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Vitamins in thermal processing

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Advances in analytical methodology, particularly high-performance liquid chromatography and immunoassays and protein-binding assays, are now making major contributions towards nutritional studies of food processing. Computer simulation of heat transfer is increasingly used in thermal process development but in nutrient prediction its use is hampered by lack of kinetic data and is mainly confined to thiamin and ascorbate. Although control over the process with respect to the severity of heating, protection from oxygen and adventitious metals, and optimisation of liquid–solid ratios are important contributors to the final nutrient quality, reactions between food components often cause 'product specific' change. Consumers need to appreciate the value of cool temperature storage for quality retention in thermally processed shelf-stable products. During cooking, leaching of water-soluble vitamins into cooking liquors is increasingly recognised as the major source of loss, but studies of cooking processes would greatly benefit from greater application of a modelling approach.

INTRODUCTION

A thermal treatment is an intrinsic part of most food processing procedures and may be employed to inactivate enzymes and toxic factors (such as lectins), to change texture and flavour or to preserve. In pasteurisation, canning, aseptic processing and cooking the main thermal treatment applied is in excess of 60°C and may exceed 200°C. The factors which control the nutrient effect can only be adequately assessed if the chemical species measured by assay methods are fully elucidated; if assay methods are amenable to the generation of sufficient data for statistical analysis; and if changes are referred to the original sample weight to accommodate water, fat and soluble solid losses. For comparison of studies the process conditions and process targets must be carefully described. Studies in laboratories where conditions are varied in a systematic manner have been very successful in indicating the vulnerable stages of a process but do not necessarily mimic plant conditions so that the extent of change may not be comparable. Laboratory studies have sometimes been carried out with fortified foods with the objective of raising the vitamin level to ease the assay problems but added vitamins are not necessarily of the same form and chemical stability as the natural content. The value per 100 g at the end of the process, which is the dietetically important quantity, is largely determined by the raw value, which is very variable.

Loss of potency may be due to chemical change into related compounds with lower potency, to irreversible binding to other food components or to degradation into inactive products. Oxygen, light and transition metals frequently play an active role in accelerating or promoting loss. Both chemical change and diffusion proceed more rapidly as the temperature is raised.

Apparent increases may occur due to the release of chemically bound forms, or to improvements in digestibility and extraction when the matrix of the food has been damaged.

ANALYTICAL ADVANCES

Vitamin biopotency is still most reliably measured by biological or microbiological assays. Although chemical methods have been successfully employed for many years for vitamin A, thiamin and ascorbic acid, microbiological assay is still the preferred method for some B vitamins because of its sensitivity. However, the relatively recent immunoassay developed for pantothenic acid (Finglas *et al.*, 1988*a*) and the protein-binding assay for folate (Finglas *et al.*, 1988*b*) are proving to be much faster than microbiological assay while giving a comparable total value. Thus, the possibility now exists for nutrient/food/process studies for which, to date, the information is very sparse. However, these 'total potency' methods give no information on individual contributors to the total activity. Vitamin activity generally resides in a group of structurally related

Table 1. Some activation energies determined at thermal processing temperatures

Food	Vitamin	E_a (kJ/mol)	Order	Range (°C)	Ref.
Orange juice	C	14 (pH 2·5) 23·6 (pH 3·0) 37·3 (pH 3·5) 16·5 (pH 4·0)	1	60–90	Ülgen & Ozilgen (1991)
Model food (bentonite glucose glycine)	C	14·6		110–150	Ghazala *et al.* (1989)
Milk	B_1	100·8	2	120–150	Kessler & Fink (1986)
Meat loaf (convective heating)	B_1	113·3	1	70–98	Skjöldebrand *et al.* (1983)
Minced meat purée	B_1	115·4	1	100–120	Feliciotti & Esselen (1957)
Minced meat purée	B_1	114·5	1	100–120	Mulley *et al.* (1975)
Buffer (pH 7)	Folate (oxid)	68·1	1	40–92	Barrett & Lund (1989)
	(nitrogen)	97·4	1	40–92	
Milk	*B. stearothermophilus* spores	288·4		90–135	Pagliarini *et al.* (1991)
	Protease inactivation	82·7			
	Colour	101·8			

compounds with varying potency and chemical stability. High-performance liquid chromatography (HFLC) has been very successful in the last decade in separating and quantifying individual vitamers and can add greatly to the understanding of changes in biopotency. The assessment of preformed vitamin A and its carotenoid precursors is a particularly good example. Woollard and Indyk (1989) found 14 retinyl esters in cows' milk whose ratio remained similar in supplemented milk powder despite an overall loss of 30% during 6 months storage at 20°C. Murphy *et al.* (1988) monitored the appearance of *cis* isomers of retinyl palmitate in fortified skimmed milk exposed to light. Pettersson and Jonsson (1990) used a calcium hydroxide column to separate the *cis* isomers of α- and β-carotene formed during the heat treatment of carrot juice. Ahmad and Ryley (unpublished results) have monitored all-*trans* and α- and β-carotene in the preparation and sterilisation of carrot purée and found that although *cis* isomers were formed during the preparation stage, the proportion of total carotenoids present as *cis* isomers was lower after sterilisation unless the product was grossly overprocessed.

