

A Study of the Apparent Diffusion Coefficients for Ascorbic Acid Losses from Peas during Blanching in Water

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ABSTRACT

This study is concerned with the loss of ascorbic acid from peas during water blanching at 50, 60, 70, 80 and 90° C for 0, 2, 4, 6, 8 and 10 min, in an attempt to elucidate the mechanisms involved in such losses.

When the agitation of the blanch water is sufficient, the surface resistance is made negligibly small, and the total resistance to the loss of ascorbic acid from peas to the blanch water is controlled by diffusion mechanism only. So the apparent diffusion coefficients (D) for ascorbic acid loss from peas were calculated after blanching under various conditions. When the temperature ranged from 50° C to 90° C, values of D were found to be in the range of 0.94×10^{-8} to 1.94×10^{-8} m² s⁻¹, having an activation energy of 18.71 kJ mol⁻¹. Also the results indicated that, if there was sufficient agitation, the leaching of ascorbic acid from peas during blanching in water was controlled by 'diffusion'.

INTRODUCTION

One of the important processes in the preparation of vegetables for freezing, canning or dehydration is blanching. The blanching process may decrease the retention of some vitamins in vegetables (Lee, 1958; Cain, 1967; Selman, 1978; Salib *et al.*, 1980).

Ascorbic acid is one of the most readily destroyed of the vitamins and its retention is often used as an index of the severity of the processing and storage conditions (Bender, 1966). Although the degradation of ascorbic

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acid during thermal processing operations has received much attention due to its instability to heat, light and metal catalysts, and oxygen (Lee *et al.*, 1976), the greatest losses of ascorbic acid are due to leaching into the processing water (Bender, 1966; Hough & Alzamora, 1984). Relatively few studies have involved ascorbic acid losses as functions of time and temperature (Selman, 1978; Lathrop & Leung, 1980; Rice & Selman, 1984).

The two contributions to the total resistance to mass transfer in the blanching of vegetables are the surface resistance due to convection, and the internal resistance due to mass diffusion (Selman *et al.*, 1983). These two can be represented by Fick's first and second laws together with a mass balance at the interface (surface),

$$\frac{\mathrm{d}c}{\mathrm{d}t} = D_{\mathrm{a}} \frac{\mathrm{d}^2 C}{\mathrm{d}x^2}$$

and

$$-D_{a} \cdot \frac{\mathrm{d}c}{\mathrm{d}x} = K(C - C_{0}) = \frac{1}{\mathrm{A}} \cdot \frac{\mathrm{d}N}{\mathrm{d}t}$$

at x = a (surface), where A = total surface area for mass transfer (m²), C = solute concentration at any point in the sample (%), $C_0 =$ concentration of blanch media (%), K = surface mass transfer coefficient (kg m⁻² s⁻¹), N = mass diffusing (kg), t = (blanch) time (s) and x = any position in the sample where the concentration is C(m).

If there is sufficient agitation of the blanching media, then the surface resistance becomes small and it can be assumed that the total resistance is due to the internal resistance only. In this case the solution to Fick's second law was used. This was given by Newman (1931) for spheres, with the average concentration obtained after integration with respect to position as a function of time, in non-dimensionalized form:

$$\frac{C - C_{\rm e}}{C_{\rm i} - C_{\rm e}} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 \left(\frac{4Dt}{d^2}\right) \pi^2\right)$$

where: C = the average concentration in sample, $C_i =$ the initial concentration of the component in sample, $C_e =$ the concentration of the component at equilibrium, D = diffusion coefficient (m²s⁻¹), d = diameter of sphere (m), t = time (s) and n = number of the term in the series solution.

Leaching, as a process in food industry, which is the transfer of solutes from a solid to an adjacent fluid, may be controlled by internal diffusion of solutes (Lathrop & Leung, 1980; Schwartzberg & Chao, 1982; Selman *et al.*, 1983; Rice & Selman, 1984).

The object of this study was to examine the mechanisms of ascorbic acid loss from peas during water blanching and to determine the apparent diffusion coefficient for the leaching of ascorbic acid from peas over a wide range of temperature and time.

MATERIALS AND METHODS

Sample collection

Fresh peas were purchased from a local supermarket. The very small and very large peas were discarded.

Measuring the diameters of the peas

The diameters of 20 randomly selected peas were determined using a micrometer.

