58.1	0.97006
4	61.9	0.95159
9	63.4	0.94575
2	71.6	0.93428

Again, regression of ln c/c_o to t_{120^oC} was done; k_{120^oC} for riboflavin was found to be 0.1357 x 10^{-4} s^{-1} with 99.9% level of significance and 0.964 correlation coefficient.

Then, the activation energy of riboflavin was calculated from:

$$Ea = \ln \left(\frac{k_{129^oC}}{k_{120^oC}}\right)\left(\frac{RTTr}{Tr - T}\right)$$

$$= \ln \left(\frac{0.2459 \times 10^{-4}}{0.1357 \times 10^{-4}}\right)\left(\frac{0.0083 \times 402 \times 393}{402 - 393}\right)$$

$$= 87\ kJ\ mole^{-1}$$

(b) Colour, Y

Same as riboflavin, the t_{129^oC} for ascorbic acid and colour Y should be the same. The c/c_o for colour, Y, corresponding to t_{129^oC} was calculated from the analytical results:

Run no.	t_{129^oC}, min	$(c/c_o)_{exp}$, colour Y
6	24.3	0.8130
1	34.3	0.7916
8	35.6	0.7782
5_2	36.5	0.7578
10	40.6	0.7352

Regression analysis gave k_{129^oC} of 1.0633×10^{-4} s^{-1} with 99.9% significance and 0.989 correlation coefficient.

At 120°C processing temperature:

Run no.	t_{120^oC}, min	$(c/c_o)_{exp}$, colour Y
7	57.8	0.9010
4	61.6	0.8753
9	63.1	0.8269
2	71.2	0.7684

Regression analysis gave k_{120^oC} of 0.4660×10^{-4} s^{-1} with 99.9% significance and 0.973 correlation coefficient.

The activation energy was 120.9 kJ $mole^{-1}$ for colour Y.

(c) Viscosity

The method as in riboflavin was used.

At 129°C processing temperature:

Run no.	t_{129^oC}, min	$(c/c_o)_{exp}$, viscosity
6	24.3	0.8130
1	34.3	0.7916
8	35.7	0.7782
5	36.5	0.7578
10	40.6	0.7352

Regression analysis gave k_{129^oC} of 1.2348×10^{-4} s^{-1} with 99.9% significance and 0.996 correlation coefficient.

At 120°C processing temperature:

Run no.	t_{120^oC}, min	$(c/c_o)_{exp}$, viscosity
7	57.8	0.9010
4	61.6	0.8753
9	63.1	0.8269
2	71.2	0.7684

Regression analysis gave k_{120^oC} of 0.4633×10^{-4} s^{-1} with 99.9% significance and 0.932 correlation coefficient.

The activation energy was 143.6 kJ $mole^{-1}$ for viscosity.