Vitamin B_6 assay provides another excellent example of the effectiveness of HPLC. It has long been known that pyridoxal is converted to pyridoxamine during thermal processing and that the stability of vitamin B_6 varies according to the food (Archer & Tannenbaum, 1979). Gregory III *et al.* (1986) using radio-labelled products and ion pair chromatography on protein hydrolysates showed that loss of B_6 activity during heating of caseinate model systems, chicken liver and chicken muscle could be attributed to binding to protein with the formation of inactive pyridoxyl lysine.

THERMAL STABILITY

In 1977, Benterud showed data for the degradation of vitamins in which the thermal effect was isolated from other effects by heating in a water-free carbohydrate melt which protected them from air. Tocopheryl acetate, riboflavin and nicotinamide suffered no loss. At 100 and 110°C for 15 min the rest suffered up to 10% loss. At 120 and 130°C only thiamin mononitrate and folic acid suffered major loss. Although the fortification forms used in this experiment were not necessarily the forms found naturally in foods, the results serve as a baseline for a discussion of interactions with the environment provided by the food and packaging.

The effect of heating on some vitamins in some foods has been studied in sufficient depth to be able to cite rate constants (usually first-order) or decimal reduction times (which are based on the assumption of a first-order rate of change) and temperature dependence (activation energies E or z† values). Table 1 lists some activation energy values for foods and solutions plus some comparative data for microorganisms, enzymes and other chemical changes (Farrer, 1955; Feliciotti & Esselen, 1957; Laing *et al.*, 1978; Ruddick *et al.*, 1980; Horak & Kessler, 1981; Mnkeni & Beveridge, 1983; Fernandez *et al.*, 1986; Lappo, 1986; Villota & Hawkes, 1986; Ghazala *et al.*, 1989). The data in Table 1 indicate that microorganisms are more vulnerable than physical and chemical changes and enzyme inactivation to increased temperature. Therefore, for thin layers which can rapidly achieve the process temperature, greater retention of original chemical properties including nutrient retention is achieved with a high-temperature short-time (HTST) process than with a low-temperature long-time process of equivalent lethality as illustrated in Table 2 for pouches (Komatsu & Yamaguchi, 1975; Castillo *et al.*, 1980). It is quite possible to render a food commercially sterile without inactivating enzymes, an effect which if it occurs in ultra-high temperature

† the 'z' value is the temperature change in °C, required to cause a 10-fold change in a particular property—the population of a particular microorganism or the concentration of a vitamin. It assumes first-order kinetics.

Table 2. Pouches HTST B_1 retention—seasoned spitchcock $F_0 = 3\text{–}4^{a,b}$

Temperature (°C)	Time (min)	% B_1 retention
Unsterilised		100·0
155	1·1	99·4
150	1·4	98·2
145	1·9	98·1
130	3·5	85·3
115	23·0	17·2

[a] From Komatsu *et al.* (1975), permission requested.
[b] $F_0 = \int 10^{(T-T_r)/z}\,dt$ (min).
where T_r is reference process temperature of 121·1°C, T is temperature of slowest heating point in package, z is the temperature coefficient for the spores of *Clostridium botulinum* (the temperature increase in °C required to cause a ten-fold reduction in the population).

An F_0 value of 2·5 min is the minimum for safety. In practice, a higher value is obtained to increase the safety margin. Calculation of the F_0 value enables the lethality of different heat treatments to be compared.

(UHT) milk is referred to as 'lipase taint'. It is also possible to sterilise foods such as beans without cooking them. Consequently, there is often a sensory or safety requirement of such importance that the optimum process for nutrient retention is not an option. Thus, some loss of vitamins is an inevitable consequence of heating food. Within this constraint much can be, and indeed is, done to ensure that the final product is of high quality with respect to its vitamin content.

'IN-CONTAINER' PROCESSING

Probably the most important factor in any thermal process is whether heat is transferred within the food by conduction or convection. In a conduction-heated food without agitation there will be a temperature gradient from the surface, which is at the process temperature, to the centre so that it is inevitable that the outer layers of the product receive a more severe process than the centre (Fig. 1).

Mathematical predictions of the retention of thiamin in a few conduction-heated foods and of ascorbic acid in a conduction heated model system have been made by several workers and verified in the laboratory. These predictions suggest that processing in a thin layer would be advantageous, a factor which has been verified by work in cans (Table 3, Teixeira *et al.*, 1975), and that the processing temperature for optimum thiamin retention depends on the package dimensions. Ohlsson (1980) calculated that for conduction-heated food sterilised in cylindrical containers, the best processing temperature range was 116–119°C for both thiamin and sensory quality for the range of can sizes commonly used. Figure 2 shows the nutritional consequences for a range of processes of equivalent lethality for a beef purée fortified with thiamin. Saguy and Karel (1980) predicted that a variable retort profile in which the retort temperature was initially low but increased rapidly towards the end of the process time would give increased thiamin retention.

