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PRELIMINARY STUDIES OF CHEMICAL REACTIONS AS INDICES OF HEAT LETHALITY

By

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"The process by which wants are satisfied is also the process by which wants are created. The more wants that are satisfied, the more new ones are born".

\- Galbraith

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INTRODUCTION

In commercial canning, food put into a container always contains micro-organisms that would cause spoilage if they were not subsequently destroyed. When the destruction of the spores of a certain organism in food has reached a certain pre-established point, the food is said to be sterile with respect to that organism and the object of heat processing canned foods is the attainment of sterility with respect to the most resistant micro-organisms present that would bring about spoilage.

Since the discovery of the principle of sterilisation by heat and the initial development of the art of heat processing by Appert at the beginning of the 19th century, considerable progress had been made in the fields of processing techniques and their evaluation. Standard methods have evolved for determining minimum processing conditions necessary to attain commercial sterility in products. However, as yet, there are no sensitive and reliable methods which do not involve the use of thermocouples for temperature measurement to check on under or over-processing during the routine sterilisation of canned products. The preparation of cans with inserted thermocouples and the recording of temperatures is too laborious and time consuming to become a routine check on processing and so the need for a more convenient method is obvious.

The purpose of this investigation was to carry out preliminary studies to ascertain the possibility of using chemical reactions occurring in model systems or food products as indices of heat lethality and so determine if correlations between a chemical index and heat lethality can be established and have commercial application.

In order to carry out this study, it is first necessary to briefly review theoretical aspects pertaining to the heat processing of canned foods.

THE HEAT PROCESSING OF CANNED FOODS

A can of heat processed "canned" food contains a "sterilised" product that at room temperature will remain microbiologically unspoiled indefinitely and depending on the type of food, will have a marketable quality shelf life of 6 months to 2 years. The majority of canned foods are heat treated to prevent microbiological and enzymatic spoilage and concurrent with the heat treatment, we may find loss of nutrients, e.g. thiamine destruction, and chemical reactions occurring, e.g. non enzymic browning.

Just as the rate of a chemical reaction depends on time, temperature and concentrations of reactants, so the lethal effect of heat on bacteria is a function of the time and temperature of heating and the bacterial population in the product. To design or evaluate an in-package heat process, it is necessary to know the heating characteristics of the system under study, the number of spoilage organisms present and the thermal resistance characteristics of the spoilage organisms.

HEATING CHARACTERISTICS OF CANNED FOODS

1. Conduction Packs

Products heating by conduction within a stationary container do not move or change their location during the process. During heating, heat from the surrounding medium, e.g. steam under pressure, is transferred almost immediately to the outermost layer of food in the container and is then conducted from particle to particle inward toward

the centre of the food mass from all points of the container wall. During the initial phase of heating there is a constant temperature portion of food near the centre of the container. The temperature of the food near the container wall rises during this lag period. Subsequent to the lag period the temperature from the centre to the can wall rises on a smooth curve. If heating is allowed to continue long enough the entire contents will eventually reach the temperature of the surrounding steam and the last portion of food to reach this temperature will be at the geometric centre of the container (the point of slowest heating or critical point).

If at the end of any given heating time the container is plunged into cooling water, heat transfer within the container is reversed in direction and the contents cool until equilibrium is reached with the surrounding medium. Because temperature rise during heating and temperature drop during cooling are logarithmic in order cooling to a non-lethal temperature is accomplished in considerably less time than is required to heat the food, (i.e. from the lowest temperature which is lethal, to the highest temperature attained during the process). Therefore, even though the temperature drops less rapidly at the centre than at any other points in the container during cooling, there is a small volume of food at the centre which receives a less severe heat treatment than any other food in the container and the severity of heat treatment increases progressively from the centre, in any direction, to the wall of the container.

2. Convection Packs

Foods which heat by convection exhibit much more rapid heating than do foods which heat by conduction. In the case of convection heating, transfer of heat in the food mass is aided by product movement within the container and for a condition of ideal convection heating, temperatures throughout the container of food during processing would be identical at all times, i.e. the temperature at any point in the container at any time is the same as the temperature at the critical point.

