Effect of temperature, starch and plasticizer concentrations on color parameters of ulluco (Ullucus tuberosus Caldas) edible films

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Abstract. The growing concern about limited natural sources and pollution has aroused the interest of developing bio-packaging based on agricultural polymers. The Andean tuber ulluco (Ullucus tuberosus Caldas) is a promising source of starch that can be used in the production of edible films or coatings for preserving the quality of food products. Color is an important feature for edible films production due to can alter the visual perception of the coated product. In this study, the effect of drying temperature (T) (40 to 60°C), starch concentration (SC) (2.0 to 3.0% w/v) and glycerol concentration (GC) (1.0 to 3.0% v/v) on the color parameters (L*, a* and b*) of ulluco edible films was evaluated. A composite central design was used to combine five levels of the three factors (T, SC and GC). Artificial neural network (ANN) were applied to establish mathematical models that could represent the dependence of the factors on the color parameters. The edible films showed luminosity values between 87.4 and 90.3. Results indicated that the higher T, the lower a* and b* parameters and the higher luminosity of the films. Likewise, the lower G, the higher luminosity of edible films. Sensibility analysis shows that SC has an important influence on L*, a*, b* parameters. Statistical results indicated that the ANN approach provided an accurate estimation ($R^2_{adj} = 0.885$ and $MSE = 0.054$) of the color parameters. ANN use a feed-forward architecture with five neurons in the hidden layer, hyperbolic-tangent transfer function, and Bayesian regularization backpropagation as training algorithm. ANN could be an alternative tool for modelling the complex relationship between the color parameters and the temperature, starch and plasticizer concentrations on ulluco edible films.

1. Introduction

Over the last twenty years has been growing the global concern about pollution generated by the indiscriminate use of non-renewable products. As result, many researches are focused on the development of products that can use as food packaging and replace petroleum based materials. Bioplastics are an alternative solution for this issue, they are obtained from natural polymers and their demand has been increased, by 2019 their production is expected to be around 5.5 million metric tons [1].
Biodegradable films can be produced from different materials such as starch, cellulose derivatives, chitosan, gums and animal or plant based proteins [2]. Among these materials, starch is one of the most promising due to their biodegradability, biocompatibility, low cost and wide availability in renewable sources. Starch-based films have been studied in a wide range at experimental level, and present suitable characteristics for their use as food packaging such as transparency, odorless and tasteless [3]. In addition, starch-based films can extend shelf life of food by acting as barrier against mechanical damages or controlling gases exchange [4].

Color properties of edible films are an important feature in packaging, since they can alter the visual perception of food products [5]. However, the performance of edible films based on starch may vary, this is related to its chemical structure, specifically to the amylose/amylopectin ratio, which depends on the botanical source of starch [6]. Basiak, Lenart, and Debeaufort [6] studied the effect of starch type on the color properties of edible films, found that the starch amylose content has a negative effect on transparency of wheat, corn and potato starch based films.

Ulluco (Ullucus tuberosus C.) is an Andean highland tuber that normally is cultivated between 2400 and 4250 meters above sea level. Ulluco tubers are small (2-15 cm) and have oblong or spherical shape, the color tuber skin may vary from yellow, orange, red, magenta to purple, while, the pulp is white or yellow [7]. Ulluco tuber is rich in carbohydrates, protein, fiber and vitamin C [8]. In Colombia, the tuber is consumed in natura and used in typical preparations. The use of the tuber is related to old indigenous traditions of paeces, muiscas and lanches from the Andean zones from Cauca, Nariño, Boyacá and Cundinamarca departments [9]. According to Cruz et al. [10] ulluco starch has suitable characteristics, such as high gel stability, for being use in food applications. However, there is not enough information about the possible industrial uses, making it difficult to take full advantage of this raw material. Therefore, the addition of value to ulluco would have a positive impact on the regional rural economy.

In this context, the aim of this work was to evaluate the effect of drying temperature (40°C to 60°C), ulluco starch concentration (2% to 3% w/v) and glycerol concentration (1% to 3% w/v) on the L*, a* and b* parameters of ulluco starch based edible films using artificial neural network (ANN).

2. Materials and Methods
2.1. Materials
Ulluco tubers were purchased in a local market in the city of Ibagué (Colombia). The samples were selected and washed, and those that showed mechanical damage on the surface were discarded.