The success of these exercises is dependent on accurate prediction of the time–temperature profile at many

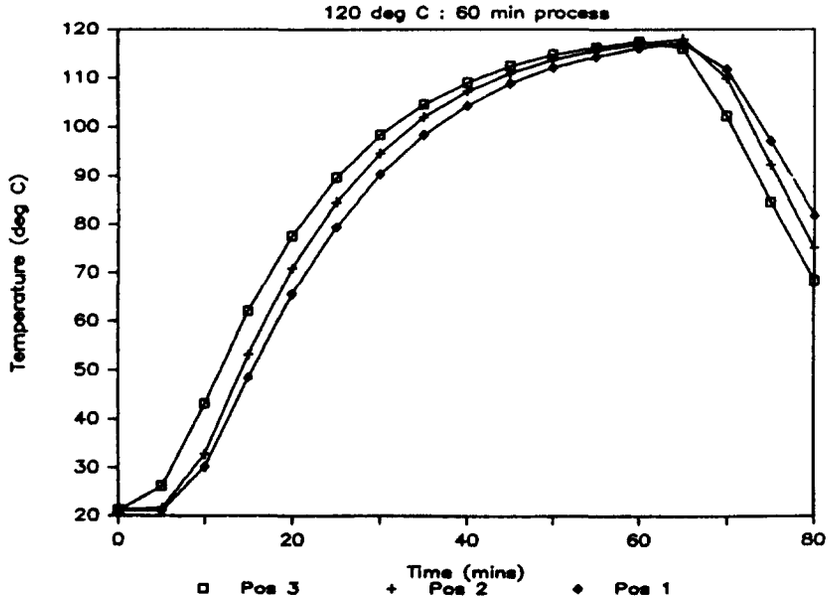

Fig. 1. Time–temperature profiles at different locations within a can of food heated and cooled by conduction. Can height 9·5 cm. Can end-plate diameter 7·5 cm. The temperature differences would be greater in larger cans. (From Lappo (1986)).

	Height from end plate (cm)	Distance along radius (cm)
Thermocouple position 1 (geometric centre of can)	4·75	3·25
Thermocouple position 2	2·375	3·25
Thermocouple position 3	2·375	2·78

Table 3. Effect of container dimension on % thiamin retention in a conduction heating pack[a]

L/D^b	Process time at 121·1°C[c]/min	% thiamin retention
0·096	30	68
0·143	38	63
0·495	75	45
0·767	90	40
1·270	89	41
1·710	83	43
2·960	68	49
5·760	52	56
13·750	38	63

[a] From Teixeira *et al.* (1975), reproduced by permission of the *Journal of Food Science.*
[b] *L*, length; *D*, diameter.
[c] All processes are of equivalent lethality (5 log reductions of initial population of Bacillus stearothermophilus spores).

points throughout the package, which can only be achieved with an adequate heat-transfer model and with accurate knowledge of the thermal characteristics of the food and the surface heat transfer coefficient from the heating medium to the package. These demanding requirements coupled with very limited kinetic data limit this otherwise very successful approach. No predictions have been made for folate since adequate kinetic data are not available, a consequence of prior analytical problems. Day and Gregory (1983) showed that lactose, protein, iron and ascorbate increased the stability of folic acid and 5-methyl-tetrahydro-folic acid, but could not determine the reaction order in a model infant formula. Barrett and Lund (1989) reported pseudo-first-order kinetics of oxidative degradation in a solution in which the experimental design had eliminated oxygen mass transfer limitations.

Temperature prediction has most often utilised the general differential equation for two-dimensional unsteady-state heat conduction in finite difference form. This requires knowledge of the steam temperature, the cooling water temperature, the initial food temperature, the package dimensions and the thermal diffusivity of the food.

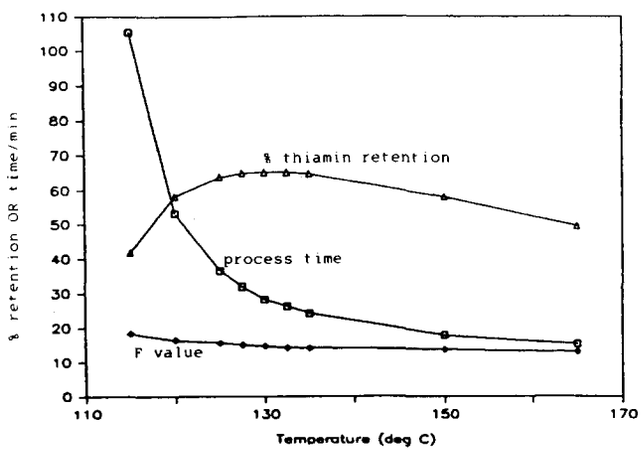

Fig. 2. Prediction of process time and percentage thiamin retention for equivalent lethality at different process temperatures. (Beef purée baby food. Can size 6·52 × 4·5 cm (209 × 202). Lethality target 5 log reduction of *B. stearothermophilus.*).

The general equation for two-dimensional unsteady-state heat conduction into a finite cylinder is (Teixeira *et al.*, 1969; Lappo, 1986)

$$dT/a\ dt = d^2T/dr^2 + dT/r\ dr + d^2T/dy^2 \quad (1)$$

where T is the temperature at time t, r is the radial distance from the centre, y is the vertical distance from the centre, and a is the thermal diffusivity.