APPENDIX 6.1 Quality Retention Calculation Program Based on Second Order Kinetics

```
      $OPT=1
            DIMENSION T(15,15),TH(15,15),B(10),XJIB(10),BRA(10),XJ0B(10),
          *  C(15,15,40),TAVE(20,20),AVET(20,20),V(15,15),TAVER(20,20),
          *   FNEA(20,20,40),RK(40),EA(40),RETEN(40),RATIO(40)
            COMMON XJ0(200),ARG(200)
            DATA ARG/0.0,0.1,0.2,0.3,0.4,0.5,0.6,0.7,0.8,0.9,1.0,
          * 1.1,1.2,1.3,1.4,1.5,1.6,1.7,1.8,1.9,2.0,
          * 2.1,2.2,2.3,2.4,2.5,2.6,2.7,2.8,2.9,3.0,3.1,3.2,3.3,3.4,3.5,
          * 3.6,3.7,3.8,3.9,4.0,4.1,4.2,4.3,4.4,4.5,4.6,4.7,4.8,4.9,5.0,
          * 5.1,5.2,5.3,5.4,5.5,5.6,5.7,5.8,5.9,6.0,6.1,6.2,6.3,6.4,6.5,
          * 6.6,6.7,6.8,6.9,7.0,7.1,7.2,7.3,7.4,7.5,7.6,7.7,7.8,7.9,8.0,
          * 8.1,8.2,8.3,8.4,8.5,8.6,8.7,8.8,8.9,9.0,9.1,9.2,9.3,9.4,9.5,
          * 9.6,9.7,9.8,9.9,10.0,10.1,10.2,10.3,10.4,10.5,10.6,10.7,10.8,
         * 10.9,11.0,11.1,11.2,11.3,11.4,11.5,11.6,11.7,11.8,11.9,12.0,
          * 12.1,12.2,12.3,12.4,12.5,12.6,12.7,12.8,12 9,13.0
          * ,13.1,13.2,13.3,13.4,13.5,13.6,13.7,13.8,13.9,14.0,14.1,14.2,
          * 14.3,14.4,14.5,14.6,14.7,14.8,14.9,0.0,0.0,0.0,0.0,0.0/
            DATA XJ0/1.0,0.9975,0.9900,0.9776,0.9604,0.9385,0.9120,
          * 0.8812,0.8463,0.8075,0.7652,0.7196,0.6711,0.6201,0.5669,
          * 0.5118,0.4554,0.3980,0.3400,0.2818,0.2239,0.1666,0.1104,
          *  0.0555,0.0025,-0.0484,-0.0968,-0.1424,-0.1850,-0.2243,
          * -0.2601,-0.2921,-0.3202,-0.3443,-0.3643,-0.3801,
          * -0.3918,-0.3992,-0.4026,-0.4018,-0.3971,-0.3887,
          * -0.3766,-0.3610,-0.3423,-0.3205,-0.2916,-0.2693,-0.2404,
          * -0.2097,-0.1776,-0.1443,-0.1103,-0.0758,-0.0412,-0.0068,
          * 0.0270,0.0599,0.0917,0.1220,0.1506,0.1773,0.2017,0.2238,
          * 0.2433,0.2601,0.2740,0.2851,0.2931,0.2981,0.3001,0.2991,
          * 0.2951,0.2882,0.2786,0.2663,0.2516,0.2346,0.2154,0.1944,
          * 0.1717,0.1475,0.1222,0.0960,0.0692,0.0419,0.0146,
          * -0.0125,-0.0392,-0.0653,-0.0903,-0.1142,-0.1367,-0.1577,
          * -0.1768,-0.1939,-0.2090,-0.2218,-0.2323,-0.2403,-0.2459,
          * -0.2490,-0.2496,-0.2477,-0.2434,-0.2366,-0.2276,-0.2164,
          * -0.2032,-0.1861,-0.1712,-0.1528,-0.1330,-0.1121,-0.0902
          * ,-0.0677,-0.0446,-0.0213,0.0020,0.0250,0.0477,0.0697,
          * 0.0908,0.1108,0.1296,0.1469,0.1626,0.1766,0.1887,0.1988,
          * 0.2,0.2129,0.2167,0.2183,0.2177,0.2150,0.2101,0.2032,
          * 0.1943,0.1836,0.1711,0.1570,0.1414,0.1245,0.1065,0.0875,
          * 0.0679,0.0476,0.0271,0.0064,1.0,1.0,1.0,1.0,1.0/
            DATA B/2.4048,5.5201,8.6537,11.7915,14.9309,18.0711,0.,0.,0./
            DATA XJIB/0.5191,-0.3403,0.2715,-0.2325,0.2066,-0.1890,0.,0.,0./
            READ(5,/)DC,DX,DIFF1,DIFF2,DIFF3,DT,SC,SX,TI,TA,TC,TIMES,
          * CTIME,TLIMIT,AX,AC,CI,TREF,NLEVEL
         9  READ(5,/)(RK(NL),EA(NL),NL=1,NLEVEL)
                   WRITE(6,/)(RK(NL),EA(NL),NL=1,NLEVEL)
            WRITE(6,30)DIFF1,DIFF2,DIFF3,TI,TA,TC
