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Multivariate accelerated shelf-life testing: a novel approach for determining the shelf-life of foods

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In order to meet consumers' expectations for high-quality products, food industries must conduct shelf-life studies that many times include the assessment of several analytical and sensory properties. However, whenever a new product is to be launched onto the market, defining which are the most relevant properties to monitor, as well as their cut-off criterion, is the subject of strong debate. Besides, for products with long estimated shelf-lives, accelerated studies have to be conducted and a third parameter has to be estimated: the acceleration factor which defines the correlation between the different storage conditions. In this study we propose a new approach for determining the shelf-life of industrialised food products, the Multivariate Accelerated Shelf-Life Test (MASLT), in which a Principal Component Analysis (PCA) is performed and the scores of the time-related components are taken for estimating the multivariate rate constants (k^m), the multivariate acceleration factor (α^m) and the multivariate activation energy (Ea^m). The method was successfully applied to a single-concentrated industrialised tomato product for which the actual shelf-life was estimated to be 28 months. Pseudo-zero-order kinetics resulted in the multivariate parameters $\alpha^m_{35,25} = 2.7$ and $Ea^m = 150\,kJ{\cdot}mol^{-1}$. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: principal component analysis; chemometrics; kinetics; food degradation; sensory analysis

1. INTRODUCTION

Due to regulatory issues and consumer demands, industrialised food products need to clearly state their shelf-lives, that is the time within their characteristics are kept at acceptable levels, in their packages. Nowadays consumers demand products with superior appearance, texture, taste and flavour whilst keeping their nutritional value. Thus, food companies need to carry out kinetic studies whenever a new or modified product is to be launched onto the market.

There are several ways of conducting shelf-life studies reported in the literature [1–5] but most of them are based on the kinetic theory, by which the rate of degradation of a product is expressed as [1–3,6]:

$$v = \frac{dP}{dt} = kP^n \quad (1)$$

where v is the reaction velocity, P denotes any property of interest, n determines the reaction order and k is the rate constant (k is negative if P decreases with time). It was determined by experience that, for foods, most properties obey pseudo-zero- or pseudo-first-order kinetics ($n = 0$ or $n = 1$) [1,3,4].

Nevertheless, conducting a complete shelf-life test over the whole estimated validity of an industrialised product with long shelf-life can be quite resource-consuming and significantly delay its launch onto the market. In order to overcome this issue food scientists conduct accelerated shelf-life studies, which consist of submitting the product to relatively severe conditions of storage. These tests rely on the fact that k is temperature-dependent. Thus, the harsher conditions to which products are submitted usually refer to some relatively higher temperature of storage. As most degradation reactions are Arrhenius-like, the higher the temperature, the faster products achieve high degradation levels [1–4].

In accelerated tests, data are collected for various storage conditions at different times and kinetic charts (sometimes called shelf-life charts) are built. By evaluating the reaction velocity profile it is possible to determine the reaction order and then convert the results from accelerated tests to actual market conditions. For this, a proportionality constant

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between different storage temperatures is determined as [1–3]:

$$\alpha_{T+\delta T,T} = \frac{v_{T+\delta T}}{v_T} \quad (2)$$

in which $\alpha_{T+\delta T,T}$ is the acceleration factor, $v_{T+\delta T}$ and v_T are, respectively, the reaction velocities for the accelerated and market test conditions. When the degradation process of products stored at different temperatures follow the same reaction order, Equation (2) simplifies to:

$$\alpha_{T+\delta T,T} = \frac{k_{T+\delta T}}{k_T} \quad (3)$$

Labuza [1] has also defined a proportionality constant called Q_{10} which is a particular case of Equation (2):

$$Q_{10} = \frac{v_{T+10}}{v_T} \quad (4)$$

and which can be further simplified for reactions of the same order.

In the equations above, T can be set as the actual market temperature. For products commercialised in several markets with distinct climates different α values can be determined.

Another important kinetic parameter determined in shelf-life studies is the activation energy (Ea), which is the minimum amount of energy needed for a reaction or degradation process to occur. The activation energy is linked to the rate constants at different temperatures by the equation [1,6]:

$$k = Ce^{-Ea/RT} \quad (5)$$

in which C is the pre-exponential or frequency term, R is the gas constant and T is expressed in kelvins.