2.2. Starch Extraction
Extraction of ulluco starch was performed according to the methodology describe by Valcárcel-Yamani et al. [11].

2.3. Experimental design
A central composite inscribed design (CCI) was used to determine the effect of drying temperature T (°C), starch concentration SC (% w/v) and glycerol concentration GC (% w/v), on the optical properties of ulluco edible film. Five levels of each factor were combined to obtain a 15 formulations design matrix (Table 1). Each formulation was prepared by duplicated and the experiments were carried out by triplicated, totalizing 90 experiments.

| Table 1. Effect of SC, GC and T on optical properties of ulluco starch edible film |
### Table 1: Results of the Color Parameters L*, a*, and b* of Ulluco Edible Films

| Sample | SC (% w/v) | GC (% w/v) | T (°C) | L*      | a*      | b*      |
|--------|------------|------------|--------|---------|---------|---------|
| 1      | 2.2        | 1.4        | 44     | 88.8 ±0.57 | -0.23 ±0.03 | 2.90 ±0.06 |
| 2      | 2.2        | 1.4        | 55     | 89.2 ±0.53 | -0.31 ±0.02 | 2.95 ±0.06 |
| 3      | 2.2        | 2.6        | 44     | 87.5 ±0.27 | -0.30 ±0.00 | 3.06 ±0.04 |
| 4      | 2.2        | 2.6        | 55     | 88.2 ±0.30 | -0.36 ±0.02 | 3.28 ±0.06 |
| 5      | 2.8        | 1.4        | 44     | 89.2 ±0.19 | -0.10 ±0.02 | 2.87 ±0.06 |
| 6      | 2.8        | 1.4        | 55     | 89.1 ±0.26 | -0.04 ±0.02 | 2.75 ±0.03 |
| 7      | 2.8        | 2.6        | 44     | 88.3 ±0.27 | -0.16 ±0.01 | 2.99 ±0.02 |
| 8      | 2.8        | 2.6        | 55     | 90.3 ±0.32 | -0.22 ±0.01 | 3.03 ±0.10 |
| 9      | 2.0        | 2.0        | 50     | 88.8 ±0.24 | -0.06 ±0.01 | 2.89 ±0.04 |
| 10     | 3.0        | 2.0        | 50     | 89.1 ±0.21 | -0.24 ±0.01 | 2.99 ±0.04 |
| 11     | 2.5        | 1.0        | 50     | 88.8 ±0.37 | -0.44 ±0.02 | 2.97 ±0.05 |
| 12     | 2.5        | 3.0        | 50     | 87.4 ±0.11 | -0.26 ±0.02 | 3.02 ±0.03 |
| 13     | 2.5        | 2.0        | 40     | 87.6 ±0.16 | -0.28 ±0.02 | 3.05 ±0.02 |
| 14     | 2.5        | 2.0        | 60     | 87.7 ±0.17 | 0.12 ±0.01  | 2.93 ±0.05 |
| 15     | 2.5        | 2.0        | 50     | 87.8 ±0.38 | 0.07 ±0.01  | 2.92 ±0.07 |

**SC**: starch concentration; **GC**: glycerol concentration and **T**: temperature

### 2.4. Film Preparation
Ulluco starch films were prepared by casting following the methodology described by Tumwesigye, Montañez, Oliveira, & Sousa-Gallagher [12], with some modifications. Starch at different concentrations (Table 1) was dissolved in distilled water using magnetic stirring for 5 min. The mixture was heated to 95°C and held at this temperature above 5 min, until a clear viscous gel was obtained. The mixture was cooled down to 50°C and then glycerol (Merck, Millipore, MA, USA) was added at different concentrations (Table 1). 30 g of solution were transferred to a Petri dish of 8.5 cm diameter. The samples were dried for 24 h in an oven with forced air at different temperatures (Table 1). Moisture films were stabilized in a desiccator cabinet (DH-1002, Acequilab, Colombia) at 54% RH for 24 h, prior to analyzes.

