KINETIC MODELING OF MEAT COLOR EVOLUTION DURING HEATING

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***Abstract*— During cooking, both temperature and time have a large effect on physical properties of meat, mainly due to protein denaturation. This work intends to evaluate a computer vision system to measure color changes and to develop a kinetic model to predict them during meat cooking. Pieces of semitendinosus muscle were heated by immersion in a thermostatic bath at constant temperature (from 40 to 100ºC). Superficial color was measured using a computer vision system (*CVS*) and a colorimeter, and represented by means of the *CIEL*a*b** color space. A kinetic model was developed to describe color changes during heating. The correlation coefficient between experimental and predicted values was 0.998 for colorimeter and 0.987 for *CVS* values. In addition, the dependence with the temperature of the fitting parameters was determined. The kinetic constants present a typical Arrhenius dependence. These results encourage coupling the kinetic model to a cooking model previously developed.**

***Keywords*— meat; color kinetics; cooking.**

I. INTRODUCTION

Meat color is the first quality attribute that consumers perceive and is associated to freshness and safety issues (Mancini and Hunt, 2005). Besides, it is also used as an indicator of the degree of doneness (Pathare and Roskilly, 2016), although it does not consider the internal temperature, the most reliable criteria to ensure microbiological safety.

Meat cooking can be defined as the heating up to a temperature sufficiently high to denature proteins. Both temperature and cooking time have a large effect on physical properties and technological quality of meat such as texture, water content and water holding capacity, flavor development, proteins coagulation, inactivation of enzymes and color changes (Tornberg, 2005). Regarding this last one, thermal denaturation of the main proteins groups (myosin, actin, actomyosin, titin) produces an intense coagulation and a release of water, which affects the optical properties of meat (Xia *et al*., 2008). Therefore, during a first stage the meat becomes whiter, causing an increase of lightness (*L** value in the *CIEL*a*b** color space). This behavior has been reported in different kinds of meats: fish (Nakamura *et al*., 2011; Matsuda *et al*., 2013; Hosseinpour *et al*., 2013; Yu *et al*., 2014); pork (Lien *et al*., 2002); and beef (Pakula and Stamminger, 2012; Kondjoyan *et al*., 2014). A second stage is characterized by a decrease of *L** values (Goñi, 2010), due to the gelatinization of collagen at prolonged heating times (Xia *et al*., 2008). In addition, at this stage the combination of high temperature and low water content promotes Maillard reactions (Yu *et al*., 2014), which confer the product desirable flavors and lead to a further decrease of *L**. Besides, the variation of red color (represented by *a** color value) is crucial for meat products. During heating the myoglobin denaturation influences the absorption properties (AMSA, 2012; Røssvoll *et al*., 2014). Initially, a variation from deep red to pink (temperature T near 60°C) is observed, later, to a greyish color (T between 60 and 70 °C), and finally, to a light brown (T between 70-80 °C, Lawrie and Ledward, 2006; Kondjoyan *et al*., 2014). Also, the oxidation state of myoglobin has a deep impact in the color kinetics, due the so-called premature browning, where the meat looks cooked at lower temperatures than the normal ones (Hunt *et al*., 1999; King and Whyte, 2006).

Several authors developed kinetic models to predict color variations during meat processing. Concerning fish products, Kong *et al*. (2007) studied the variation of superficial color during salmon heating, pointing out two phases: a fast lightening followed by a slow browning, this last one modeled with zero order kinetics. Hosseinpour *et al*. (2012) described color changes during shrimp drying using zero and first order kinetics. Matsuda *et al*. (2013) modeled with first order kinetics the changes in superficial lightness of red sea bream during heating, dismissing the initial increase in *L**. Yu *et al*. (2014) followed the actin and myosin denaturation during grilling of red sea and suggested first order kinetics with temperature dependent variables. Regarding red meat, Portanguen *et al*. (2009) employed successive first order kinetics to predict the initial phase (lightness increase) followed by the browning stage during cooking. Pakula and Stamminger (2012) developed a method to measure color variation (using *CIE XYZ* space) to determine the degree of cooking. These authors indicated that lightness recording is sufficient to characterize color kinetics. Kondjoyan *et al*. (2014) analyzed color evolution relating it to protein denaturation. They described both consecutive stages (whitening followed by browning), and represented both of them with first order kinetics.