In practice, in order to properly conduct an accelerated shelf-life test one has to specify the properties to monitor, the storage conditions and the cut-off criteria for each property. Usually, the decision regarding the two former aspects is made on the basis of the prior experience and/or on information available in the literature. Defining the best cut-off criterion is rather more complicated. Despite some parameters being defined by legislation or other local market needs, it is usually up to the researcher to define which criterion to use. The issue becomes even more complicated when several variables are studied because each one demands its own criterion and, especially for sensory characteristics, it is not easy to state which is the most relevant for defining the final validity date of the product.

Multivariate techniques of analysis present a set of useful tools for shelf-life studies in which many different properties need to be monitored. One of the most applied techniques is Principal Component Analysis (PCA), which aims at finding a new set of axes in multivariate space that better describe the structure in the data. These new axes are called Principal Components (PC) and are built by linear combinations of the original variables [7–9].

PCA and other data-reduction techniques were previously applied to shelf-life studies solely as variable selection techniques [10–13], or for studying the relationship between sensory attributes and instrumental analysis [14–17]. However, the potential of the PC-scores was never exploited as formal parameters (P in Equation (1) for shelf-life determination.

The objective of this article is to describe a novel multivariate approach for shelf-life determination of food products which uses PCA. The ability of the Multivariate Accelerated Shelf-Life Test (MASLT) method to give reliable shelf-life estimates whilst improving data interpretability is presented for a single-concentrated, processed tomato product in a complete 30 months study which included sensory and analytical data. Previous studies reported in the literature for similar products were conducted for shorter periods of time [18–23].

2. THE MULTIVARIATE ACCELERATED SHELF-LIFE TEST (MASLT) METHOD

2.1. Assumptions and general properties

The MASLT is based on compressing the space spanned by the original variables via PCA and then using the scores as properties for further shelf-life assessment. The data set has to be properly arranged prior to PCA analysis in order to retain the information related to time and storage conditions. This arrangement is described in section 2.2. below. As PCA can be considered a weighted least squares procedure, the multivariate parameters can be interpreted as loadings-weighted averages of the kinetic parameters obtained from the original properties.

The main assumption of MASLT is that the degradation reactions are the main source of variation in the data set because samples initially have the same composition and the storage conditions are properly controlled. Thus, PCA should be driven by time-related phenomena. Besides, as PC are extracted in a decreasing order of explained variance, it is expected that the first few PC account for the degradation reactions and that subsequent PC describe noise or processes not related to product degradation.

If higher-order PC present a relationship with time whilst the first ones do not, one should carefully examine what are the most important variables responsible for the lower-order PC, as time-uncorrelated variations might bring new insights about product degradation. On the other hand, it can flag that something went wrong during storage as the variation in the data set is not being described by time-related processes.

Another assumption of the MASLT is that PCA can accommodate non-linear processes in the scores of the time-related PC [7–9]. This is especially important for shelf-life studies where pseudo-first-order processes are dominant. How these non-linearities are being accounted for by the PCA can be determined by evaluating the loadings of the variables of first-order kinetics.

An important characteristic of the MASLT is that samples presenting large scores values do not necessarily vary with time: they might present the same extreme values during the whole study. This is particularly true if samples are stored at low temperatures in which degradation reactions are virtually stopped.

A scaling pre-processing is necessary prior to PCA when the original variables under study present different scales.

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This procedure can bring some detrimental effects to the subsequent multivariate shelf-life study as variables with low variability in time will be emphasised whilst those with high variability might have its importance diminished in the PCA. As this is an intrinsic characteristic of any scaling procedure [24], one should be careful in controlling the storage conditions and data acquisition in order to minimise these detrimental effects.

2.2. The MASLT algorithm

Following the traditional convention in linear algebra, in this work vectors are represented by boldface lower case, matrices by boldface upper case, scalars by italic lower case letters and sequences by italic subscripts.

1) For each storage condition, collect the instrumental and sensory data in a $\mathbf{X}_T \in \Re^{NxK}$ matrix, where N is the number of points in time where evaluations were conducted and K is the number of variables included in the study;
2) Stack the $\mathbf{X}_T$ matrices on top of each other, in order of increasing temperature, to form a single $\mathbf{X} \in \Re^{cNxK}$ matrix, where c denotes the number of storage temperatures (Figure 1). This structure of $\mathbf{X}$ is necessary in order to keep samples spread in a single multivariate space which would reveal time and temperature dependencies in the PCA;
3) If the variables present different scales, auto-scale [8,24,31] the $\mathbf{X}$ matrix to obtain $\mathbf{Xa}$. The columns of $\mathbf{Xa}$ have means equal to zero and unit variance:

$$xa_{n,k} = \frac{x_{n,k} - \bar{x}_k}{s_k} \tag{6}$$

where $\bar{x}_k$ and s_k are, respectively, the mean and the standard deviation of the elements of the k-th column of $\mathbf{X}$ and $xa_{n,k}$ and $x_{n,k}$ are typical elements of $\mathbf{Xa}$ and $\mathbf{X}$.