3. "Broken Heating" Packs

Certain foods exhibit "broken" heat penetration curves due to a change in consistency within the pack when a certain temperature is reached. An increased rate of heat penetration could result from the transformation of a conduction pack into a convection pack and similarly, a decreased rate of heat penetration could result from the transformation of a convection pack into a conduction pack. The critical point in a container of food of this type bears the same significance to the respective state the food is in as discussed above.

DEATH OF BACTERIAL SPORES

The first modern critical approach to the problem of death of bacterial spores under the influence of heat appears to be that of Bigelow and Esty (13) who define thermal death point in relation to time (i.e. thermal death time) as the time at different temperatures necessary to completely destroy a definite concentration of spores in a medium of known hydrogen ion concen-

tration. Using the concept of thermal death time, they demonstrated that with any given spore suspension, the thermal death time was a function of the spore concentration and that the thermal death time for a given spore concentration decreased with increase in temperature. Using the same data Bigelow (11) demonstrated the logarithmic relationship between temperature and thermal death time, that is, when the survival and destruction points for any given suspension and spore concentration were plotted upon a logarithmic scale against the corresponding temperatures on a linear scale, essentially straight lines were obtained.

Ball (5,6) on developing the mathematical methods used for the calculation of processes for canned foods pointed out that the thermal death time curves of Bigelow (11) could be characterised by a point and a slope. The reference point chosen was the time to destroy the organism at 250°F and this was designated by the symbol F. The slope of the thermal death time curve symbolised by Z was defined as the number of degrees required for the curve to traverse one log cycle. This is the equivalent of the number of degrees the temperature must be raised or lowered from a given reference temperature to produce a tenfold decrease or increase in destruction time.

The lethal rate L was defined as the reciprocal of the thermal death time.

The above procedures are concerned with survival and destruction times for some given initial spore concentration, and the basic presupposition of this work is, that there is a time for a given temperature and suspension medium for any initial spore concentration of a given organism at which all of the organisms are dead.

Very early in the studies of the death of micro-organisms under adverse influences attention was given to the number of survivors remaining in relation to time, and attempts were made to measure the "rate of death" of bacterial suspensions, exposed to some adverse environmental factor such as chemicals or high temperature. In 1910 Chick (24) showed that the rate of death of micro-organisms was of logarithmic order, that is, the number of surviving organisms plotted on a logarithmic scale against time on a linear scale gave a straight line. The logarithmic order of death of micro-organisms under various influences has been extensively reviewed by Rahn (97,98) and considerable additional evidence substantiating logarithmic death has been presented.

Evidence for a non logarithmic order of death has been reviewed by Rahn (97,98) and a non logarithmic order of death of spores of food spoilage organisms has been reported (101,106).

It is evident that only in the case of straight line survivor curves can simple mathematical treatment, formulation and extrapolation of the results to other conditions or initial numbers be carried out. No satisfactory expression has been found to express resistance when the survivor curve is not a straight line. For this reason, death of bacterial spores is generally considered logarithmic (9,98,120) and this allows it to be described mathematically in the same manner as a unimolecular or first order bimolecular chemical reaction. In a unimolecular reaction only one substance reacts and its rate of decomposition is directly proportional to its concentration while in a first order bimolecular reaction one reactant is in such great excess that variation in its concentration is negligible and rate of decomposition of the second reactant is directly proportional to its

concentration.

The rate of a first order reaction is expressed by

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

$$\text{or} \quad -\frac{dc}{c} = k\,dt \qquad \ldots\ldots\ldots\ldots \text{(1)}$$

where c = concentration of reacting substance

t = time

$^{dc}/_{dt}$ = rate of change of concentration of reactant

k = rate constant

Integrating equation (1) between the limits, concentration c_1 at time t_1 and c_2 at a later time t_2, we have

$$-\int_{c_1}^{c_2} \frac{dc}{c} = k \int_{t_1}^{t_2} dt$$

$$-\quad \ln c_2 - (-\ln c_1) = k(t_2 - t_1)$$

$$k(t_2 - t_1) = \ln \frac{c_1}{c_2}$$

This can be modified to give

$$t = \frac{2.303}{k} \log \frac{c_o}{c} \qquad \ldots\ldots\ldots\ldots \text{(2)}$$

