



Evaluation of quality during storage of apple leather

Natalia A. Quintero Ruiz^{a,b}, Silvana M. Demarchi^a, J. Facundo Massolo^a, Luis M. Rodoni^a, Sergio A. Giner^{a,b,c,*}

^a Centro de Investigación y Desarrollo en Criotecología de Alimentos (CIDCA – UNLP – CONICET), Calle 47 y 116, (B1900 AJJ) La Plata, Argentina

^b Facultad de Ingeniería, Universidad Nacional de La Plata, Calle 1 y 47, La Plata, Argentina

^c Comisión de Investigaciones Científicas (CIC), Provincia of Buenos Aires, Calle 526 e 10 y 11, La Plata, Argentina

ARTICLE INFO

Article history:

Received 30 August 2011

Received in revised form

2 February 2012

Accepted 9 February 2012

Keywords:

Fruit leather

Storage

Apple

Dehydration

Quality

ABSTRACT

Fruit leathers, a dehydrated snack, have the potential to increase fruit solids consumption especially in the young. Two apple puree formulations containing sugar and citric acid and one containing potassium metabisulphite (100 mg SO₂/kg final product) were prepared by hot-air drying at 60 °C to a water activity of 0.7 (moisture content = 25 kg water/100 kg of final product). The fruit leathers were then subjected to a storage trial and remained stable for a period of 7 months at 20 °C. Changes in organoleptic and nutritional parameters such as Browning Index (BI) and antioxidant activity (AA), respectively, were evaluated. The effect of temperature was studied by accelerated storage tests at 30 °C. Using the kinetic constants at both temperatures, a Q₁₀ coefficient was calculated as 2.55 for BI and 16.26 for AA, leading to estimated activation energies of 68.9 and 206.1 kJ mol⁻¹, respectively.

© 2012 Published by Elsevier Ltd.

1. Introduction

Fruit leathers are dehydrated, restructured fruit-based products prepared by the acid - sugar - high methoxyl pectin gelation. They are eaten as candy or snacks, and presented as flexible strips or sheets. Due to their novel and attractive appearance, and because they do not normally require cold storage to avoid microbial growth, fruit leathers constitute a practical way to increase fruit solids consumption, especially for children and young people. In recent years, their popularity has increased: they are becoming an industrial product, evolving from their origins as a homemade preparation produced by enthusiasts (Raab & Oehler, 1976).

Earlier research work on the subject described the physico-chemical properties, sensory attributes and processing of these pectic gels (Chan & Cavaletto, 1978; Moyls, 1981). The latter author focused on the drying conditions, evaluating equipment characteristics such as the spacing between trays and the fluid-dynamic regime of the drying air. Bains, Ramaswamy, and Lo (1989) evaluated the effect of drying commercial purees at high temperatures with various air velocities and relative humidities. They found that high temperatures (85–94 °C), high air velocity (4.1 m s⁻¹) and low

relative humidity (5%) caused a decrease in drying time. However, the organoleptic quality of fruit leather dried at the lower temperature of 70 °C was considerably better than that of the product dried at 90 °C or 121 °C. Vijayanand, Yadav, Balasubramanyam, and Narasimham (2000) compared the evolution of quality of conventional mango leather with that of guava leather, the latter being obtained by dehydration of an enzymatically-treated puree. Colour, texture, sensory acceptability and non-enzymatic browning were analysed. They concluded that both products maintained a high acceptability after 90 days at 27 °C. Finally, in the last decade, publications on fruit leathers have explored the use of combined drying technologies, showed experimental studies and mathematical models on drying kinetics and, assessed the influence of various additives on drying rate and product quality (Fiorentini, Leiva Díaz, & Giner, 2008; Gujral & Khanna, 2002; Jaturonglumert & Kiatsiriroat, 2010). Knowledge of the quality changes that occur during storage is essential for producers of fruit leather, the distribution chain and retail markets. However, the literature offers scarce information on the deteriorative changes that occur to apple fruit leathers on storage, and so the purpose of this work was (1) to evaluate the organoleptic as well as nutritional changes during storage at 20 °C of an apple leather prepared from a base formulation developed earlier (Leiva Díaz, Giannuzzi, & Giner, 2009), (2) to explore the effect of temperature, by means of accelerated storage tests (Labuza & Riboh, 1982)

* Corresponding author. Facultad de Ingeniería, Universidad Nacional de La Plata, Calle 1 y 47, La Plata, Argentina. Tel.: +54 221 4249287.