4) Perform a PCA on the $\mathbf{Xa}$ matrix, obtaining the scores ($\mathbf{T}$) and loadings ($\mathbf{L}$) matrices as well as the variance table for each PC. Select the first R PC that possess higher variances and evaluate their structure via scores and loadings charts.

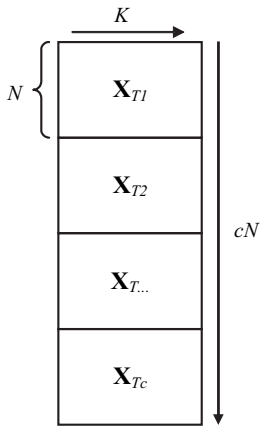

Figure 1. The **X** matrix structure. *N* is the number of points in time where evaluations were conducted, *K* is the number of variables included in the study and *c* is the number of storage conditions.

5) Split the $\mathbf{T} \in \Re^{cN \times R}$ matrix into the c distinct $\mathbf{T}_T \in \Re^{N \times R}$ matrices.
6) Build up shelf-life charts (PC scores vs. time) for the first R PC and identify the A ones which are time-related.
7) For each of the time-related PC, identify their reaction order and determine the multivariate kinetic parameters (k^m, Ea^m and $\alpha^m_{T+\delta T,T}$) using the PC scores as properties (refer to Eqs. 1, 3 and 5 above).

The loadings of the PCA can then be used to simultaneously calculate the cut-off criteria for the A time-related PC as follows:

8) Place the reference values for each property into the $\mathbf{x}$ vector and pre-process it using the parameters determined in step 3 to obtain $\mathbf{xa}$.
9) Use the loadings matrix to calculate the cut-off criteria, that is the maximum acceptable scores for each time-related PC:

$$\mathbf{t}^{\mathrm{T}}_{\mathrm{crit}} = \mathbf{xa}^{\mathrm{T}}\mathbf{L}_{Tm} \tag{7}$$

where $\mathbf{xa}^{\mathrm{T}}$ is the row vector of reference values and $\mathbf{L}_{Tm}$ is the $N \times A$ loadings matrix of the time-related PC at the market storage condition.

10) Calculate the time equivalence between the accelerated and the market temperatures using $\alpha^m_{T+\delta T,T}$ and t_{crit} for each of the A multivariate properties.

3. EXPERIMENTAL

3.1. Samples preparation and storage

Tomato concentrate samples with 18 NTSS (Natural Tomato Soluble Solids) were prepared in a pilot-plant by properly diluting a 29-NTSS tomato paste processed during the Brazilian tomato season. Salt and sugar were added according to typical formulations found in the Brazilian market. The product was heated to 120°C by 5 min and placed in 300 g steel-metal cans internally covered with an acrylic/epoxy resin. Sterilisation was performed in boiling water (ca. 98°C) for 15 min.

Samples were stored at 8, 25 and 35°C in three different Marconi MA 035 climatic chambers. Temperatures were controlled using the Flycon v.1.0 software. Maximum temperature variation in the chambers was ±0.6°C.

3.2. Physical–chemical and sensory analysis

Four instrumental parameters, namely lycopene, β-carotene, colour and vitamin C, as well as eight sensory attributes—visual colour, sweetness, saltiness, sourness, consistency, green tomato taste, bitter taste and over-ripened tomato taste were monitored.

Quantitative Descriptive Analysis (QDA) was performed by a trained 24-person panel [25,26]. Panellists were selected according to their ability in describing and distinguishing several tomato taste and consistency attributes related to ageing. The scales for sensory attributes ranged from 0 (none) to 10 (maximum). For colour, 0 meant yellow-green, 5 dark red and 10 brown.

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In order to get unbiased assessments of the taste and consistency-related attributes, colour was evaluated separately under daylight (D65 illuminant) whilst the other sensory parameters were scored under red light to eliminate colour influence. Despite being trained, dark samples could bring negative psychological effects to the assessors, which would interfere in the evaluation of the other attributes. Analysis of variance (ANOVA) followed by the Tuckey-HSD test [25,27] was performed in order to identify and remove any outlier assessors in the sensory evaluations. Panel drift was avoided by constant training and validation schemes with reference samples.