On the other hand, online color measurement appears to be a very appropriate method for industrial food processes monitoring (Goñi and Salvadori, 2017). In this sense, a computer vision system has many advantages in contrast to the traditional colorimeter: very small as well as very large samples can be handled in a single measurement (Rodríguez-Pulido *et al*., 2012), it does not require direct contact with the sample, and it can be used remotely.

Taking into account this background, the aims of this work are to evaluate a computer vision system to measure color changes during meat cooking, and to develop a kinetic model that represents them. Thus, the kinetic model can help to predict the cooking time related to a desired degree of doneness.

II. METHODS

A. Sample preparation

Beef semitendinosus muscle were purchased in a local market of La Plata (Argentina), and chilled at 4 ºC for 24 hrs. Slices of 6 mm thickness and 8.2 ± 0.5 g (approx.) were packed into polyethylene bags (60 μ). Samples were cooked by immersion in a thermostatic bath (6 l capacity, Vicking Masson D, Argentina) at constant temperature (from 40 to 100 ºC). The heating times were 2, 4, 6, 8, 10, 15, 20, 30 and 60 minutes (at temperatures of 90 ºC or higher maximum heating time was 30 minutes). Given the small thickness of the samples and the bath volume, it was assumed that the sample surface reaches almost instantaneously the bath temperature. After cooking, samples were introduced in a water-ice mixture during 30 seconds to stop the color changes. Then they were smoothly dried using absorbent paper.

B. Color measurements

Superficial color was measured using a *CVS* (Goñi and Salvadori, 2017), which consists on an image acquisition chamber, an illumination system, and a digital camera (Sony Alpha a3500, Japan). The samples were placed in the middle of the chamber floor, together with a X-Rite ColorChecker (X-Rite Inc., USA), which allows calibrating the *CVS* by means of an empiric conversion model between the *RGB* (red, green and blue) and the *CIEL*a*b** color spaces. The images (3000x4000 pixels, acquired with the same white balance) were processed using computational tools developed ad-hoc (Goñi and Salvadori, 2016). Besides, the surface color was measured with a colorimeter (Konica Minolta CR-400, Japan; D65 illuminant, 8 mm aperture, 2º standard observer), in order to corroborate *L*a*b** values, four measures were taken from both sides of the meat slice.

C. Modeling of color changes

The color of a meat sample subjected to a thermal treatment is assumed time and temperature dependent, and is expressed as a combination of two independent mechanisms (Goñi, 2010):

$$C(t) = C^I(t) + C^D(t) \tag{1}$$

where C refers to each color parameter L^*, a^* or b^*, and superscripts I and D refers to the increase and decrease mechanisms, respectively. Each mechanism is modeled independently. Taking into account published results and some preliminary tests, fractional first order variation was considered for both mechanisms, according to Eqs. (2) and (3):

$$C^I(t) = C^I_\infty + (C^I_0 - C^I_\infty)^{e^{-k_I t}} \tag{2}$$

$$C^D(t) = C^D_\infty + (C^D_0 - C^D_\infty)^{e^{-k_D t}} \tag{3}$$

where subscripts *0* and ∞ refer to the initial and the equilibrium (at prolonged times) values, and k_I and k_D are the kinetic constants. Color values at initial and final time are:

$$\begin{cases} C(t=0) = C_0 \\ C(t=\infty) = C_\infty \end{cases} \tag{4}$$

Therefore, the initial and final conditions for each mechanism are established according to the set of Eq. (5); and operating on Eq. (5), Eq. (4) is obtained.

$$\begin{cases} C^I(t=0) = C^I_0 = \alpha C_0 \\ C^D(t=0) = C^D_0 = (1-\alpha) C_0 \\ C^I(t=\infty) = C^I_\infty = \beta C_\infty \\ C^D(t=\infty) = C^D_\infty = (1-\beta) C_\infty \end{cases} \tag{5}$$