In finite difference analysis the cylinder is assumed to be divided into a two-dimensional grid of $n \times m$ elements, such that the volume is divided into a series of concentric rings (Teixeira *et al.*, 1969). As the volume in each ring is very small, the heat transfer at each ring is assumed to be steady state. The new temperature at a node (i,j) in the grid is calculated by

$$\begin{aligned} T_{new}(i,j) = {} & a\ dt/dr^2(T(i-1,j) - 2T(i,j) + T(i+1,j)) \\ & + a\ dt/2r\ dr(T(i-1,j) - T(i+1,j)) \\ & + a\ dt/dy^2(T(i,j-1) - 2T(i,j) + T(i,j+1)) \end{aligned} \quad (2)$$

The change in concentration at each node for a first-order reaction is

$$c_{new}(i,j) = c_{old}(i,j) - K_0 \Delta t\ e^{-E/RT} \quad (3)$$

where K_0 is the pre-exponential factor, E is the Arrhenius activation energy, and C is the ln (concentration).

Other methods of predicting the time–temperature profile have been used. Prediction of vitamin losses in the thermal processing of conduction heated foods has been reviewed by Lund (1977), Paulus (1989), Richardson *et al.* (1989) and Ryley *et al.* (1990). This was originally introduced by Hayakawa (1969) and Teixeira *et al.* (1969). If it is applied to well-defined systems, good correlation with experimental results has been acheived. The essence of the theory is a mathematical model to predict temperature at any point in the food during the process. Its application is limited mainly by lack of kinetic data but represents a valuable approach to understanding causes of loss and indicates the direction for possible improvements in processing methods.

Particulates are sterilised in syrup or brine heat mainly by convection with consequent reduction in process times so that overall losses during the sterilisation process are less than in a conduction-heated food processed at the same temperature to the same lethality. However, soluble nutrients are leached into the liquor and if diffusion rates are known the loss can be predicted by making the simplifying assumption that all parts of the can are at the same temperature.

Ryley *et al.* (1989) predicted the loss of riboflavin from soya beans in brine during different canning processes and found good agreement with experimental values (Table 4). Abdel-Kader (1990) monitored ascorbic acid, thiamin and riboflavin in commercially canned potatoes in brine after sterilisation and 6 months storage and confirmed that although the amount in the brine remains static the quantity in the solids continues to drop. The continuation of the loss may be taking place in the potato itself or by further diffusion into the liquor if equilibrium between the food and the brine has not been reached.

Table 4. Comparison of predicted and experimental riboflavin retention during the canning of soya beans[a,b]

Process temperature (°C)	Process time (min)	Retained in solid predicted (%)	Retained in solid experimental (%)	F_0 value
109	4·8	77·7	76·2	0·65
109–113·5	19·2	62·1	61·0	2·87
109–111·5	14·4	59·9	59·8	1·78
118–123·5	20·4	58·9	59·3	25·7
120–121·5	31·8	57·2	58·5	33·1
119	30·0	35·7	34·2	21·7

[a] From Abdel-Kader (1985).
[b] Can size A1, 7 × 11 cm (211 × 400). Used own kinetic data.

Figure 3 (De Saucedo, 1982) shows loss during storage in both conduction heating and in particulates in brine and indicates that increased retention achieved by processing in a thin layer in pouches is maintained during storage. DeSouza and Eitenmiller (1986) canned spinach and found 14% of total folate in the can liquid immediately after processing and this increased to 18% after 3 months storage.

Flame sterilisation offers a means of attaining an HTST process for particulate foods within a can. It requires the can to be rotated over a gas burner to improve heat transfer through the foods. It is mainly applied to particulates without covering liquid or with only a small quantity of covering liquid, the main requirement being for the contents to be mobile.

Table 5. Percentage vitamin retention in flame sterilisation

	Vitamin	Pre-cook	Flame sterilisation	Still retort
Tuna flakes[a]	B_1	58	32	9
	B_2	88	74	60
	Niacin	96	83	68
Whole peeled tomatoes[b]	C		15·8	11·8

[a] Data taken from Seet *et al.* (1983).
[b] Data taken from Leonard *et al.* (1975).

Studies with precooked diced tuna (Seet *et al.*, 1983) indicated a significant gain for thiamin retention but much smaller benefits for riboflavin and niacin (Table 5). This difference in behaviour between the three vitamins is readily explained by their relative thermal stabilities. Likewise, whole peeled tomatoes showed a significant improvement in vitamin C retention (Leonard *et al.*, 1975). Flame sterilisation is limited to small cans because of the high internal pressures generated but offers advantages for particulate foods for which aseptic packaging is still at an early stage. Flame sterilisation has been reviewed by Richardson (1987) and Heil (1989). While the scientific literature describes its use for peaches, diced potatoes, pears, whole-kernel corn,