            WRITE(6,39)DC,2.0*DX,1/SC,1/SX
```

```
     *   F12.10,//," THERMAL DIFFUSIVITY IN LATER COOLING(MM/S)=",
     *   F12.10,//,"  INITIAL TEMPERATURE(C)=",F12.2,//
     *   "  RETORT TEMPERATURE(C)=",F12.2,//
     *   "   COOLING TEMPERATURE(C)=",F12.2,//)
  39  FORMAT("   CAN RADIUS(M)=",F12.5,/
     *   "   CAN HEIGHT(M)=",F12.5,/
     *   "  SIZE OF DIMENSIONLESS SPACE INCREMENT IN R DIRECTION=",
     *   F12.5,/
     *   "  SIZE OF DIMENSIONLESS SPACE INCREMENT IN X DIRECTION=",
     *   F12.5,///)

         DO 102 NL=1,NLEVEL
        DO 102 II=1,SX
        DO 102 JJ=1,SC
         AVET(JJ,II)=TI
 102    C(JJ,II,NL)=CI
          WRITE(6,/)CO
      TIME=0
      NN=(TIMES+CTIME)/DT
      DO 42 N=1,NN
      TIME=TIME+DT
      FOC=DIFF1*TIME/DC/DC
      FOX=DIFF1*TIME/DX/DX
      DO 58 I=1,SX+1
      DIX=FLOAT(I-1)/SX
      IF(FOX.LT.0.03)GO TO 110
      CALL SLAB(FOX,YL,DIX)
     GO TO 80
 110   XL=DIX*DX
        CALL LSLAB(FOX,YL,DX,XL)
  80   DO 58 J=1,SC+1
      DIC=FLOAT(J-1)/SC
      IF(FOC.LT.0.02)GO TO 120
      DO 49 JJ=1,6
  49   BRA(JJ)=B(JJ)*DIC
      CALL CYLND(FOC,YC,B,BRA,XJOB,XJIB)
      GO TO 90
 120   IF(DIC.LT.0.1)GO TO 100
      R=DC*DIC
      CALL LCYLND(FOC,YC,DC,R)
      GO TO 90
 100   YC=1.0
  90   YHEAT=YC*YL
      TH(J,I)=(1-YHEAT)*(TA-TI)+TI
```

```
      IF(TIME.LE.TIMES)GO TO 200
      TDEL=TIME-TIMES
       A=FLOAT(I-1)*DX/SX
       ALIMIT=DX/AX
       X=FLOAT(J-1)*DC/SC
       XLIMIT=DC/AC
       IF(T(J,I).LT.TLIMIT)GO TO 800
       IF(A.GT.ALIMIT)GO TO 300
       IF(X.GT.XLIMIT)GO TO 300
       CFOC=DIFF2*TDEL/DC/DC
       CFOX=DIFF2*TDEL/DX/DX
       GO TO 400
  800   CFOC=DIFF3*TDEL/DC/DC
        CFOX=DIFF3*TDEL/DX/DX
       IF(A.GT.ALIMIT)GO TO 400
       IF(X.GT.XLIMIT)GO TO 400
        GO TO 500
 300  CFOC=DIFF1*TDEL/DC/DC
      CFOX=DIFF1*TDEL/DX/DX
 400  CIX=DIX
      IF(CFOX.LT.0.03)GO TO 145
      CALL SLAB(CFOX,CYL,CIX)
      GO TO 155
  145  CXL=CIX*DX
      CALL LSLAB(CFOX,CYL,DX,CXL)
  155  CIC=DIC
      IF(CFOC.LT.0.02)GO TO 165
      DO 55 JJ=1,6
   55  BRA(JJ)=B(JJ)*CIC
      CALL CYLND(CFOC,CYC,B,BRA,XJOB,XJIB)
      GO TO 175
  165  IF(CIC.LT.0.1)GO TO 185
       CR=DC*CIC
      CALL LCYLND(CFOC,CYC,DC,CR)
      GO TO 175
 185  CYC=1.0
175  YCOOL=CYC*CYL
     T(J,I)=TH(J,I)+(TC-TA)*(1-YCOOL)
     GO TO 58
500  CIX=DIX
      IF(CFOX.LT.0.03)GO TO 245
      CALL SLAB(CFOX,CYL,CIX)
      GO TO 255
  245  CXL=CIX*DX
      CALL LSLAB(CFOX,CYL,DX,CXL)
  255  CIC=DIC
      IF(CFOC.LT.0.02)GO TO 265
      DO 355 JJ=1,6
   355  BRA(JJ)=B(JJ)*CIC
      CALL CYLND(CFOC,CYC,B,BRA,XJOB,XJIB)
      GO TO 275
```

```
  265  IF(CIC.LT.0.1)GO TO 265
         CR=DC*CIC
       CALL CCYLND(C,DC,CYC,DC,CR)
       GO TO 275
  285    CYC=1.0
  275  YCOOL=CYC*CYL
        T(J,I)=YCOOL*(TLIMIT-TC)+TC
       GO TO 56
  200  T(J,I)=TH(J,I)
   58  CONTINUE
         DO 42 NL=1,NLEVEL
           DO 42 I=1,SX
           DO 42 J=1,SC
           TAVE(J,I)=(T(J,I)+T(J,I+1)+T(J+1,I)+T(J+1,I+1))/4