Finally, from Eqs. (1) to (5), the kinetic model is expressed as following:

$$C(t) = C_\infty + (\alpha C_0 - \beta C_\infty) e^{-k_I t} + ((1-\alpha) C_0 - (1-\beta) C_\infty) e^{-k_D t} \tag{6}$$

The parameters k_I, k_D, α, β, C_0 and C_∞ must be obtained by fitting experimental color data. Particularly, the kinetic constants (k_I and k_D) can be related to temperature (expressed in K) using the Arrhenius equation:

$$k_{I\,or\,D} = k_{I\,or\,D,0} e^{\left(-Ea/RT\right)} \tag{7}$$

Additionally, it has been reported that the final color (C_∞) strongly depends on the temperature, on the oxidation state of the meat and, in less extend, on the cooking method. In order to relate C_∞ with temperature, the color values measured at the longest processing time at each temperature were considered.

Noteworthy that the non-linear fitting procedure can have multiple and equivalent solutions (for the same set of experimental data) relying on the starting point. In this sense, several fittings were performed to ensure a suitable solution.

D. Statistical Analysis

The experimental data was subjected to statistical analysis, evaluating the error between the two devices used to measure the color. In this sense, the average absolute residuals (Eq. (8)), and the total color difference ΔE (Eq. (9)) were calculated.

$$\left|\Delta C\right| = \frac{1}{m}\sum_{i=1}^{m}\left|C_{E,i} - C_{F,i}\right| \tag{8}$$

$$\Delta E = \frac{1}{m}\sum_{i=1}^{m}\sqrt{\left(L^*_{E,i} - L^*_{F,i}\right)^2 + \left(a^*_{E,i} - a^*_{F,i}\right)^2 + \left(b^*_{E,i} - b^*_{F,i}\right)^2} \tag{9}$$

The subscripts E refers to *CVS* value and subscript F refers to colorimeter value. Also, Eqs. (8) and (9) were

used to evaluate the error of the fitting procedure. In this case, the subscripts *E* and *F* refer to experimental and fitted values, respectively, being the experimental values those obtained with the *CVS* or with the colorimeter. The subscript *i* refers to each sampling time, and *m* is the number of samples at each cooking temperature.

III. RESULTS

Figure 1 shows the variation of each color parameter at two different processing temperatures, comparing both devices. An increase in L^* values is observed in all tests, despite the temperature.

Particularly when the treatment temperature is low (Fig. 1A) L^* value increases slowly, reaching a constant value at prolonged times. At higher processing temperatures (Fig. 1B), the increase in L^* is faster and after reaching a maximum, it decreases gradually, being the final value always above the initial one (raw sample). Similar behavior was reported by Pakula and Stamminger (2012) and Kondjoyan *et al*. (2014). Heating induces protein denaturation, causing in turn increase of structural inhomogeneities, higher scattering and increase of luminosity (Xia et al., 2008).

Regarding the parameter a^*, a decrease in all thermal treatments is recorded, down to a stable value, confirming the tendency informed by Vaudagna *et al*. (2002), who studied the effect of temperature in sous vide beef cooking. In other words, meat samples become less red. Higher processing temperatures cause a faster decreasing rate, in concordance with the statement of Pathare and Roskilly (2016), who found that between 50 and 80 ºC the redness decreases significantly, and above 80 ºC myoglobin denatures completely. The changes on a^* values are highly associated with the myoglobin pigment and its modifications (Xia et al., 2008).

The parameter b^* did not present a significant variation, only a slight increase. Similar behavior of parameters a^* and b^* with the temperature was reported by Lien *et al*. (2002) but referring to pork meat.

In summary, the L^* behavior is mainly due to structural changes, whereas a^* and b^* changes are more related to modifications of the chemical compounds.

Table 1 shows the color differences between both devices, calculated using Eqs. (8) and (9). A good correlation was found, except for a^* values measured at low temperatures, where an appreciable difference was obtained, also shown in Fig. 3. As the cooking temperature increases, this difference becomes smaller, being less noticeable at the highest processing temperatures.

