COLOUR AND CHLOROPHYLL'S DEGRADATION KINETICS OF FROZEN GREEN BEANS (*PHASEOLUS VULGARIS, L.*)

R.C. Martins[1] and C.L.M. Silva[2]

1,2 Escola Superior de Biotecnologia-Universidade Católica Portuguesa,
Rua Dr. António Bernardino de Almeida, 4200-072 Porto, Portugal
[1]email: rmcm@morango.esb.ucp.pt [2]email: crislui@esb.ucp.pt

ABSTRACT

Colour changes and chlorophyll's degradation of frozen green beans (*Phaseolus vulgaris, L.*, variety bencanta) were studied during 250 days of storage at -7, -15 and -30°C. Chlorophyll's a and b losses were modelled by a first order reaction kinetics. Colour Hunter *a* and *b* co-ordinates and total colour difference were successfully described by a first order reversible model. The temperature effect was well mathematically described by the Arrhenius law, for both quality parameters.

1. INTRODUCTION

The visual aspect of frozen vegetables is the consumer's first quality judgement, and colour is one of the most important sensory attributes, that influences the quality perception. The colour of frozen vegetables is lost during storage, as well as other important quality attributes, such as vitamins and texture.

Colour measurement of green vegetables is a good method to evaluate their quality. Consequently, the analytical measurement of colour, that has became widely used in several research fields, is a valuable instrument to give an accurate measurement of colour. There are several colour co-ordinate systems used in the food research, but the Hunter *Lab* and CIE $L^*a^*b^*$ systems are the most widely used, because they are based on colour perception. The *L* defines the position of light-dark axis, *a* the green-red axis and *b* the blue to yellow axis. Colour changes can also be assessed by the total colour difference (TCD_H) (Shin and Bhowmik, 1995) or colour difference (Drlange, 1994):

$$TCD_H = \sqrt{(L - L_0)^2 + (a - a_0)^2 + (b - b_0)^2} \quad (1)$$

where L, a, b are the Hunter coordinates and L_0, a_0 and b_0 the corresponding initial values. The distance in the colour space can be related with the human ability to distinguish colours, therefore TCD_H differences can be used to classify colour differences (DrLange, 1994).

Frozen green beans, previously blanched, suffer colour changes along storage. This loss of colour is attributed to the fading of the vivid green colour of chlorophyll's until an olive brown, characteristic of pheophytin (Dietrich et al., 1959; Shin and Bowmik, 1995; Steet and Tong, 1996). This phenomena is mostly related to a common alteration of chlorophyll's (pheophytisation) where the centre magnesium is replaced by hydrogen. The formation of pheophytin alters the absorbance spectrum in the visible band changing the natural blue-green and yellow-green band of Chlorophyll's a and b, respectively (Steet and Tong, 1996).

During frozen storage, low protein foods (e.g. milk or green beans) exhibit a pH decrease (Fennema et al., 1973). This may lead to an increase in the rate of acid catalysed reactions (e.g. pheophytisation).

Modelling chlorophyll losses and colour changes

As mentioned before, the major pathway of chlorophyll's degradation is by direct pheophytisation to pheophytin's and, consequently, in mechanistic terms, this process can be represented by a first order reaction kinetics, following Arrhenius behaviour with the storage temperature (Villota and Hawkes, 1992):

$$\frac{C}{C_0} = \exp(-k_{ref}.e^{-\frac{Ea}{R}\left[\frac{1}{T}-\frac{1}{T_{ref}}\right]}.t) \tag{2}$$

where C is the concentration of chlorophyll a or b at time t, C_0 the initial concentration, k_{ref} the kinetic rate at the absolute reference temperature, T_{ref}, T the absolute temperature, R the gas constant and Ea the Arrhenius activation energy.

Colour changes in green vegetables were previously modelled by Steet and Tong (Steet and Tong, 1996). Their approach to model the evolution of $-a$ with storage time, for pureed green peas during thermal treatment, was made by using a first order reversible (or fractional) model:

$$\frac{C-C_{eq}}{C_0-C_{eq}} = \exp(-k_{ref}.e^{-\frac{Ea}{R}\left[\frac{1}{T}-\frac{1}{T_{ref}}\right]}.t) \tag{3}$$

where C is the $-a$ at time t, C_0 the starting value of $-a$, C_{eq} the $-a$ at infinite storage time, when all chlorophyll is converted into pheophytin, and k_{ref} the kinetic rate at the reference temperature. This model assumes that the initial and final colour co-ordinates are not dependent on the storage temperature.

2. MATERIALS AND METHODS

Frozen green beans were stored at -7, -15 and -30°C. Colour and chlorophyll's were analysed along 250 days. The Hunter *Lab* co-ordinates were measured using a tristimulus colorimeter (model CR300, Minolta Corporation, Japan). A spectophotometric procedure, developed by Vernon (Vernon, 1960), was used to determine chlorophyll's a and b, and pheophytin's a and b.

A specially made program was written in Matlab 4.0 (The MathWorks Inc., 1993), to estimate the kinetic parameters by the one-step optimisation procedure (Arabshahi and Lund, 1985).

3. RESULTS AND DISCUSSION

Chlorophyll's a and b degradation were observed during the 250 days of frozen storage for the three studied temperatures. The degradation of both chlorophyll's a and b followed first order kinetics with an Arrhenius behaviour with temperature. Good correlation coefficients between the fitted model and experimental data and low parameter variance were obtained (*Table 1*).

The high activation energies of chlorophyll's a and b degradation and colour changes, enables frozen storage to kinetically constrain destruction, which makes frozen storage at low temperatures a good mean of preservation. However, the high activation energies also makes these quality parameters very sensitive to temperature fluctuations (or abuses), and in particular for colour changes.

Colour loss occurs at significant fast rates only at high storage temperatures (larger than –15°C), attaining great colour differences after 15 to 30 days of storage time. The characteristic equilibrium olive brown colour, was only observed at the storage temperatures of -7 and -15°C. Both Hunter *a* and *b* colour parameters followed a fist order reversible kinetics, and regression

results are presented in *Table 2*. The Hunter L value did not change significantly, leading to a random pattern with an average value of 37.96±3.82 during storage time.
This research work lead to the conclusion that chlorophyll's content is not a good colour index of frozen green beans. The results emphasise that colour is a more important quality parameter to assess the visual quality of frozen stored green beans.

Table 1. Estimated kinetic parameters for degradation of chlorophyll's in frozen stored green beans.

Chlorophyll	**Ea** [kJ/mol]	$k_{-15°C}\times10^{-2}$ [days^{-1}]	$C_0\times10^{-2}$ [mg/g]	$s_{model}\times10^{-3}$ [mg/g]	R^2 [pred/exp]
a	48.730±1.273	4.793±0.001	4.559±0.063	4.607	0.9961
b	49.595±1.938	4.795±0.002	2.572±0.096	6.995	0.8302

Table 2. Estimated kinetic parameters for colour loss in frozen stored green beans.

Colour Parameter	**Ea** [kJ/mol]	$k_{-15°C}\times10^{-3}$ [days^{-1}]	C_0	C_{eq}	s_{model}	R^2 [pred/exp]
a	103.053±0.072	6.600±0.000	-11.931±0.072	-6.329±0.083	1.389	0.8388
b	55.329±1.785	22.189±0.349	13.099±0.117	10.101±0.072	1.557	0.6871
TCD_H	106.272±1.049	5.999±0.000	3.745±0.095	7.486±0.117	1.872	0.6145

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