As lycopene, β-carotene and vitamin C were expressed in dry-weight (dw), moisture (%) was determined in triplicate by using a Fanem EV8 oven (Fanem, Co., São Paulo, Brazil) at 70°C under vacuum (~20 kPa absolute pressure) given by an Edwards E2M8 vacuum pump, until constant weight (~4 h).

Lycopene and β-carotene (mg·kg^{-1}·dw) were determined in duplicate by using a Shimatzu HPLC (Shimadzu, Kyoto, Japan) equipped with a CTO-10A column oven, a Sil-10A automatic injector, LC-10AD pumps and a SPD-10AV UV-visible detector at 473 nm. Separation was achieved using a RP18 Zorbax ODS column (5 μm, 15 × 0.46 cm) and the mobile phase was MetOH/THF/H_2O (67:27:6), isocratic at 1.0 mL/min. Sigma-Aldrich standards where used for building analytical curves for lycopene and β-carotene. For the extraction procedure, the method suggested by Sadler and colleagues [28] was applied.

Vitamin C (mg/100 g·dw) was determined in duplicate by HPLC using the same chromatographic system as described above, but using a Supelco HS C18 column (150 × 2.1 mm, 5 μm) with the detector set at 260 nm in order to avoid interference [29]. Mobile phase was KH_2PO_4 (pH 2.3), isocratic at 0.4 mL/min. Extraction followed the procedure described by Nisperos-Carriedo *et al*. [30] and Sigma-Aldrich L-ascorbic acid standard was used for building analytical curves.

Colour was measured in duplicate by a model PC2Δ HunterLab colorimeter (HunterLab, Inc., Reston, USA) with a CIE type C illuminant at 45°/0° geometry. Calibrations with black and white standards were performed prior to the measurements and periodically checked using a tomato-red standard ($L = 26.18$, $a^* = 27.3$ and $b^* = 12.7$). The ΔE value, that is the deviation of the colour from its initial reading, was calculated according to the equation:

$$\Delta E_{t,T} = \sqrt{(L_{t,T} - L_{0,T})^2 + (b_{t,T} - b_{0,T})^2 + (a_{t,T} - L_{0,T})^2} \quad (8)$$

where $L_{t,T}$, $a_{t,T}$ and $b_{t,T}$ correspond to the sample reading at time t and temperature T, whilst $L_{0,T}$, $a_{0,T}$ and $b_{0,T}$ are the readings of the sample at $t = 0$ for the same temperature T.

Table I. Desirable reference values for the tomato single-concentrated product

Variable	Reference value
ΔE	6
Lycopene (mg·kg^{-1}·dw)	1400
β-Carotene (mg·kg^{-1}·dw)	40
Vitamin C (mg/100 g·dw)	170
Sweetness	3.5
Saltiness	4.5
Sourness	5.5
Consistency	7.0
Green tomato taste	1.5
Bitter taste	1.0
Over-ripened tomato	2.5
Colour	6.0

3.3. Shelf-life analysis

Physical–chemical and sensory assessments were conducted at $t = 0$ and 1, 2, 3, 4, 6, 8, 10, 13, 18, 22, 24 and 30 months after production. Thus, in this study $N = 13$, $K = 12$ properties and $c = 3$ storage conditions.

Multivariate constant rates (k^m), activation energies (Ea^m) and acceleration factors ($\alpha^m_{35,25}$) were calculated using the MASLT method. Univariate parameters were also determined and compared to the multivariate results. The cut-off criteria were calculated using the reference values given in Table I.

All the calculations were performed using Matlab Software v. 6.1 (The MathWorks, Co., Natick, USA), with routines implemented by the authors.

Table II. Initial and final values for the shelf-life parameters of tomato concentrate*

		Time = 30 months		
	Time = 0	8°C	25°C	35°C
Instrumental colour (ΔE)	0.33 ± 0.02	0.36 ± 0.03	7.34 ± 0.07	18.44 ± 0.09
Lycopene (mg·kg^{-1}·dw)	1650 ± 216	1648 ± 152	1434 ± 105	913 ± 132
β-Carotene (mg·kg^{-1}·dw)	52 ± 9	51 ± 3	47 ± 7	40 ± 10
Vitamin C (mg/100 g·dw)	386 ± 12	382 ± 14	138 ± 9	56 ± 5
Sweetness	3.84 ± 0.16	3.89 ± 0.22	3.50 ± 0.28	3.18 ± 0.17
Saltiness	5.04 ± 0.09	5.12 ± 0.06	4.88 ± 0.16	4.72 ± 0.27
Sourness	6.18 ± 0.22	6.13 ± 0.35	4.94 ± 0.30	3.01 ± 0.27
Consistency	8.46 ± 0.13	8.16 ± 0.19	6.19 ± 0.20	5.51 ± 0.13
Green tomato	1.12 ± 0.16	1.09 ± 0.22	1.11 ± 0.31	1.30 ± 0.37
Bitter	1.10 ± 0.46	1.32 ± 0.26	1.95 ± 0.30	2.66 ± 0.23
Over-ripened tomato	2.21 ± 0.25	2.42 ± 0.19	1.32 ± 0.13	2.10 ± 0.18
Colour	4.87 ± 0.42	4.97 ± 0.33	6.80 ± 0.46	10.00 ± 0.82