E-mail address: saginer@ing.unlp.edu.ar (S.A. Giner).

Nomenclature		Y	Absolute colour green coordinate
a^*	CIELab green-red colour coordinate	Z	Absolute colour blue coordinate
a_w	water activity	<i>Subscripts</i>	
b^*	CIELab blue-yellow colour coordinate	0	zero-order model
BI	browning index	1	first-order model
C	measured quality parameter in Eq. (9)	as	asymptotic value
h	reaction order in Eq. (9)	i	initial value
k_c	kinetic constant (month^{-1})	L	logistic model
L^*	CIELab lightness (black-white) coordinate	n	reference value
p	fitting coefficient in Eq. (13)	<i>Abbreviations</i>	
Q_{10}	temperature coefficient	AA	antioxidant activity
R	gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)	ABTS	2,2-azinobis-(3-ethylbenzthiazoline-6-sulphonic acid)
r^2	coefficient of determination	BI	browning index
s_y	standard deviation	CAE	chlorogenic acid equivalent (μmol)
T_k	temperature (K)	KMBS	potassium metabisulphite
t_m	time (month)		
X	Absolute colour red coordinate		

2. Materials and methods

2.1. Materials

Ripe green apples (*Malus domestica* Borkh. L, cv. Granny Smith) and commercial sucrose were purchased in a local market in La Plata, Argentina. Citric acid, potassium metabisulphite and ethanol 96° were obtained from Química Anedra, while 2,2-azinobis-(3-ethylbenzthiazoline-6-sulphonic acid) (ABTS), chlorogenic acid and potassium persulphate were provided by Sigma–Aldrich.

2.2. Apple leather formulation

The apple puree and leathers were prepared from a base formulation and procedure developed by Leiva Díaz et al. (2009). The main ingredients were (all expressed in % w/w): apple puree, prepared from green apples, 60.8; sucrose, 13.8; citric acid solution (concentration, 0.302 mol/l, similar to that in lemon juice), 2.3; distilled water, 23.1 and potassium metabisulphite (KMBS) 0.0057 (The control sample did not contain KMBS). Peeled apple cubes, were then thermally treated for 10 min in a food steamer to inactivate polyphenol oxidase (PPO) and also to impart an adequately soft golden colour and mechanical resistance to the leathers (possibly achieved by allowing time for pectins to diffuse out of the broken tissue and dissolve in the acid medium). A metabisulphite concentration of 173.7 mg/kg final product (based on the final product composition) was required to attain 100 mg/kg final product of SO_2 , which is only 10% of the limiting value accepted for dehydrated fruit products by the Codex Alimentarius (FAO-WHO, 2010).

An outline of the experimental work is presented in Fig. 1. Once the dehydration process was finished, gels were hermetically packaged for storage at 20 °C for 7 months. The packaging used was CRYOVAC M7340 (Sealed-Air, USA), a high-barrier, metallised-plastic material providing protection against light and with very low permeability to gases and water vapour.

2.3. Determination of moisture content

Samples of 7 g were kept in a Mettler LP 16 Moisture Analyzer set at 105 °C until reaching constant weight. This procedure follows the AOAC method 984.25 (AOAC, 1998).

2.4. Soluble solids content

The sample was prepared according to AOAC Method 932.12 (AOAC, 1998) and measurements were carried out in a Bellingham–Stanley R30-200 Abbé refractometer.

2.5. pH measurement

The sample was conditioned according to AOAC method 981.12 (AOAC, 1998). An Alpha PW-40 electrode, calibrated with buffer solutions of pH 4 and 7, was employed, which was connected to an Altronix TPA-V, pH meter with digital display.