### 2.5. Color
Film color was determined by Minolta colorimeter (Cr 410, Konica Minolta, Japan) in the CieLab scale. Standard white plate was used to calibrate the equipment (Y=86.6, x=0.3153, y=0.3228). The L*, a*, and b* values were evaluated by reflectance measurements. In these system, L* is the luminosity (from black to white), and the horizontal axes a* and b* are the chromatic coordinates (from -a*: greenness, +b*: bluish to -a*: redness, +b*: yellowness) [5].

### 2.6. Artificial Neural Network (ANN) model
ANN was used to determine the effect of temperature (T), starch concentration (SC) and glycerol concentration (GC) on the L*, a* and b* parameters of ulluco edible films. A feed-forward neural network was developed and trained by Bayesian regularization backpropagation (trainbr) algorithm (Table 2). Transfer function log-sig was used. Three-layer basic architecture was modelling, the input layer with three neurons reflecting the independent variables (T, SC, GC), a hidden layer with five neurons and the output layer representing the dependent variables (L*, a*, b*). All the experimental data were used for ANN modeling. ANN training and simulation were carried out by the Neural Network Toolbox of Matlab® R2016b (The Mathworks Inc., Natick, MA, USA) software. Both input and output
Data were normalized within the range [-1,1] by the ‘‘mapminmax’’ function of Matlab® which helps to reduce network error by balancing the order of magnitude of the inputs [13].

ANN performance was evaluated by the adjusted coefficient of determination ($R^2_{adj}$) (Equation 1) and the mean square error ($MSE$) (Equation 2).

$$\begin{align*}
R^2_{adj} &= 1 - (1 - R^2) \frac{n-1}{n-m} \\
MSE &= \frac{1}{n} \sum_{i=1}^{n}(x^*_i - x_i)^2
\end{align*}$$

where $x^*_i$ represents the experimental values; $x_i$ represents the estimated values; $n$ is the number of experimental or estimated values and $m$ is the number of estimated parameters (biases and weights).

The best ANN configuration was selected for $L^*$, $a^*$ and $b^*$ parameters, first, according to the highest $R^2_{adj}$ and the lowest $MSE$, and secondly, considering the lowest number of hidden-layer neurons and the simplest network architecture. $R^2_{adj}$ evaluated how successful each ANN explained the variation in the experimental data by adjusting the coefficient of determination ($R^2$) based on the number of biases and weights [14].

Moreover, the selected ANN configurations were submitted to a residual analysis, to assess the adequacy of ANN models [15], and were submitted to a global sensitivity analysis by the Sobol’ method [16], to quantify the effect of factors and their interactions on the responses.

### Table 2. Parameters of artificial neural network (ANN)

| Properties | ANN architecture | Transfer function | Neurons (hidden layer) | Number of parameters | $R^2$   | $R^2_{adj}$ | $MSE$   |
|------------|------------------|--------------------|------------------------|----------------------|--------|------------|--------|
| Color      | Feed-forward     | Logsig             | 5                      | 38                   | 0.901  | 0.885      | 0.054  |

$ANN$: artificial neural network and $MSE$: mean square error

### 3. Results and discussion

Edible films color is an important characteristic for consumers acceptability as packaging material. Films with high gloss and transparency leads to a good visual food presentation [3]. In general, ulluco starch edible films had good appearance and clarity. Ulluco films were homogenous and easily removed from the plastic petri dish. As exposed Figure 1, the film does not alter food natural colors, which shows good characteristics for being applied as food packaging.

The effect of $SC$, $GC$ and $T$ on the $L^*$, $a^*$ and $b^*$ parameters are shown in the Figure 2. $L^*$ values ranged between 87.4 and 90.3 (Table 1). The highest $L^*$ value was shown by sample prepared with 2.8% of $SC$, 2.6% of $GC$ and 55°C of $T$. The luminosity values obtained in this work were higher than those reported for babassu mesocarp starch edible films ($L^* = 76$) [17] and mucilage-based films produced with $Cereus hildmannianus$ ($L^* = 86$) [18].
Sensitivity analysis (SA) allows the calculation of two factors $Si$ and $STi$ (Table 3), the first order sensitivity index ($Si$) measures only the main effect contribution of each input factor on the output variance. However, the second index ($STi$) shows the contribution of the main factor interactions between them and the rest [16]. Table 3 shows that $SC$ was the factor with the greatest sensitivity on $L^*$ values, which is consistent with the values obtained of ulluco edible films at 2.8% and 3% of $SC$ (Table 1). However, SA also shows that the interaction between $SC$ and $GC$ parameters have effect on $L^*$ values. Fig. 2 illustrate these results, when $SC$ increased and $GC$ decreased the luminosity of the edible films are higher, this could be explained since the increase in plasticizer concentration ($GC$) leads to a polymeric chain compaction that can modified the refractive index and restricting the passage of the light through the film matrix [19]. Moreover, $T$ parameter does not show a sensitivity effect on luminosity.
Table 3. First-order-effect and total-effect sensitivity indices corresponding to SC, GC and T