*Values expressed as mean ± standard deviation.

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4. RESULTS AND DISCUSSION

4.1. Analytical and sensory results

Table II shows the initial and final values for the 12 variables monitored during the tomato shelf-life study at the three different temperatures. It can be seen that none of the properties, either analytical or sensory, presented significant quality loss for samples kept at 8°C. This corroborates the common assumption in some shelf-life studies that samples kept at low temperatures have most of their degradation reactions stopped and can thus be regarded as being fresh-like standards. This also shows that the training scheme of the sensory panel was effective in avoiding drift.

Most of the physical–chemical parameters presented significant changes at room and warm temperatures of storage. Colour (ΔE) followed pseudo-zero-order kinetics (Figure 2a) and had an increase of about 20 times for samples stored at 25°C and 55 times for those kept at 35°C. Besides being easy to measure, colour is an important parameter to monitor during shelf-life because a linear relationship between colour degradation and the formation of furosine, a Maillard reaction by-product, was previously reported for tomato products [23].

Vitamin C decreased by ca. 64% and about 85% for samples stored at 25 and 35°C, respectively. Despite the conversion of ascorbic acid to its oxidised forms being somehow expected during storage [22,32], lower degradation rates were previously reported in the literature [22] for tomato juice. This might be due to the fact that vitamin C follows a pseudo-first-order reaction (Figure 2b) and its initial concentrations are higher in tomato concentrates.

Carotenoids showed some decrease as well, but to a rather lesser extent than vitamin C. Lycopene decreased by 13% and 45% whilst β-carotene diminished by 9.6% and 23% for 25 and 35°C, respectively.

Regarding sensory properties, sweetness, saltiness, green and over-ripened tomato tastes presented no significant changes. Green tomato ratings were low because the tomato concentrate was manufactured with an off-season tomato paste, the product then being subjected to two heating stages and an over-ripened tomato taste did not develop during storage.

Sourness and bitterness, as well as consistency, presented moderate changes during storage. Sourness decreased as the bitter taste increased. In fact, panellists described the overall taste of products stored at 35°C as 'cardboard-like' at the end of the study. The consistency decreased with time because of both, hydrolysis of the glycosidic bonds and breakage of the ester bonds from the pectin fibres which give tomato its structure [32–34].

As for the instrumental measurements, colour was the most affected sensory attribute during storage. Perceptible (but acceptable) changes in colour were detected by the sensory panel at 20 and 6 months for samples stored at 25 and 35°C, respectively.

4.2. Applying the MASLT method to processed tomato products

In PCA, two principal components have accounted for 80% of the variation in the original data set, a reasonable amount of information considering the intrinsic variability of the original properties (10–15%, refer to Table II). Figure 3a shows the scores chart for the first two PC. Samples are labelled with their respective times (t_i) in order to visualise the correlation of each PC with time-related degradation. Samples stored at 8°C presented a slight change in PC2 but this variation does not seem to be related to storage. Nevertheless, as observed in the analysis of the data from Table II, samples stored at this temperature presented no variation with time at all.

Despite not presenting variation in time, high scores values were obtained for samples stored at 8°C. This was expected since these samples were stored at an extreme condition and have received the lowest (or highest) values for each property (refer to section 2.1. above).

The loadings chart in Figure 3b reveals the key attributes responsible for product degradation. It can be seen that those variables which increase in time have positive PC1 loadings whilst those which decrease present negative values. As in the previous analysis from data in Table II, green tomato, over-ripened tomato and salt presented smaller contributions to PC1 than the other attributes. As these variables presented no significant variation with time and as they contribute the most to PC2 it can be concluded that most of the information brought by this PC is related to noise.