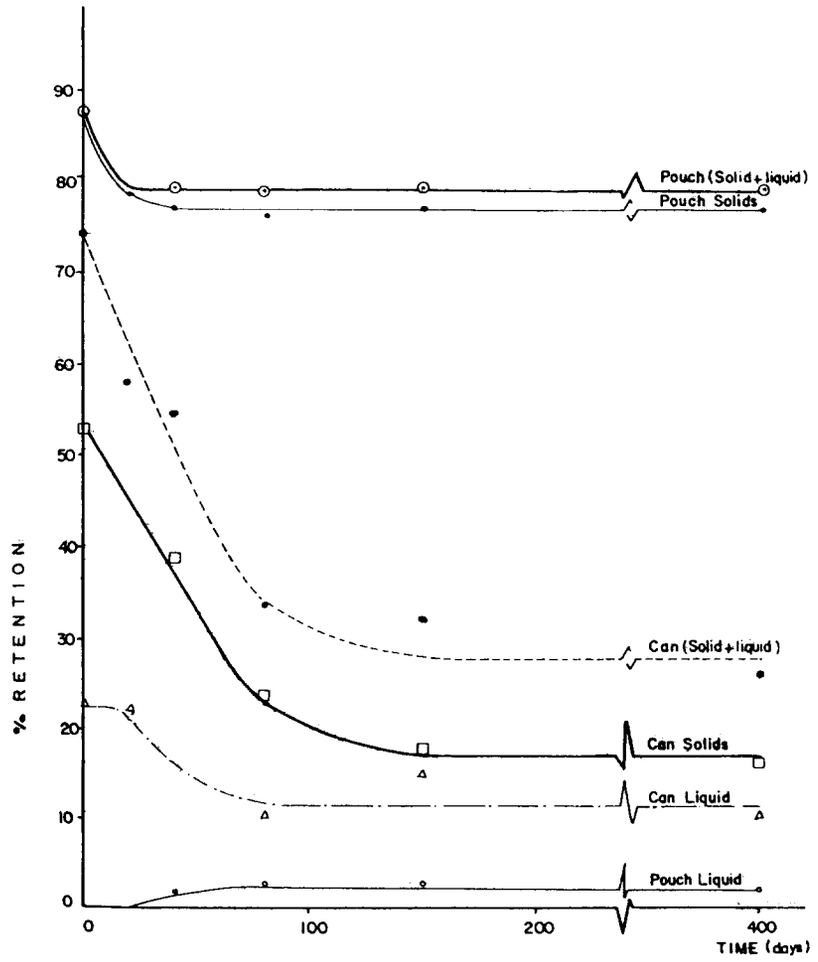

Fig. 3. Ascorbic acid retention in Jersey new potatoes after sterilisation and during storage at +20°C.

mushrooms and fruit cocktail, in practice it appears to be mainly used for mushrooms for which it shows greatly reduced shrinkage.

ASEPTIC PACKAGING

Thermally sterilised products have lost ground in the market-place with the introduction of frozen and chilled foods. Perhaps an exception is aseptically packed fruit juice, an area of food processing which expanded more rapidly in Europe than in the US.

Aseptically packaged foods are packaged after heat treatment. The heat treatment is applied to a thin layer of the food in a heat exchanger or by direct steam injection. Such conditions enable HTST processes to be used without overheating as the product can be rapidly heated and cooled throughout so that the conditions for minimising chemical change with adequate lethality can be achieved. The product is cooled prior to packaging into sterile containers, often cartons at atmospheric pressure. These packages are likely to have a higher content of residual and headspace oxygen than 'in-container' processed products which are exhausted at blanch temperatures and vacuum seamed prior to processing. During storage, only cans, glass and retortable pouches are impermeable to air.

Predictably, the only nutrients which have generated any work are vitamin C and to some extent folate. To quote André (1984), the factors which aid vitamin C retention in food subjected to HTST sterilisation are low pH, low oxygen tension in the headspace and in solution, low levels of metallic ions and storage at suitably low temperatures.

Milk and fruit juice are particularly suited to aseptic packaging both because of their low viscosity and because the aim is to preserve the 'fresh' taste. It is generally accepted that the thermal process prior to packaging maintains the vitamin concentration of most vitamins close to the pre-processing value. Particulate foods are still mainly processed 'in-container' but Lee *et al.* (1990), using a computer model of HTST processing of potato cubes in water, have reported on the sensitivity of a range of properties including thiamin retention to variations in the processing conditions. Particle size and thermal properties were the most important factors influencing thiamin retention.

However, problems of vitamin retention in aseptically processed foods arise during storage and can be attributed to dissolved and headspace oxygen, oxygen and light permeability of the packaging material and to commodity-specific reactions which are only dependent on storage temperature.

VITAMIN C IN THERMALLY PROCESSED FRUIT JUICE

Nagy (1980) reviewed knowledge of the vitamin C status of heat-treated citrous orange juice.

Storage temperatures in excess of 28°C cause markedly accelerated rates of destruction in canned products (Fig. 4). The loss during storage can be related to the log of the storage time but significant deviations are found at temperatures above 30°C. The temperature effect is different for grapefruit and orange juice. Grapefruit follows the Arrhenius law in giving a linear plot of log of rate constant against $1/T$ but for orange juice the plot shows two different gradients indicating a change in kinetics around 28°C. Here, the rate of loss follows a quadratic function better than a first order and this is attributed to the effect of breakdown products on the degradation. Vitamin C loss is greater in orange juice than in grapefruit juice at the same storage temperature. The loss in canned grapefruit juice has been considered to be primarily anaerobic because of the low levels of dehydroascorbic acid (DHA) and diketogulonic (DKA) found (Smoot & Nagy, 1980) but it remains unclear if this is because of the low oxygen pressure of the environment or if it is a characteristic of grapefruit juice. Orange juice from cans and bottles contains only small amounts of DHA and DKA but on exposure to air this increases. Deaeration procedures only reduce the dissolved oxygen to about 0·05% prior to the process, so that there is a relatively rapid rate of loss of vitamin C in the first 2 weeks attributed to aerobic oxidation followed by a much slower loss. The loss of vitamin C in enamelled cans or glass is greater than that in plain cans, attributed to competition for oxygen by the metal of the can. Storage in plastic or waxed-paper cartons impermeable to oxygen resulted in markedly more rapid loss relative to glass.