Blanching

The shelled peas were stored at 4°C overnight before blanching. Duplicate pea samples of 10 seeds were blanched in distilled water at 50, 60, 70, 80 and 90°C for periods of 0, 2, 4, 6, 8 and 10 min. Since it was desired to maintain a constant ascorbic acid content in the blanch water, the mass of the blanch water used was 50 times the mass of the pea seeds. The blanch medium was maintained using a thermostatically-controlled, agitated water bath. Water temperature fluctuations were within ± 0.5 °C. After the required blanch time, the samples were removed and stored at -20°C until ascorbic acid analyses were performed.

Ascorbic acid analysis

Visual titration with 2,6-dichlorophenol indophenol solution was used for the determination of ascorbic acid in peas (Freed, 1966; Osborne & Voogt, 1978; AOAC, 1980). Pea samples were extracted using 5% metaphosphoric acid. Sample extraction and titration were completed as soon as possible.

RESULTS AND DISCUSSION

The ascorbic acid contents in peas after leaching at these different temperatures (50, 60, 70, 80 and 90°C) and times (0, 2, 4, 6, 8 and 10 min) are

presented in Fig. 1. A similar pattern of decreasing ascorbic acid concentration was observed at each temperature, and the rate of decrease of ascorbic acid concentration appeared to increase as temperature increased. Also the results indicate that, as temperature increased, the concentration decreased rapidly, especially during the first two minutes.

This was in agreement with similar observations reported by Fenton *et al.* (1936) and Guerrant *et al.* (1947). They suggested that this large initial loss might have been due to the combined leaching and enzymic oxidation of ascorbic acid during the initial heating period. At higher temperature (90°C), the concentration of ascorbic acid in peas, after 4 min, came very close to the concentration after 10 min, but at lower temperature (50°C) there were still substantial differences between these concentrations. This indicated that, as would be expected, the ascorbic acid loss occurred by the diffusion process, and that diffusion was dependent on temperature; so at lower temperatures, the equilibrium conditions were not reached.

Calculation of apparent diffusion coefficients of ascorbic acid in peas

Selman (1978) and Lathrop & Leung (1980) suggested that the leaching of ascorbic acid from peas is independent of agitation rates and controlled primarily by diffusion rather than mass transfer. So, in this case, the solution of Fick's law, as given by Newman (1931) was used for unsteady diffusion in



Fig. 1. Percentage ascorbic acid content of peas after the given blanch time at 50, 60, 70, 80 and 90°C.

a sphere as follows and assumes constant diffusivity, no resistance to mass transfer in the medium surrounding the solid, and no chemical reaction.

$$\frac{C - C_{\rm e}}{C_{\rm i} - C_{\rm e}} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[-n^2 \left(\frac{4Dt}{d^2}\right) \pi^2\right]$$
(1)

where d = diameter of sphere (m), and the average radii of the peas was 8.8 mm. Equation (1) leads to eqns (2) and (3):

$$\ln\left(\frac{C-C_{\rm e}}{C_{\rm i}-C_{\rm e}}\right) = \ln\frac{6}{\pi^2} - \frac{4\pi^2 Dt}{d^2}$$
(2)

$$\ln\left(\frac{C-C_{\rm e}}{C_{\rm i}-C_{\rm e}}\right) = -Kt \tag{3}$$

If $\ln (C - C_e/C_i - C_e)$ was plotted versus time (t), a straight line was obtained and its slope equals

$$\frac{-4\pi^2 D}{d^2} = -K \tag{4}$$

So, the leaching mechanism of ascorbic acid from peas can be described by eqn (3), where (K) is a constant and dependent on the internal diffusion coefficient (D). When $\ln (C - C_e/C_i - C_e)$ was plotted against time (t) at different temperatures, and assuming the C_e that gave the best straight line, it was noticed that sometimes the results gave a straight line and sometimes did not, i.e. the results did not give a good agreement with the theory because the correct value of C_e was unknown, especially at lower temperature. Since eqn (3) will lead to eqn (5), then

$$\ln\left(\frac{\mathrm{d}c}{\mathrm{d}t}\right) = \ln\left[-K(C_{\mathrm{i}} - C_{\mathrm{e}})\right] - Kt \tag{5}$$

Equation (5) describes the calculation of the reaction rate (K), independently of C_e . Plotting $\ln (dc/dt)$ against time (t), at different temperatures will give a straight line of slope = -K, and intercept = $\ln [-K(C_i - C_e)]$.