Another advantage of using the loadings plot is that it visually presents the correlations between variables. For

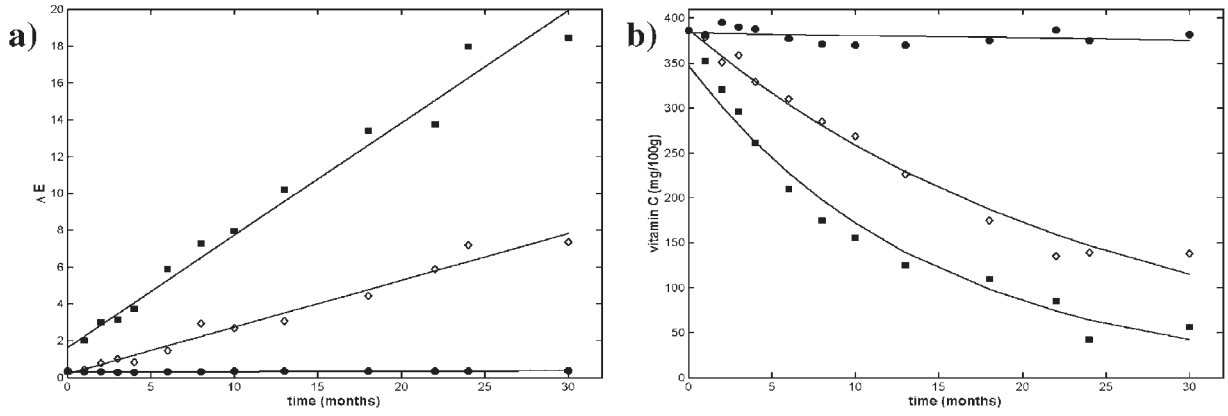

Figure 2. Univariate kinetic charts of (a) colour and (b) vitamin C, exemplifying pseudo-zero and pseudo-first-order kinetics, respectively. (●) stands for samples kept at 8°C, (◇) for 25°C and (■) for 35°C.

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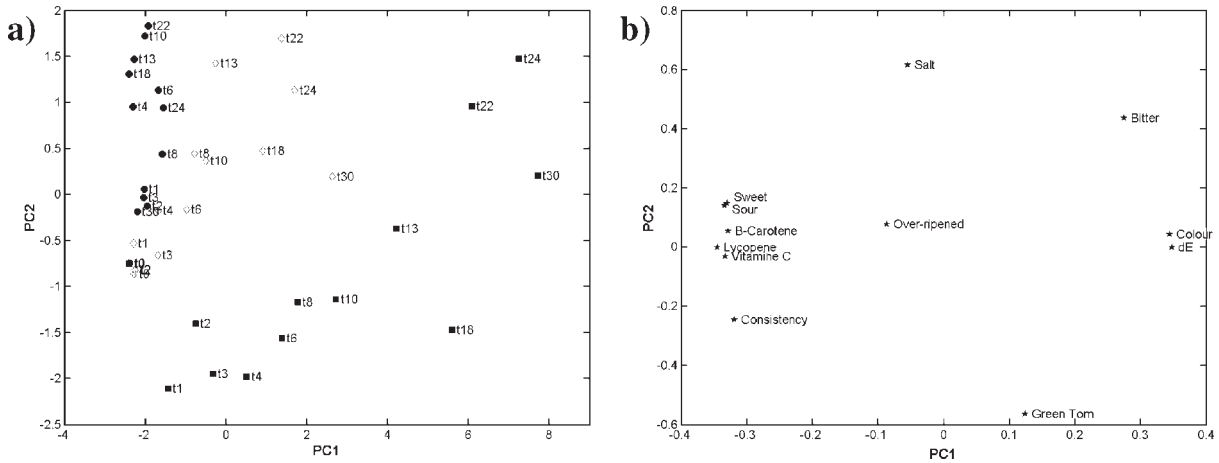

Figure 3. PC1 (68%) versus PC2 (12%) charts for (a) scores and (b) loadings. In (a), (●) stands for samples kept at 8°C, (◇) for 25°C and (■) for 35°C.

instance, sensory and instrumental colour (ΔE), as well as β-carotene and vitamin C, presented significant correlation coefficients (Table III). High correlations are especially interesting between sensory and instrumental variables because one can, for instance, take the quick and objective instrumental colour measurement and have information on the response of the subjective, time and resource-consuming sensory colour evaluation.

Constant rates, α-values and activation energies were individually determined for the parameters selected via PCA (green tomato, over-ripened tomato and salt were excluded).

