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A MALST method comparison over univariate kinetic modeling for determination of shelf-life in cereal snack of dried apples

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Abstract

A Multivariate Accelerated Shelf-Life Testing (MALST) study in cereal of dried apple snack incubated at 18°C, 25°C and 35°C. Quality attributes were analyzed until 18 months. The data obtained were used to modeling univariate and multivariate kinetic, through Principal Componenent Analysis PCA. PCA could explain the interaction between attributes; which would imply that model reflected in terms of variability, biochemical phenomena associated with the deterioration of the product. There was a good relationship between both models in the Shel-life estimated with the comparative advantage that MALST method could model simultaneously the complete and "all at once" phenomenon of deterioration.

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Keywords: MALST; PCA; Multivariate Kinetic, Scores, Shelf Life

1. Introduction

Nowadays consumers demand products with superior appearance, texture, taste and flavour whilst keeping their nutritional value [1, 8]. For this purpose, the formal determination of shelf-life is a key factor in the research and development of food since provides information regarding the time that the product aptly retains its attributes [1-5]. This determination is usually performed by measurement of quality attributes [6], alternating accelerated ageing methods under extreme conditions [7]. The most usual model to this purpose is Arrhenius equation, since it relates temperature with the reaction velocity

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(k) [2]. However, the shelf-life determination becomes complex when multiple attributes must be studied simultaneously in a food system, since each one has an own specification related with the date of expiration. For these cases, the use of multivariate statistical techniques could be more suitable [8]. In this sense, accelerated shelf life testing methods have incorporated multivariate tools, called Multivariate Accelerated Shelf Life Testing (MALST).

In this context, the objective of this research was comparatively assessing shelf-life of an absolutely new product in market which is a snack-cereal of dried apple type, through traditional univariate method and multivariate accelerated method.

Nomenclature

Aw	Activity water
Humidity	% Moisture
PCA	Principal Component Analysis
k^{m}	Multivariate reaction rate (Scores*h^{-1})
Ea^{m}	Multivariate Energy of activation (cal/mol)
$\alpha^{m}_{T+\delta T,T}$	Acceleration factor
Tc	Cut off criteria

2. Materials and Methods

Samples of a new product in the market of dried Apple snack type from an exporting agribusiness (Maule, Chile) packed in multi-laminated bags were used. They were incubated at 18 °C, 25 °C and 35 °C. Considered quality attributes were Aw (Aqua LAB at 20 °C ± 0.3 °C), moisture (AOAC 2000-934 06), content of SO2 (method Monier Williams), taste, color, aroma, sensory texture and color CIE-Lab (colorimeter Minolta CR-200b). Analyses were conducted over 18 months of incubation.

Univariate analysis: in this stage, univariate degradation kinetics were studied according methodologies proposed by [2, 3].

Multivariate analysis: data of quality attributes were modeled using the method proposed by [8]. This method is based on application of Principal Component Analysis (PCA) based NIPALS algorithm, modified by [9]. PCA was performed on quality attributes matrix for three storage conditions of temperature, jointly and separately. With these values, multivariates kinetic were adjusted multivariate, for each of the multivariate properties. All calculations and adjustments were made with SIMCA-P+ 12 (Umetrics, Umeå, 2009), Sigmaplot 11 (Systat Inc., 2009) and Excel 2003 (Microsoft, 2003).

3. Results and Discussion

Scores plot (Fig. 1) from PCA shows the evolution of the attributes used at three temperatures. PCA is an unsupervised exploratory tool to visualize the main variations between samples, sample clustering, and the relation between the samples and variables. PCA is a technique that, by the reduction of the data dimensionality, allows their visualization retaining as much as possible the information present in the original data. So, PCA transforms the original measured variables into new uncorrelated variables called principal components. Each principal component is a linear combination of the original measured variables. Thus, the behavior pattern underlying the studied variables could be explored.