Studies on fruit juices since 1980 have centred around the characteristics of aseptic packaging and of single versus concentrated juice, the mechanism of the loss and its relationship to non-enzymic browning. The process is distinguished from hot filling by the higher levels of oxygen encountered by the product during processing and packaging, the means by which the equipment and packages are sterilised, the oxygen content of the headspace, and, because of the wider range of suitable materials, the permeability of the

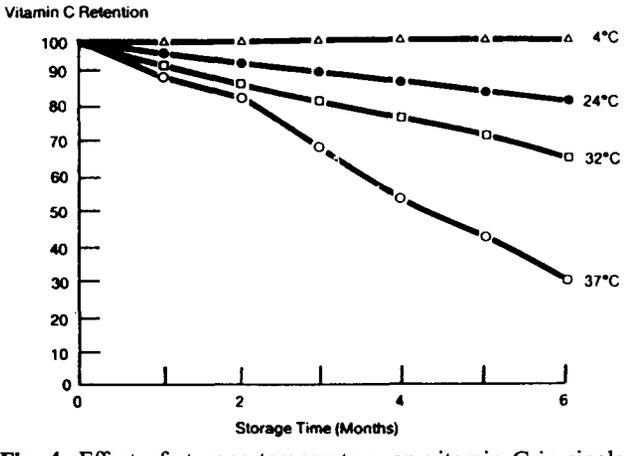

Fig. 4. Effect of storage temperature on vitamin C in single-stretch canned orange juice. (From Nagy (1980), reproduced by permission of American Chemical Society.)

package and the surface lining of the package.The low pH of fruit juice means that only a pasteurisation level is required so that the profile by which the process is applied is not a major factor in determining the vitamin C level at the start of storage. However, heating in the presence of oxygen is deleterious so that the effect of oxygen has received considerable attention.

Ascorbic acid degradation in heat treated citrous products is due to non-enzymic aerobic and anaerobic reactions. Degradation has been shown to be directly proportional to the initial concentration of dissolved oxygen in model systems (Kefford *et al.*, 1950; Singh *et al.*, 1976). The reaction is speeded up in the presence of suitable catalysts such as transition metal ions which exhibit stable paramagnetic states and are thus able to react with triplet molecules such as oxygen (Kanner & Shapira, 1988). In an experiment with grapefruit juice in which only reduced ascorbic acid was measured, Kanner and Shapira (1988) showed that both ascorbic acid and browning proceeded more rapidly the higher the initial oxygen concentration, but significant browning only occurred after most of the ascorbic acid had been reduced. The same authors reported inhibition of ascorbic acid degradation in citrous juices by sequestrants, so supporting the concept of the importance of the role of metal ions. Thus, the most important processing factors which affect the loss of vitamin C in fruit juices are the dissolved oxygen and headspace oxygen, the permeability of the packaging and the seal, and the temperature of storage. The idea that shelf-stable foods can benefit from cool storage (Fig. 4) is not promoted to any extent. Direct steam heating gives a product with approx. 1 ppm oxygen regardless of the starting value whereas in indirect heating the level of oxygen at the beginning of storage depends on good deaeration prior to processing. Ohta *et al.* (1983) working with satsuma mandarin juice concluded that headspace volume and storage temperature were more important than pasteurisation time and temperature.

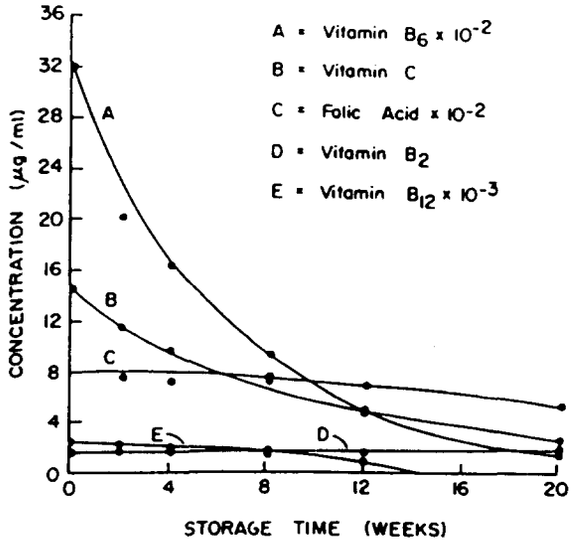

Fig. 5. Degradation of vitamins in UHT milk during storage. (From Oamen *et al.* (1989), reproduced by permission of the *Journal of Dairy Science*.)

The importance of deaeration seems to be a variable factor (Graumlich *et al.*, 1986) and may be less significant for concentrates. Saguy *et al.* (1978) found the rate of loss of vitamin C from grapefruit juice unaffected by deaeration. Orange juice concentrate stored at 12, 17, 25 and 37°C for 150 days showed a marked acceleration at 37°C commensurate with a change from first- to second-order kinetics above 25°C so that the degree of destruction was dependant on the starting concentration (Kanner *et al.*, 1982).