Table III. Correlation coefficients between variables

Variables	r
ΔE and visual colour	0.9866
Lycopene and β-carotene	0.9323
Sourness and sweetness	0.8902
Vitamin C and lycopene	0.8435

Table IV shows that degradation speed increases by a 1.4–3.9 factor, depending on the attribute. It also shows that β-carotene, vitamin C and sour taste followed pseudo-first-order kinetics (refer to Figure 2b).

Once all the kinetic parameters were calculated for the main properties, which α-value to take for estimating the shelf-life at different market conditions? There are several approaches for solving this issue in the literature. One can take, for instance, the lower value and conduct the accelerated study for a longer period. Nevertheless, this would inevitably demand valuable resources and, most importantly, time before product launch. Another alternative would be to take the highest α-value and conduct the shelf-life study for a shorter time. This approach is risky because in practice a single-property study is being conducted. Besides, which cut-off criteria to take for each property? Which variable is more relevant? This is a quite hard decision especially when sensory variables are included in the study. The multivariate approach proposed herein gives fewer, if

Table IV. Univariate rate constants for the variables selected by the loadings chart

Variable	Kinetics order n	Temperature (°C)	Rate constant[a] k	$\alpha_{35,25}$	Activation energy (kJ·mol^{-1})
ΔE	Zero	25	0.2541	2.4	164
		35	0.6107		
Lycopene (mg·kg^{-1}·dw)	Zero	25	−7.3931	3.5	114
		35	−25.7720		
β-Carotene (mg·kg^{-1}·dw)	First	25	−0.0028	3.9	67
		35	−0.0108		
Vitamin C (mg/100 g·dw)	First	25	−0.0405	1.7	128
		35	−0.0704		
Sweetness	Zero	25	−0.0104	2.0	128
		35	−0.0203		
Sourness	First	25	−0.0086	2.6	280
		35	−0.0228		
Consistency	Zero	25	−0.0729	1.4	121
		35	−0.0989		
Bitterness	Zero	35	0.0317	1.7	51
		25	0.0547		
Colour	Zero	25	0.0701	2.7	144
		35	0.1888		

[a] k is given in months^{-1} for pseudo-first-order reactions and in [unit] month^{-1} for pseudo-zero-order reactions.

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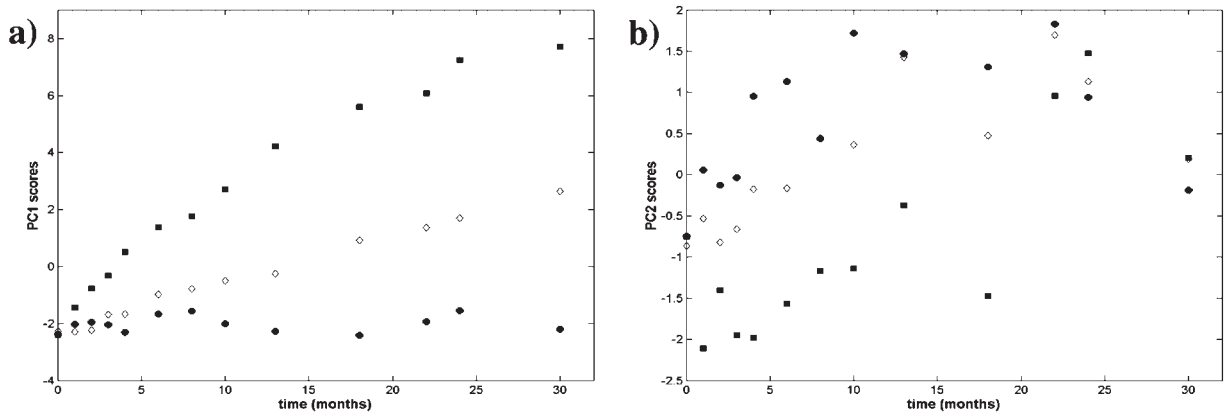

Figure 4. Behaviour of the first two PC as a function of time for samples stored at (●) 8°C, (◇) 25°C and (■) 35°C.

not a single acceleration coefficient, which can be interpreted as a weighed average of all the properties under study.

Figure 4 shows the scores versus time charts for the first two PC. It clearly shows that only PC1 is time-structured ($A = 1$) and thus this is the most suitable PC for estimating shelf-life parameters.

In Figure 5 the PC1 versus time chart together with the LS regression fits is shown. Pseudo-zero-order kinetics gave reasonable adjustments (Table V), the slope of the curves corresponding to the rate constant (k^m) for each temperature.