It is worth to mention that the *CVS* allows measuring the color on the entire sample surface in a single measure, whereas multiple measurement points must be employed with the colorimeter. Furthermore, the sample has not uniform color, and then it is easier to obtain average color values from the *CVS*. For instance, Fig. 2 depicts the color predicted from *CVS* (Goñi and Salvadori, 2016) for one sample (which has been segmented to delete extreme data like fat, etc.); the minimum and maximum for each color parameter are also showed.

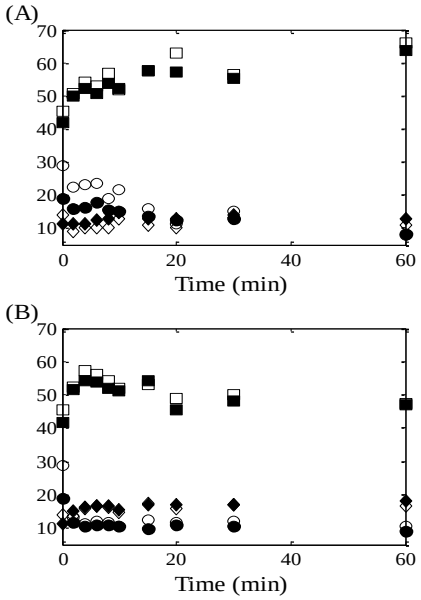

Figure 1. Experimental values of L^* (■, □), a^* (●,○) and b^* (♦,◊) during cooking at A) 50 ºC and B) 80 ºC. Full symbols: *CVS*; Empty symbols: colorimeter.

Table 1. Color differences between both devices for each treatment.

T (ºC)	$\|\Delta L^*\|$	$\|\Delta a^*\|$	$\|\Delta b^*\|$	ΔE
40	1.02±1.15	6.38±2.45	2.77±1.73	7.31±2.44
50	2.15±1.73	4.52±3.06	2.04±0.60	5.91±2.54
60	3.43±1.23	2.44±2.83	1.16±1.12	4.86±2.34
70	2.99±1.36	2.71±2.95	0.97±0.70	4.65±2.49
80	1.76±1.01	2.11±2.84	0.89±0.79	3.21±2.75
90	2.94±0.85	2.16±3.22	0.85±0.78	4.32±2.88
100	1.99±1.31	1.93±3.08	0.95±0.79	3.34±3.00

Figure 3 shows the complete set of samples cooked at 40 ºC and the color provided by each device (depicted as *RGB* patches predicted from the corresponding $L^*a^*b^*$ values). In general, a^* value of the raw sample measured with the *CVS* was near 10 points higher than the one measured with the colorimeter

Figure 4 shows the graphic interface built to perform the fitting procedure. A successful fitting for each treatment was obtained.

Table 2 shows ΔE values of each processing condition, and each device. Furthermore, the correlation coefficient between the whole group of experimental and predicted values was 0.987 for the measurements with the *CVS* and 0.998 for the ones with the colorimeter.

Even though the individual fitting was promising, the fitting parameters (k_I, k_D, α, β and C_∞) did not present a clear dependence with the processing temperature. For this reason, a single fitting including the complete experimental dataset was performed.

First, the equilibrium values C_∞ were fitted with temperature through simple mathematical relationships. Figure 5 shows the experimental values, measured with the *CVS*, and the result of the fitting process to characterize this dependence. Then, these equations (not shown) were included in the global fitting procedure.