in which c_o = initial concentration of reactant

c = concentration after reaction time t

From the survivor curve let a represent the initial number of cells (comparable to c_o in equation (2)) and b represent the number of surviving

cells (comparable to c in equation (2)) after heating time t. Then

$$t = \frac{2.303}{k} \log \frac{a}{b}$$

The time required to destroy 90% of the cells is the time required for the survivor curve to traverse one log cycle. If this time is represented by D (decimal reduction time) the slope of the survivor curve may be expressed as

$$\frac{\log a - \log b}{D} = \frac{1}{D}$$

Substituting in the general equation of a straight line

$$y = mx$$

we obtain

$$\log a - \log b = \frac{1}{D} t$$

$$t = D(\log a - \log b) = D\log \frac{a}{b} \qquad \text{............ (3)}$$

in which t = time of heating

D = time to destroy 90% of cells

a = initial number of cells

b = number of cells after heating time t

On comparing equations (2) and (3) the similarity between the expression for a first order chemical reaction and the expression for logarithmic destruction on bacterial spores can be seen.

PROCESS EVALUATION

1. The General Method

This method described by Bigelow, *et al.* (12) is essentially a graphical procedure for integrating the lethal effects of various time-

temperature relationships existent in a container of food during processing. The time-temperature relationships for which the lethal effects are integrated are those represented at the point of greatest temperature lag during heating and cooling of the product. This point was found to be at or near the geometric centre of the container.

The rate of destruction of an organism per minute at any given temperature (T) in a process is the reciprocal of the time in minutes (t) required to destroy the organism at that temperature. From the thermal death time curve, the following relationship can be obtained.

$$\frac{\log t - \log F}{\log 10} = \frac{250 - T}{Z}$$

$$\log \frac{t}{F} = \frac{250 - T}{Z}$$

$$\text{i.e.} \quad \frac{t}{F} = \text{antilog} \, \frac{250 - T}{Z} \qquad \ldots\ldots\ldots\ldots \; (4)$$

where Z = slope of thermal death time curve in ^{o}F

F = minutes to destroy the organism at $250^{o}F$

T = temperature under consideration (^{o}F)

$^{t}/_{F}$ = time to destroy the organism at temperature (T) if $F = 1$

$^{F}/_{t}$ = lethal rate at T

Since F and Z are known from the thermal death time curve, equation (4) can be solved and the lethal rate determined.

Since thermal reduction times were used to replace thermal death times, the Z concept was retained and so, if the values of thermal reduction time (for some constant reduction of spore numbers) or the decimal reduction time (D) are plotted against temperature (T), then the curve has the same slope

as the logarithm thermal death time versus temperature curve

$$\text{i.e. } \frac{1}{Z} = -\frac{d\ (\log d)}{T}$$

$$\text{or } \log (D_2/D_1) = -(T_2 - T_1)/Z$$

However, lethal rate L is defined as the reciprocal of the thermal reduction time.

$$\text{Hence} \quad \frac{L_2}{L_1} = 10^{(T_2 - T_1)/Z} \qquad \text{............ (5)}$$

Lethal rate values have been tabulated (15,120).

From the survivor curve, the destruction of spores can be represented

$$\log \frac{No}{N} = L\theta$$

$$\text{or} \quad d \ \log \frac{No}{N} = Ld\theta$$

$$\text{whence} \quad \log \frac{No}{N_1} = \int_{\theta_o}^{\theta_1} Ld\theta$$

The F value of a process can be defined as the time at 250°F which accomplishes the same reduction in spore numbers as the process

i.e. $$F = D_{250} \log \frac{No}{N_1}$$

therefore $$F = D_{250} \int_{\theta_o}^{\theta_1} L d\theta$$

$$= \int_{\theta_o}^{\theta_1} \frac{L}{L_{250}} \, d\theta$$

Substituting equation (5) we have

$$F = \int_{\theta_o}^{\theta_1} 10^{(T - 250)/Z} \, d\theta$$

Hence by plotting lethal rate against time, a lethality curve is obtained and the area under this curve represents the total lethal value of the process. This area is expressed in terms of equivalent time at 250°F by dividing into it a unit area representing the equivalent of one minute at 250°F (or Fo = 1 minute). The resulting value is the Fo value of the process in minutes. For example, the heat process required to destroy *Clostridium botulinum* in low acid products must have an Fo of not less than 2.78 minutes. That is, the area of the lethality curve must be greater than 2.78 times the unit

area to ensure adequate processing.