Applying the reference values of Table I in Equation (8), a critical PC1 score value of 1.7 was obtained (refer to Figure 5), which corresponds to a 28-month shelf-life for samples stored at 25°C. Nevertheless, as it is common practice in the food industry to apply a reduced shelf-life to industrialised products in order to account for sources of variation not included in the study, such as transportation and temperature oscillations [1–3], the commercial shelf-life of the concentrated tomato product was set at 24 months.

Given that the overall degradation reaction followed pseudo-zero-order kinetics for samples stored at 35 and 25°C, $\alpha^m_{35,25}$ was determined to be equal to 2.7. This means that, for an estimated shelf-life of 24 months, future MASLT have to be conducted for 10 months for concentrated tomato products. Higher temperatures might be used in order to get faster estimates but a new acceleration factor would have to be determined.

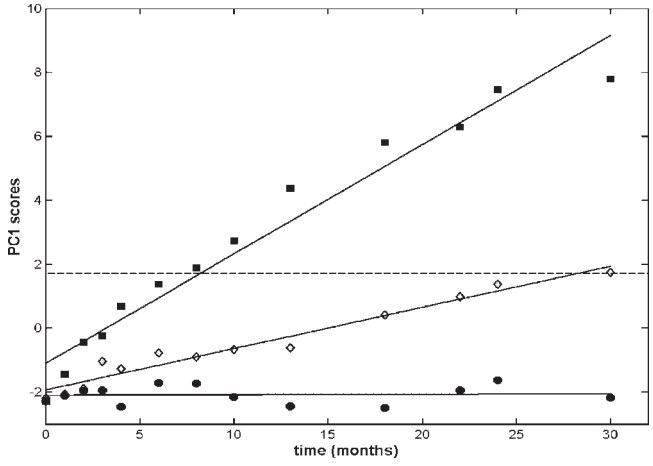

Figure 5. Multivariate kinetic chart of samples kept at (●) 8°C, (◇) 25°C and (■) 35°C. The dashed line represents the multivariate cut-off criterion.

Table V. Multivariate rate constants and activation energy for processed tomato concentrate

Temperature (°C)	Rate constant k^m (PC1 score month^{-1})	r^a	Activation energy Ea^m (kJ·mol^{-1})
8	0.0016	0.059	150 ± 30 ($r = 0.984$)
25	0.1290	0.979	
35	0.3418	0.978	

[a] 'r' stands for the correlations coefficient between measured and predicted values.

As previously stated, the multivariate coefficients can be interpreted as loadings-weighted estimates of the univariate parameters, that is k^m, α^m and Ea^m are linear combinations of the individual values of k, α and Ea. The univariate kinetic parameters of Table V were multiplied by the PC1-loadings and $\alpha^*_{35,25} = 2.79$ and Ea$^* = 147$ kJ·mol^{-1} (the asterisk is used to differentiate the loadings-weighed average parameters from those obtained for the individual properties) were obtained, in accordance with the values of the multivariate approach.

5. CONCLUSIONS

The MASLT has proven its value by successfully determining the actual shelf-life of commercial concentrated tomato products. By reducing the kinetic study to a single variable, it provided a significant simplification and reduction of the number of calculations performed (when compared to the univariate approach), whilst giving information on what are the main parameters affecting product degradation in a direct and visual fashion. This is especially interesting when results have to be presented to non-technical personnel.

The method has also significantly simplified the decision-making process by the definition of a single acceleration factor and cut-off criterion. This is extremely advantageous since, in industry, scientists, managers and marketers often struggle to define individual criteria for each measured property. In the present study, a flexible, desirable profile was applied.

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6. FUTURE WORK

The work presented herein is the first application of the MASLT method. Its validity has to be proven with a larger number of applications.

Modifications of the method can also be sought. For instance, the convenience of adding extra constraints to the PCA model can be devised. One obvious constraint would be to maximise covariance of the scores with time. In this first application the method was kept as simple as possible.

In this study it was assumed that all the variables had equal importance to product degradation and/or acceptability, but in some cases one might know in advance that some variables are more relevant than others. Another modification which could be interesting in these cases is to give higher weights to the loadings of variables which are known in advance to be more relevant. The scores would then be rotated, but the fit would be unchanged.

The MASLT makes it possible to conduct real multivariate shelf-life studies. For example, sensory panels can be used to determine the acceptability of a given product based on a wide range of parameters which could be used as acceptability profile $\mathbf{x}$. It even makes it possible to apply instrumental methods such as spectroscopy and chromatography for directly estimating the shelf-life of a product, thus improving the whole data acquisition process in these studies.

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