Not all studies show dissolved oxygen to be important. Robertson and Salmaniego (1986), working with pasteurised lemon juice stored at 36°C, considered the degradation of ascorbic acid to be largely anaerobic with a better fit to second order kinetics over a storage period of 6 weeks and with a half-life of about 28 days. Kennedy *et al.* (1992) recently showed that ascorbic acid in single-strength orange juice in cartons was sensitive to the level of dissolved oxygen but that when the headspace and dissolved oxygen were in equilibrium the loss continued anaerobically, but both mechanisms were proceeding simultaneously. They confirmed that at 37°C the rate of loss was much better described either by zero- (Smoot & Nagy, 1980) or second-order rather than first-order kinetics.

The presence of headspace oxygen is enhanced by aseptic filling at ambient temperature so that the atmosphere in the chamber at the time of filling is that of the package. If the chamber and material has been sterilised with hydrogen peroxide then there may be residues which accelerate degradation, although Toledo (1984) reported that residual peroxide up to 0·1 g/ml had no effect but at 1 g/ml the half-life of ascorbic acid was significantly reduced.

Wilson and Shaw (1987) found market values in the range of 33–44 mg/100 ml for 1–6 weeks prior to expiry and 29–22 mg/100 ml for 1–7 weeks after expiry. It is of interest to compare this with the similar global figure in UK composition tables of 39 mg/ml for mixed cartons, cans and frozen samples. Sizer *et al.* (1988) attributed oxidative losses in a (worst situation) litre package of aseptically packaged orange juice as follows:

- saturated with oxygen to 8 ppm
- 70 ml headspace
- oxygen penetration 1 mg/month
- peroxide residue 0·1 ppm
- stored at 20°C for 6 months

the losses of ascorbic acid would be

- 8 mg/100 ml due to dissolved oxygen
- 20 mg/100 ml due to headspace oxygen
- 6 mg/100 ml due to penetration of oxygen packaging
- 0·05 mg/100 ml due to peroxide.

Product-specific degradation (independent of the above) was estimated as 65% of total loss by comparing tetra briks stored in air and anaerobic surroundings. The amount penetrating the package is small compared with the headspace effect.

ASEPTICALLY PROCESSED MILK

In whole milk the vitamins of interest are A, B_1, B_2, B_6, folate and B_{12}, and the effect of thermal processing on vitamins as reviewed by Schaafsma (1980) indicated the expected superiority of UHT (Table 6).

Vitamin C in milk is probably not of dietetic importance but its presence in milk is essential for the protection of folate. All studies of aseptically packaged milk show a concurrent loss of vitamin C in the milk and of dissolved and headspace oxygen during storage, with the rate of loss of ascorbic acid being greater the higher the initial level of dissolved oxygen (Thomas *et al.*, 1975; Oamen *et al.*, 1989). Losses of folic acid during processing were negligible in samples with medium (5·2 ppm) and low (less than 1 ppm) dissolved oxygen. High initial concentration of oxygen (8·4 ppm) resulted in 18% loss of folic acid during processing and a further rapid loss to <6% of the initial value during storage for 28 days at 23°C in the dark (Thomas *et al.*, 1975). Oamen *et al.* (1989) also reported negligible losses during heat treatment but heavy losses of vitamin B_6 and B_{12} during storage (Fig. 5).

Vitamin A is essentially stable in whole milk both during processing and storage (Ford *et al.*, 1969). Since then there have been studies relating to the stability of vitamin A in fortified processed milk with varying levels of fat (Le Maguer & Jackson, 1983; McCarthy *et al.*, 1985; Gaylord *et al.*, 1986; Lau *et al.*, 1986; Dolfni & Kueni, 1991). This can be attributed to the increasing popularity of skimmed milk and subsequent efforts to fortify it, combined with the problems of oxygen and light permeation into aseptically processed packages. The loss due to the thermal (UHT) process has received less attention than the loss during storage but Dolfini and Kueni (1991) reported a loss of 40% of the amount added to very low fat milk (0·04%). Le Maguer and Jackson (1983) working with 2% fat white and chocolate milks reported that, during storage, losses were greater from a 1-litre carton (36%) than from a 250-ml carton (25%) after 28 weeks at 20°C. Fat is protective. Losses of the order of 50% of the initial processed value in 3 months during storage at 5°C have been reported by Dolfini and Kueno (1991) for fat content of 0·5% and in 8 days at 26°C (Lau *et al.*, 1986) for a fat content of 0·15%. Increasing the non-fat milk solids also has had a protective effect (Gaylord *et al.*, 1986). Zahar *et al.* (1987) related the stability of added retinyl palmitate to the melting point of the oil used as a carrier.

Table 6. Vitamin losses in milk during processing (%)[a]

	B_1	B_6	Folate	B_{12}	C
Pasteurisation	10	0–5	5	10	5–15
UHT sterilisation	5–15	10	10–20	10–20	10–20
Boiling	10–20	5–8	15	20	15–20
Conventional sterilisation	30–40	10–20	40–50	80–100	30–50

[a] From Schaafsma (1980), reproduced by permission of the International Dairy Federation.

Lau *et al.* (1986) working with milks of varying fat content showed that the amount remaining after 3 weeks of storage at 26°C corresponded closely to the natural level present prior to fortification.

First-order rate constants for the loss of vitamin A acetate in skimmed 2% and whole milk at 4°C after exposure to light have been published by Gaylord *et al.* (1986). Murphy *et al.* (1988) showed that the half-life of all-*trans* retinyl acetate in skimmed milk stored in glass, plastic or paper carton and exposed to commercial fluorescent light at 7–10°C was 41, 61 and 1004 h, respectively.