Various modifications have been made to the General Method. For example, Shultz and Olson (117) introduced specially ruled lethal paper on which the temperature - time data are plotted directly while Patashnik (92) used a simple arithmetic summation of lethal rate values at equal time intervals.

2. Formula Methods

Ball's "Formula Method", introduced in 1923 (5) uses heating and cooling curves of a standard form. The reciprocal slopes, f_h and f_c, of the heating and cooling curves are assumed equal and the cooling curve has a lag factor or j value incorporated. The lag portion of the cooling curve is approximated to by a hyperbolic expression.

The integration is carried out using the expression

$$F = f \, Lg \, C$$

$$\text{where} \quad Lg = {}_{10}(250 - Tg)/Z$$

and C is a tabulated function of g, Z and m + g

"g" is the difference between retort temperature and maximum centre temperature Tg at the end of the heating period, and Z is the slope of the thermal death time curve. "m + g" is the difference between retort and cooling water temperature.

Ball's technique was further improved in 1928 with the retabulating of the C : g tables as $f_h/_u$: g tables

$$\text{where} \quad \frac{f_h}{u} = \frac{e^{2.303 \, g/Z}}{C}$$

"u" is the number of minutes required to destroy an organism at retort temperatures. Further parameters and modifications have been introduced to the method (7) but discrepancies are still found (46, 121).

The above formula method treats only a single point and depending on whether thermal death time or thermal reduction time data is used, indicate whether a process will achieve "sterility" or reduce the population of spores by a given ratio. They do not indicate the probability of spore survival at any point other than that considered in the analysis. Ball, one of the chief exponents of the critical point method argues that the basic problem in sterilisation rests in determining when the food at the critical point has received a sufficient quantity of heat to destroy the organisms of the most resistant type that could spoil the food. Ball assumes that when sterilisation is accomplished at the critical point, sterilisation will already have been completed at all other points and hence the sterilisation of the entire mass is accomplished (7).

However, with the introduction of the thermal reduction time concept the critical point approach received considerable criticism. To calculate the survivors, Stumbo (119) considered the contents of the container to consist of a collection of portions that constitutes a series of nested shells, designated as iso-F value shells, which are defined by the condition that all material which constitutes any one shell receives equal lethal-heat treatment. As the series progresses from the outside surfaces of the container to the shell that contains the critical point, there is a progressive decrease in lethal value for the successive shells. Stumbo applied the survivor curve to each shell independently, basing the calculation of survival on the entire

volume of the food substance which constitutes the shell as the unit volume, that is, considering each shell as defining its own unit volume. No two shells have the same volume and it is visualised that the imaginery containers gradually change in shape from cylindrical to ellipsoidal or spherical from outside to centre of the real container.

Stumbo defined the region of greatest probability of survival as the region occupied by the shell in which the number of survivors would be greatest according to the calculation. His calculation showed that the shell occupying the region of the greatest probability of survival according to the above definition, is not the shell within which is the point of lowest degree of lethal treatment. He suggested that the latter point may not be critical in consideration of the effectiveness of a sterilising process and that the effect observed at that point may not be a true criterion of sufficiency of the sterilisation of the contents of the container.

Hicks (44) in a discussion of Stumbo's first two papers points out that with a uniform spore destruction in the container, the number of spores actually subjected to the conditions at the slowest heating point will be very small. Some regions in the container receiving slightly more heat treatment will be relatively large in volume and so contain more spores. The chance of survival of a spore in such a region may therefore be greater than at the slowest heating point.

The more recent concept above of integration of the lethality of the process in terms of the whole container is only applicable to conduction packs as in convection packs all bacteria are subject to essentially the same amount of lethal heat.