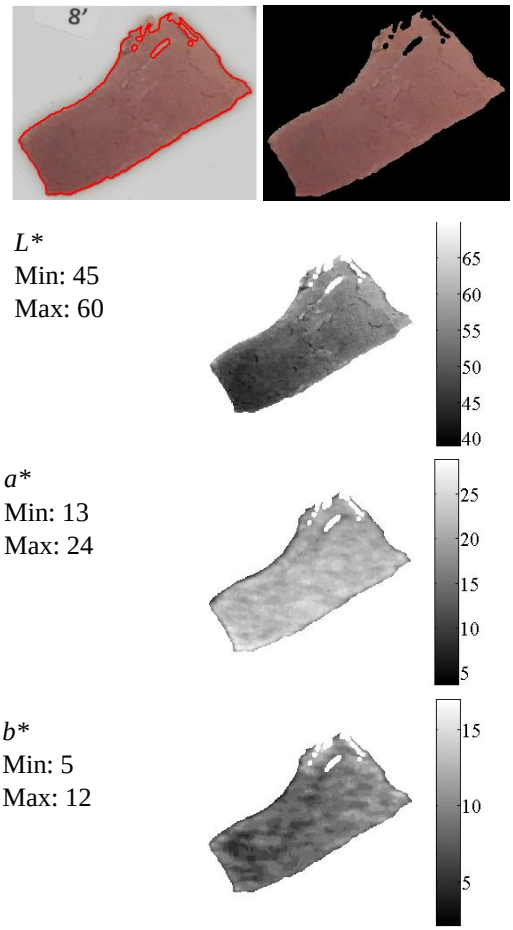

Figure 2. Experimental superficial L^*, a^* and b^* values from *CVS* for the sample treated 8 minutes at 50 ºC.

t (min)	*CVS*				*Colorimeter*			
	L^*	a^*	b^*		L^*	a^*	b^*	
0	45.3	28.8	14.0		41.7	18.8	11.5	
2	46.8	19.9	11.7		46.2	16.7	11.9	
4	46.8	22.9	9.6		46.5	15.4	14.4	
6	44.1	23.9	9.7		44.0	21.0	14.0	
8	44.8	26.5	11.7		45.0	18.2	15.7	
10	48.8	23.8	10.2		46.9	16.8	11.5	
15	48.7	24.8	8.5		48.2	15.8	11.9	
20	51.1	22.9	8.4		50.4	16.2	11.5	
30	50.1	20.3	7.7		50.2	14.9	12.0	
60	53.9	19.5	11.9		51.8	15.6	11.9	

Figure 3. Color measured with both devices for cooking at 40 ºC.

Table 3 presents the results of the global fitting procedure, considering time t and temperature T as independent variables. For L^* values, both mechanisms (increase and decrease) are significant, and adequately describe the experimental data. In this case, α and β follow a linear tendency with the processing temperature, while the kinetic constants k_I and k_D present a typical Arrhenius dependence. For the other color values, a^* and b^*, a single fractional conversion adequately represents the experimental behavior (Ec. (2)), given that including the complete model with increase and decrease terms do not improve the fitting procedure.

Table 2. Fitting errors for each experimental dataset and device.

T (ºC)	ΔE_{CVS}	$\Delta E_{Colorimeter}$
40	2.35±1.09	1.79±1.14
50	2.86±1.68	1.56±1.08
60	1.55±1.07	1.33±0.88
70	2.70±1.49	1.6±1.06
80	1.73±1.06	1.25±1.44
90	1.84±2.06	1.59±1.52
100	2.67±1.15	1.20±0.97

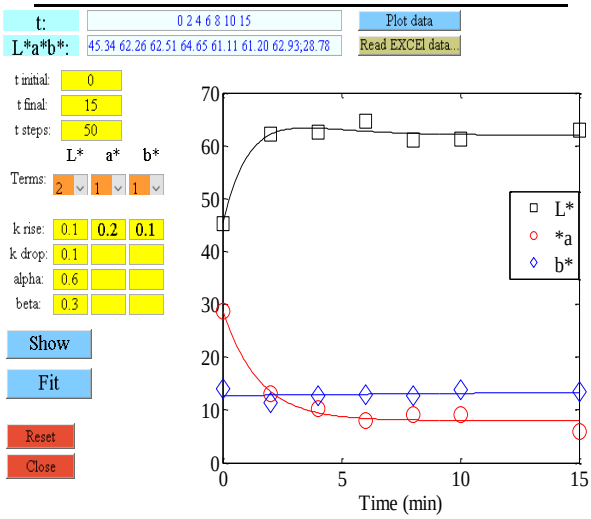

Figure 4. Graphic interface developed in MATLAB to fit the data. The data (symbols) at 70 ºC obtained with the *CVS* is depicted. Full lines represent the fitting model.