K values have been calculated using the leaching curves (concentration of ascorbic acid against time), a minimum of 10 points of times; the tangents to the curve have been drawn and the slopes of these tangents have been calculated. Related to eqn (4) and by knowing the values of (K) at different temperatures, the diffusion coefficients (D) have been calculated as follows:

$$D = \frac{Kd^2}{4\pi^2} \tag{6}$$



Fig. 2a. Graph to calculate the value of K at 50°C.



Fig. 2c. Graph to calculate the value of K at 70°C.



Fig. 2b. Graph to calculate the value of K at 60°C.



Fig. 2d. Graph to calculate the value of K at 80°C.



Fig. 2e. Graph to calculate the value of K at 90°C.

Figures 2a, 2b, 2c, 2d and 2e show the plotting of $\ln (dc/dt)$ against time (t) to obtain the leaching rate of K at different temperatures. K values were 0.289, 0.365, 0.420, 0.508 and 0.592 min⁻¹ at 50, 60, 70, 80 and 90°C. The results indicate that, during the blanching of peas, the rate of leaching of ascorbic acid from peas into the water was increased with increasing temperature.

Equation (6) concludes that the leaching of ascorbic acid from peas into the surrounding liquid is controlled by diffusion only. Table 1 shows the values of *D* at different temperatures as calculated from eqn (6) using the *K* values and a mean of diameter of pea samples of 8.8 mm. It was concluded that, with increasing temperature 50, 60, 70, 80 and 90°C, *D* increased having values of 0.94×10^{-8} , 1.193×10^{-8} , 1.37×10^{-8} , 1.66×10^{-8} and $1.94 \times 10^{-8} \text{ m}^2 \text{s}^{-1}$ respectively. These results compared favourably with those reported by Lathrop & Leung (1980).

A graph of $\ln D$ versus 1/T (Fig. 3) shows that D can be related to temperature by an Arrhenius equation:

$$D = D_0 \exp\left(-E_a/RT\right) \tag{7}$$

where $D = \text{diffusion coefficient } (\text{m}^2 \text{ s}^{-1}), D_0 = \text{constant } (\text{m}^2 \text{ s}^{-1}), E_a = \text{activation energy } (\text{kJ mol}^{-1}), R = \text{universal gas constant } (8.314 \text{ J K}^{-1} \text{ mol}^{-1})$



Fig. 3. Graph of ln D (apparent diffusion coefficient at 323, 333, 343, 353 and 363 K) versus the reciprocal of absolute temperature.

| Temperature | | 1/T(K) | K | $D(m^2 s^{-1})$ | In D |
|-------------|-----|-----------|--------|------------------------|----------|
| °C | K | | values | | |
| 50 | 323 | 0.003 096 | 0.289 | 0.94×10^{-8} | - 18·480 |
| 60 | 333 | 0.003 003 | 0.365 | 1.193×10^{-8} | - 18·244 |
| 70 | 343 | 0.002916 | 0.420 | 1.37×10^{-8} | -18·104 |
| 80 | 353 | 0.002 833 | 0.508 | 1.66×10^{-8} | -17·914 |
| 90 | 363 | 0.002 755 | 0.592 | 1.94×10^{-8} | - 17.760 |
| 90 | 363 | 0.002 755 | 0.592 | 1.94×10^{-8} | - 1 |

 TABLE 1

 The Calculation of the Apparent Diffusion Coefficient D for Ascorbic Acid Loss from Peas during Blanching in Water

and T = absolute temperature (K). From this graph, the value of E_a was calculated as $18.71 \text{ kJ mol}^{-1}$. This compared well with reported activation energies for other temperature-dependent changes occurring in plant foods during processing. Chen & Johnson (1969) reported an E_a of 18.1 kJ mol^{-1} for water diffusion during drying of tobacco leaf and Rodger *et al.* (1984) estimated an E_a of 18.9 kJ mol^{-1} for the diffusion of acetic acid into fish muscle.

Generally, it can be concluded that, since a substantial amount of ascorbic acid in peas leached into the water during blanching, leaching was therefore largely responsible for ascorbic acid losses from peas into the surrounding liquid. Because of the sufficient agitation in the blanch media, the surface resistance was negligible and leaching of ascorbic acid was probably controlled by diffusion. Also, by knowing the apparent diffusion coefficients at these experimental temperatures, it is possible to determine the activation energy of diffusion, and hence the diffusion coefficients at other temperatures.

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