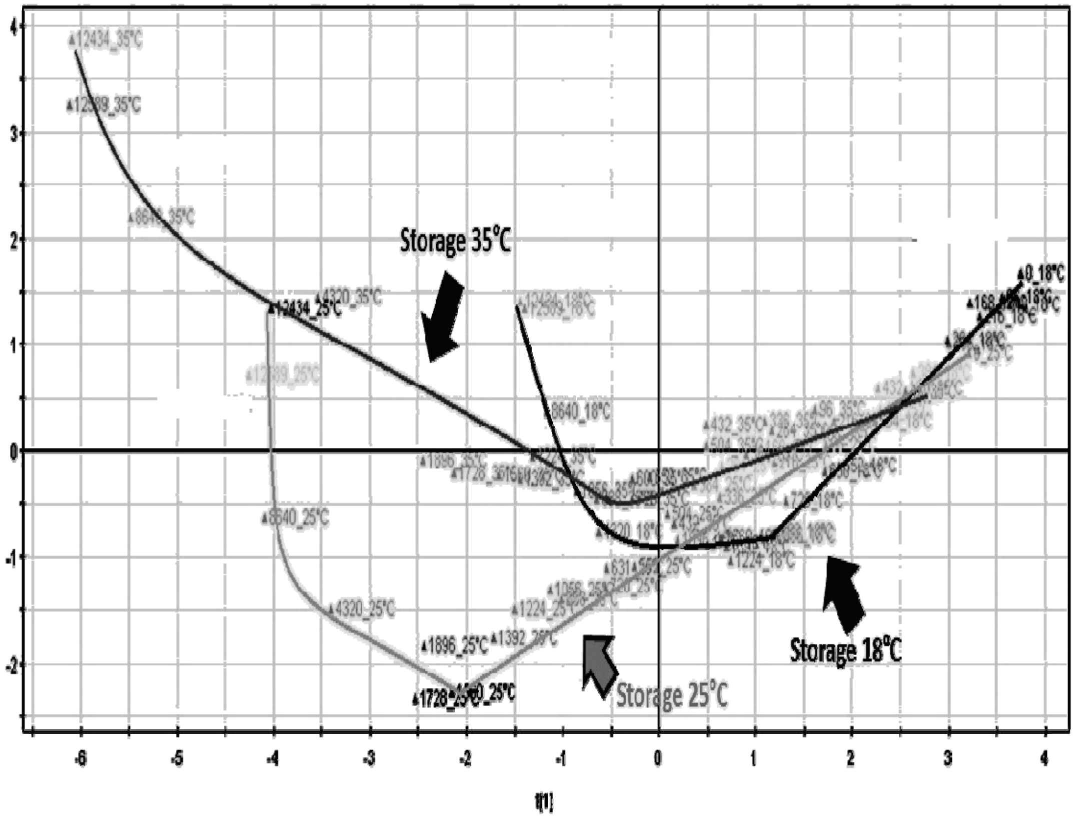

Fig. 1. Global Score Plot for three storage temperatures

The first model retained 2 Principal Component (PC) explaining 83.1% of the total variability (PC 1: 68% and PC2: 16.2%). PCA ordered the variability of samples based on the time through the first component (t1). Inspecting the graphics of contribution (not shown data) it could be appreciated the pattern of variability explained by the second component (t2). Thus, it can be explained the different behavior for the 3 temperatures of storage. Therefore, for the storage at 18°C, contribution is mainly explained by attribute Aw, while at 25°C, the color variables of and SO_2 content acquired greater importance. At 35°C the greatest contributions were associated with moisture and texture, at the final incubation times. This suggests that for each storage temperatures, there are alternating predominant mechanisms of deterioration. In this sense, some examples in literature reports that degradation of SO_2 increases significantly at 25°C [10], and the color in the range of 20°C to 30°C [11], while at 35°C, the greatest contribution of humidity and texture were associated with higher values detected in these attributes. The above, would imply that model reflected in terms of variability, biochemical phenomena associated with the deterioration of the product, taking into account moisture migration it´s a clear meaning of a mass transfer process which develops along all incubation time (more than 18 months) and may have direct impact in crispness and the beginning of other deterioration changes.

Reflecting above, Loadings Plot (Fig.2) shows the underlying interaction between attributes, appreciating that moisture and texture are related in reverse, since as humidity (moisture) increases, sensory crispness decreases. In addition, color DE is inverse to sensory color, because an increase in DE is associated to coffee shades (a rejection factor associated to enzymatic browning). The kinetic calculation was performed with the first PC related with the time, to obtain multivariate kinetic associated with 3 conditions storage (Fig.3).