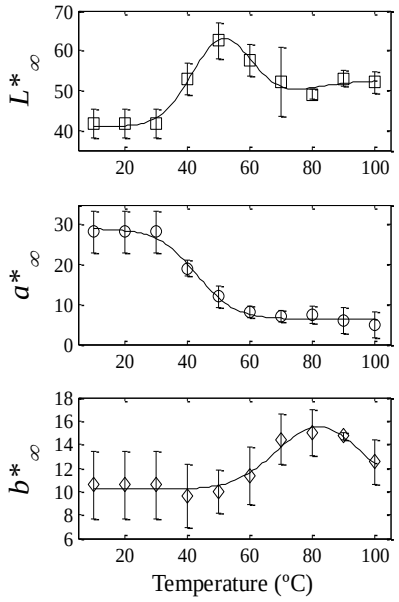

Figure 5. Equilibrium values for each color parameter L^* (□), a^* (○) and b^* (◊). Symbols: experimental data (with *CVS*); full line: fitting model.

Table 3. Fitting parameters considering the whole dataset. (T: ºC; E_a: kJ/mol; k_0: min^{-1}).

	L^*	a^*	b^*
CVS			
C_0	43.03	25.78	10.32
α	0.0354+0.959T	--	--
β	0.559+0.947T	--	--
$E_{a,I}$	40.76	64.09	38.87
$k_{I,0}$	8.05 10^5	1.56 10^9	2.14 10^5
$E_{a,D}$	39.38	--	--
$k_{D,0}$	4.84 10^5	--	--
Colorimeter			
C_0	42.35	18.24	11.56
α	12.41+0.397T	--	--
β	9.99+0.362T	--	--
$E_{a,I}$	41.38	50.39	56.42
$k_{I,0}$	1.19 10^6	6.74 10^6	1.10 10^8
$E_{a,D}$	34.43	--	--
$k_{D,0}$	9.24 10^4	--	--

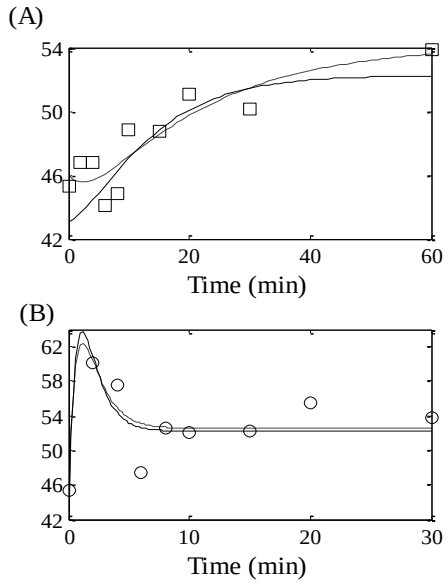

Figure 6. L^* data at 40 ºC (A) and 90 º C (B). Symbols: experimental data; dashed line: individual fitting; continuous line: global fitting.

The kinetic model successfully represents the experimental dataset obtained with both devices. As an example, Fig. 6 compares the experimental L^* values with those predicted with individual and global fittings.

The absolute average difference (Eq. (8)) for the *CVS* measurements were 1.50, 1.43 and 0.72 for L^*, a^* and b^*, respectively, with ΔE = 4.42 in average. For data measured with the colorimeter the errors were 1.85, 1.17 and 0.55, with a total average color difference ΔE = 2.31. These values were acceptable, considering that a color difference less than 2-3 cannot be detected by human eyes.

III. CONCLUSIONS

In general, the computer vision system provides color measurements more similar to the real color of the samples. The correlation between values measured with both devices was adequate, especially at high temperatures.

Regarding the kinetic model, it presents a good correlation with experimental data, and mainly, it was able to describe the increase-decrease behavior of L^* values.

The global fitting allowed the prediction of color changes as a function of time-temperature, in the range of interest of cooking. In this context, these results encourage us to couple the color kinetic model with a cooking model previously developed (Goñi and Salvadori, 2010), in order to include the evolution of this quality attribute when studying the effect of different operative conditions. Thus, the cooking time could be predicted not only based on the thermal evolution inside the piece of meat, but also based on the color evolution.

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