            TAVER(J,I)=(TAVE(J,I)+AVET(J,I))/2+273
         FNEA(J,I,NL)=EXP(-EA(NL)*((1.0/TAVER(J,I))-(1/TREF))/0.0083)
           FNEA(J,I,NL)=FNEA(J,I,NL)*RK(NL)*DT
           C(J,I,NL)=1.0/((1/C(J,I,NL))+(FNEA(J,I,NL)))
        AVET(J,I)=TAVE(J,I)
   42  CONTINUE
       DO 108 I=1,SX
       DO 108 J=1,SC
       R1=(J-1)*DC/SC
       R2=J*DC/SC
  108    V(J,I)=(22.0*(R2**2.0-R1**2.0)*DX)/(7.0*2.0*SX)
         DO 308 NL=1,NLEVEL
           SUM=0.0
           DO 208 I=1,SX
           DO 208 J=1,SC
       SUM=SUM+C(J,I,NL)*V(J,I)/((22.0*DC*DC*DX)/(7.0*2.0))
  208      CONTINUE
      RETEN(NL)=SUM
  308    RATIO(NL)=RETEN(NL)/CI
       WRITE(6,202)TIMES,CTIME
  202  FORMAT("     HEATING TIME(SEC)=",F12.1,//
    *  "     COOLING TIME(SEC)=",F12.1,//)
          WRITE(6,22)(RETEN(NL),RATIO(NL),RK(NL),EA(NL),NL=1,NLEVEL)
   22   FORMAT("     RETENTION CONCENTRATION=",F12.5,//
    *   "      RATIO OF C/CO=",F9.7,//
    *   "      REACTION RATE(1/SEC)=",E12.5,//
    *   "      ACTIVATION ENERGY(CAL/MOLE)=",E12.5,//)
       STOP
       END
```

```
      SUBROUTINE CYLND(FO,YC,B,BRA,XJOB,XJIB)
      DIMENSION B(10),XJIB(10),BRA(10),XJOB(10)
      COMMON XJU(200),ARG(200)
      DO 1 I=1,6
      IF(BRA(I).GT.14.89)GO TO 3
      DO 2 J=1,152
      IF(BRA(I)-ARG(J))5,4,2
    2 CONTINUE
    4 XJOB(I)=XJU(J)
      GO TO 1
    5 IF(J.GT.1)J=J-1
      XJOB(I)=XJU(J)+(XJU(J+1)-XJU(J))/(ARG(J+1)-ARG(J))*
    * (BRA(I)-ARG(J))
      GO TO 1
    3 XJOB(I)=(0.7979/BRA(I))**0.5*(COS(BRA(I)-0.7854)+0.125/
    * BRA(I)*SIN(BRA(I)-0.7854))
    1 CONTINUE
      YC=0
      DO 6 I=1,6
    6 YC=YC+2.0*XJOB(I)/B(I)/XJIB(I)*EXP(-B(I)**2*FO)
      RETURN
      END
      SUBROUTINE SLAB(FO,YL,D)
      YL=1.2732395*(COS(1.57143*D)*EXP(-FO*2.467401)+
    * (-1)/3.0*COS(3.0*1.57143*D)*EXP(-9.0*FO*2.467401)+
    * (+1)/5.0*COS(5.0*1.57143*D)*EXP(-25.0*FO*2.467401)+
    * (-1)/7.0*COS(7.0*1.57143*D)*EXP(-49.0*FO*2.467401)+
    * (+1)/9.0*COS(9.0*1.57143*D)*EXP(-81.0*FO*2.467401)+
    * (-1)/11.0*COS(11.0*1.57143*D)*EXP(-121.0*FO*2.467401))
      RETURN
      END
      SUBROUTINE LCYLND(FO,YC,DC,R)
      X=(DC-R)/2.0/(FO*DC**2.0)**0.5
      A=ERFN(X)
      E1=0.56428958*EXP(-X*X)-X*A
      X2=X+X
      E2=0.25*(A-X2*E1)
      YC=1-((DC/R)**0.5*A+(DC-R)*(FO*DC**3.0)**0.5/4/
    * DC/R**1.5*E1+(9*DC**2.0-7.0*R**2.0-2.0*DC*R)/
    * (32.0*DC**1.5*R**2.5)*FO*DC**2.0*E2)
      RETURN
      END
```

```
      SUBROUTINE LSLAB(FU,YL,DX,XL)
      YL=1.0
      XFU=(FU*DX**2.0)**0.5
      DO 102 I=1,3
      N=I-1
       Y1=((2*N+1)*DX-XL)/2.0/XFU
       Y2=((2*N+1)*DX+XL)/2.0/XFU
  102  YL=YL-((-1)**N*(ERFN(Y1)+ERFN(Y2)))
       RETURN
       END
       FUNCTION ERFN(X)
       DATA P,A1,A2,A3,A4,A5/0.3275911,0.25482959,-0.28449674,
     * 1.42141374,-1.45315203,1.06140543/
       IF(X.GT.0.0)GO TO 13
       X=(-1)*X
   13  T1=1.0/(1+P*X)
       T2=T1*T1
       T3=T2*T1
       T4=T3*T1
       T5=T4*T1
       ERFN=EXP(-X*X)*(A1*T1+A2*T2+A3*T3+A4*T4+A5*T5)
       RETURN
       END
```