COOKING

To quote several authors (Warthesen *et al.*, 1984; Augustin *et al.*, 1987; Rumm-Kreuter & Demmel, 1990; Somogyi, 1990), the high degree of variability of cooking conditions makes a direct comparison of the results of numerous investigations unrewarding.

The amount lost depends on the same factors as in all processing. The problem with cooking is that by its very nature the targets are less clearly defined than in preservation processes. Studies of cooking have not, on the whole, been carried out with an approach comparable to those involving preservation. Mathematicians have rarely been involved in modelling cooking. Mass balance exercises have not usually been attempted. No effort has been made to relate results to plant structure and the location of nutrients as was done for blanching (Selman & Rolfe, 1982). Because of the very wide range of foods and cooking processes anybody involved in this field is likely to be overfaced. More use needs to be made of the approach used by Skjöldebrand *et al.* (1983) for convection cooking of meat loaves, Selman and Rolfe (1982) and Garrotte *et al.* (1986) for blanching and Paulus (1979) for boiling. The current situation is that it is possible to find conflicting information on many issues.

All studies find steaming at atmospheric pressure without addition of water better than boiling, and boiling in the minimum of water better than in a large amount. However, pressure cooking has sometimes, but not always, given higher retentions of water-soluble vitamins than boiling but the dimensions of the product are probably the major variables to consider here (Table 7). The surface area in contact with water is generally agreed to be important so that leafy vegetables tend to show greater losses than root vegetables.

Augustin *et al.* (1987) found greater than 80% retention of vitamins C, B_2, folate and virtually total retention of vitamins B_1, niacin and pyridoxine in potatoes baked or boiled unpeeled. Boiling the peeled potato increased the loss of every vitamin except thiamin but the minimum retention (riboflavin) was 63%. Most other workers have found thiamin to be relatively unstable. Somogyi (1990) found losses of 11–27% in steaming, 14–35% in pressure cooking and 14–66% for boiling, depending on the vegetable, with the greatest losses occurring during the boiling of leafy vegetables like

Table 7. Vegetable cooking losses (%)[a]

	Vitamin C		Vitamin B_1	
	Potatoes	Spinach	Potatoes	Spinach
Pressure-cooked				
Whole	33·5			
Half	29·0	35	28	44
Cubed	23·9			
Boiling in a large amount of water				
Whole	14·8			
Half	22·8	66	33	62
Cubed	36·4			
Steamed	7	18	14	16

[a] From Somogyi (1990).

cabbage and spinach. While leaching appears to be the major mode of loss for niacin, ascorbic acid and riboflavin; thiamin and folate are lost both by degradation and by leaching, although folate is protected by the presence of ascorbic acid. Paulus (1989) shows very small losses of folate overall in boiling a range of vegetables but about one-third is leached into the boiling water. However, Desouza and Eitenmiller (1986) found much greater losses into blanch water with steam blanching being considerably better. However, they had used a lower vegetable to water ratio than some other workers, which emphasises the importance of controlling the factors leading to heavy leaching losses. There is some evidence of deconjugation to free folate with only free folate appearing in the liquor in the cooking of broccoli (Kajda, P. & Ryley, J., 1992, unpublished reports). Mostly folate results are very variable even on the same food sample making processing differences difficult to quantify. Apparent increases occur (Paulus, 1990; Kajda, P. & Ryley, J., 1992, unpublished results) although whether this is due to extraction difficulties from the raw food or the wide range of results is not clear. Perhaps the main result of all the cooking studies is to underline the need for more controlled studies using modelling approaches but which are less ambitious in the range of foods and processes covered.

In baking, roasting and frying, high retentions are expected except for thiamin in alkaline conditions with most damage occurring in the crust. The surface temperature rises to the process temperature but within the food the temperature does not exceed the temperature of the steam under the crust. Skjöldebrand *et al.* (1983), studying convective heating of meat loaves, predicted retentions of 75–99% but found 85–97% retentions of thiamin depending on the air speed temperature and humidity used. Unklesbay and Dawson (1988) compared rotating hot air, charbroiling and deep-fat frying on the B_6 vitamin content of beef, lamb and pork. While no difference due to heating method was established, the end-point of cooking had a significant effect particularly for thiamin and riboflavin in beef loin steaks. The rare product retained 71% of thiamin and 72% of riboflavin relative to 50% and 55% in the well-done product. Bertelsen *et al.* (1988) monitored thiamin by HPLC and pantothenic acid by immunoassay in chicken breast and thigh muscle. They identified the optimum sensory process (45 min at 190°C in a fan-assisted oven) from the range studied and reported the results both on a fresh weight and fat-free dry weight basis. The dietetic value compared well with current food table values with 79 and 86% retention on a dry weight fat-free basis for thiamin and pantothenic acid, respectively.

CONCLUSION

Thermal processing can be controlled to maximise vitamin retention within sensory and safety constraints. Product-specific changes take place in addition to those caused by interaction within the environment but which are sensitive to storage temperature. The importance of temperature for maintenance of the quality of shelf-stable foods is insufficiently emphasised and the role of light in storage changes in packaged foods may have been underestimated, particularly in glass and plastic containers.

Only a limited number of cooking exercises have adequately controlled and reported the target process, the process parameters and the mass balance data or involved food engineers to analyse the heat/mass transfer effects.

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