| Factor | $L^*$ | Difference | $a^*$ | Difference | $b^*$ | Difference |
|--------|-------|------------|-------|------------|-------|------------|
| SC     | 0.45  | 0.877      | 0.427 |            | 0.106 | 0.108      |
| GC     | 0.058 | 0.047      | 0.141 |            | 0.39  | 0.341      |
| T      | 0.04  | 0.045      | 0.076 |            | 0.06  | 0.035      |

SC: starch concentration; GC: glycerol concentration; T: temperature; $S_i$: sensitivity index and $ST_i$: total sensitivity index

SA shows that $a^*$ and $b^*$ parameters have similar behavior, both were mainly sensitive ($S_i$) to GC, followed by SC and last by T. In addition, GC and T interactions ($ST_i$) have the greater sensibility effect on $a^*$ and $b^*$ parameters. $a^*$ values ranged between -0.36 to 0.12 (Table 1), showing that ulluco edible films tend to a neutral color. Fig. 2 shows when GC and SC increased $a^*$ values decreased and slightly tends to greenness. On the other hand, the use of middle drying T produces that $a^*$ values tend to zero. Nawab et al. [3] studied the physical, mechanical and barrier properties of Mango kernel starch-gum composite films, they observed lower $a^*$ values (-0.86) compare to those obtained for ulluco edible films, indicating a higher tendency to green. This can be related to the botanical source of raw material (starch) used in the preparation of edible films.

As can be observed in Table 1, $b^*$ values were between 2.75 and 3.28, suggesting that these films tend to the yellowness. It was observed that higher $b^*$ values were obtained when GC increased (Figure 2). However, the opposite behavior was observed for SC and T variables. The results obtained in this study for $b^*$ values were lower than those reported by Saberi et al. [19] and Vargas et al. [20].

ANN is a computational and mathematical modelling technique, based on inspiration from the simulation of the biological brain [21]. ANN exhibited a good fit of the experimental data with high adjusted coefficient of determination ($R^2_{adj} = 0.885$), as well as high accuracy of the estimation (MSE=0.054). The difference between the experimental and estimated average color properties (residuals) vs the experimental are shown in Fig 3. It was observed that 72.22% of the results were between -0.11337 and 0.16324. Thus, corroborate the suitability of the proposed model to accurately predict the color properties of ulluco edible films.

![Figure 3](image_url)  
Figure 3. Residual analysis for color properties of ulluco edible films to ANN

A mathematical model for the feed-forward architecture was obtained (Equation 3).
where \( W_{ih} \) is the weight matrix from the input to the hidden layer, \( b_h \) is the bias vector of the hidden layer, \( W_{ho} \) is the weight matrix from the hidden layer to the output layer, \( b_o \) is the bias vector of the output layer, \( X \) is the matrix of the normalized input variables and \( Y \) is the matrix of the normalized output variables.

4. Conclusions
Edible films based on ulluco starch were successfully prepared and the effect of starch concentration \( SC \), glycerol concentration \( GC \) and temperature \( T \) on their color parameter (\( L^* \), \( a^* \), \( b^* \)) was study using an artificial neural network ANN. Colorimetric analysis show high \( L^* \) values, neutral \( a^* \) values and slightly yellowness films (positive \( b^* \) values). \( L^* \) values were mainly influenced by \( SC \) and by the interactions between \( SC \) and \( GC \). Nevertheless, \( a^* \) and \( b^* \) values were mainly influenced by \( SC \) and by the interactions between \( SC \) and \( T \). ANN accurately predicts the color properties of ulluco edible films. Thus, ulluco edible films has suitable color characteristics for being applied as for food coating or edible application, corroborated by their high transparency and luminosity.

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