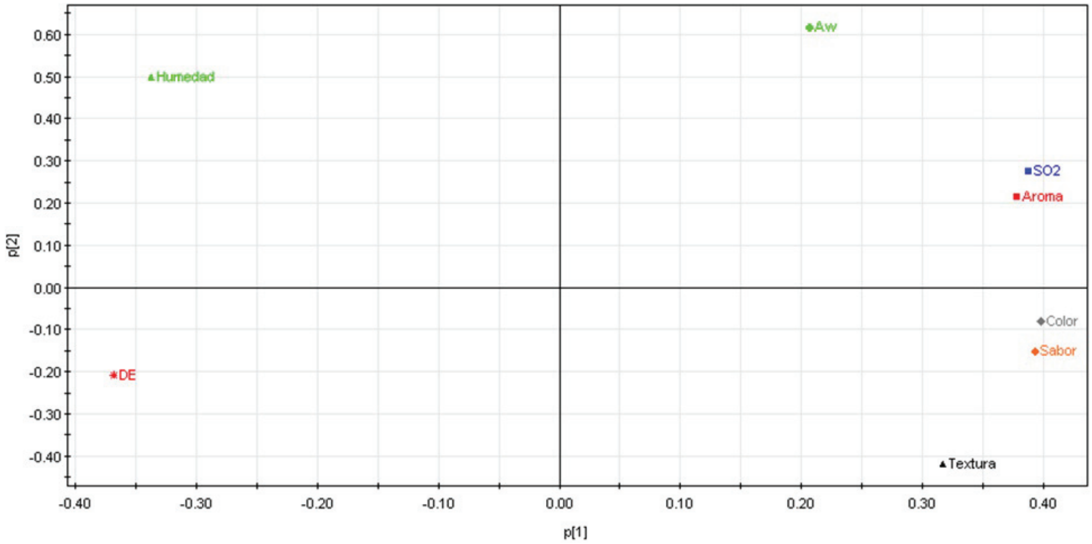

Fig. 2. Loadings Plot

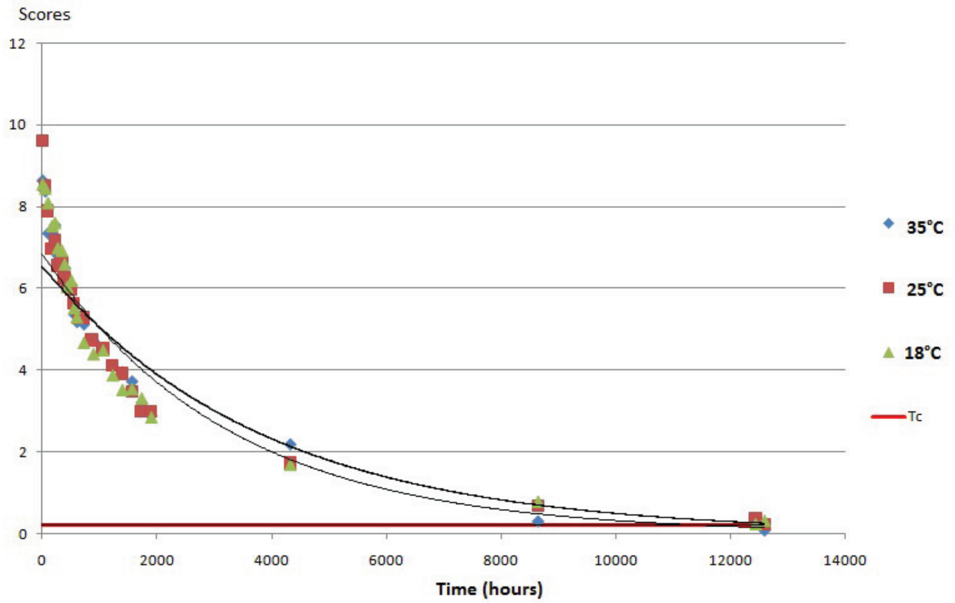

Fig. 3. Scores vs. Time plot for 3 Storage conditions (Multivariate Kinetic)

Fig. 3 shows that degradation product reflects 1st order kinetic for all storage conditions. From this graph, degradation curves were adjusted and multivariate kinetic parameters were calculated $\boldsymbol{k}^{\,m}$ (reaction rate), $\boldsymbol{Ea}^{m}$ (Activation energy expressed in cal/mol) and $a_T^m + \delta_{T.T}$ (acceleration factor) (Table 1). The stability of the product is inferred, due to the minimal increase in the rate of reaction between incubation temperatures.

From the specification values of the product (not shown values) and the Loadings matrix was obtained the Cut off criteria (Tc in figure 3), which in this case was 0.2183. It was determined that shelf-life was 18.2 months for storage to 18 ° C, 18.1 months at 25 ° C and 15.5 months at 35 °C. By comparing this value with the obtained by univariate kinetics, where the degradation only contemplates humidity as attribute, shelf-life of the product was 17.4 months, existing a difference of a few weeks in estimating one method and other.

Table 1. Multivariate kinetic parameters for three storage temperatures

Storage T°	**Rate constant k^m** (PC 1 score hours^{-1})	R^2 adjust	$\alpha^{m}_{T+\delta T,T}$	***Ea^m*** **(cal/mol)**
18°C	0,00026	0,96		1563,53
25°C	0,00026	0,96	$\alpha_{25,18 = 1}$	
35°C	0,00030	0,95	$\alpha_{35,18 = 1,15}$	

Indeed, despite the partial increase observed in the humidity in the three storage temperatures, there was not a relationship with the attribute Aw, as had been hoped. This suggests that water migrates to inside the product through packaging; water settles so in the product, which interacts with the different ingredients, whereas the product has a high content of sugars and solutes that preclude the availability of water for degradation reactions.

Due to little difference of shelf-life at 18°C and 35°C, it could be inferred the high stability of the product and a seeming "semi-independence" of the phenomena from the temperature. In the other hand, the "self-weighting" of attribute variability approach of MALST method could be considered like an important feature at the moment of take decisions about the cut-off criteria. In this meaning, the shelf-life assessment by MALST method appears advantageous to reduce the bias of select arbitrarily the quality attributes to shelf-life determination.

4. Conclusion

MALST methodology could estimate simultaneously deterioration of quality attributes of the product, showing all the interactions occurring at the product concurrently

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