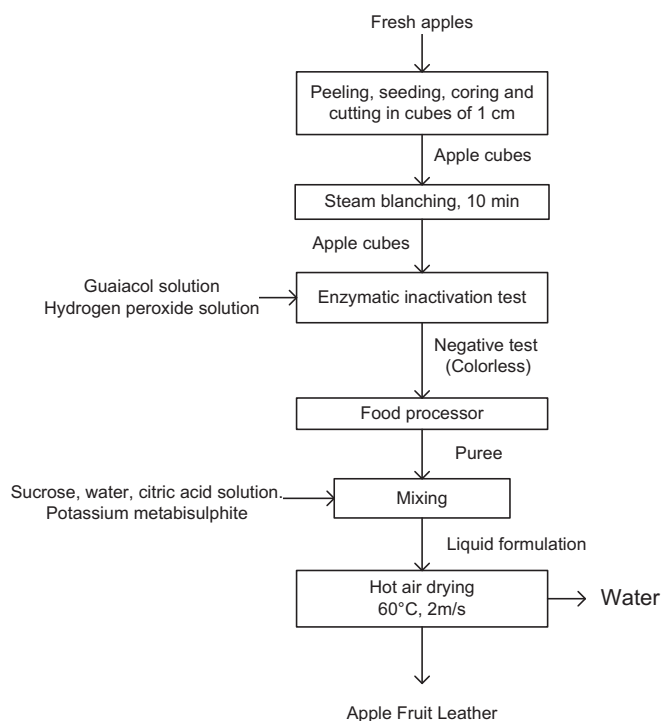


Fig. 1. Outline process chart for the production of the apple leather (dehydrated pectic gel).

2.6. Water activity determination

The water activity of samples was measured at 25 °C by the AOAC 978.18 hygrometric method (AOAC, 1998) in an AquaLab 3TE water activity meter (Decagon devices, Inc.)

2.7. Development of microorganisms

The number of colony forming units (moulds and yeasts) per gram of sample was determined in YGC agar (yeast glucose chloramphenicol) by immersion seeding on plates followed by incubation for 5 days at 25 °C (Camacho et al., 2009). Greensmith (1998) reported a value of 1000 CFU (yeast and moulds) per gram as the upper acceptable limit for dehydrated fruits.

2.8. Colour changes (Browning Index, BI)

A Konica-Minolta CR-400 tristimulus colorimeter was employed. Measured values were read in the $L^* a^* b^*$ scale (CIELab), being converted firstly to X (red), Y (green), and Z (blue) coordinates (see Eqs. (1)–(3)), (Kang, 2006) and secondly to scale x, y, Y (Eqs. (4)–(6)). Browning index, was calculated by Eq. (7), specially suited for sugar-rich products (Buera, Lozano and Petriella, 1985/1986; Gonzales, Burin, & Buera, 1999). Reference values used in Eqs (1)–(3) were $X_n = 91.97$, $Y_n = 93.8$ and $Z_n = 107.98$, respectively.

$$X = X_n \left(\frac{a^*}{500} + \frac{(L^* + 16)}{116} \right)^3 \quad (1)$$

$$Y = Y_n \left(\frac{(L^* + 16)}{116} \right)^3 \quad (2)$$

$$Z = Z_n \left(\frac{-b^*}{200} + \frac{(L^* + 16)}{116} \right)^3 \quad (3)$$

$$x = \frac{X}{(X + Y + Z)} \quad (4)$$

$$y = \frac{Y}{(X + Y + Z)} \quad (5)$$

$$Y = Y \quad (6)$$

$$BI = \frac{(x - 0.31)}{0.172} 100 \quad (7)$$

2.9. Variation of the antioxidant activity

Determinations followed the ABTS^{•+} radical cation decolorization assay method depicted in Fig. 2 (Miller, Rice-Evans, Davies, Gopinathan, & Milner, 1993; Re et al., 1999). For a measurement to be considered valid, the final value of absorbance (i.e., after a reaction time of 6 min) must decrease by 20–80% from the base value of 0.7, which corresponds to ABTS^{•+} in ethanolic solution. Determinations were carried out every month during storage, duplicate ethanolic extracts were prepared from the control and the sample with added KMBS. All extracts were kept in a freezer at –20 °C until the storage trial was complete and then all samples were analysed in the same laboratory session. The results are expressed as Chlorogenic acid equivalents (CAE), as this phenolic compound is dominant in apples (Wu et al., 2007). To this end, a calibration curve was prepared with standard solutions of chlorogenic acid of various concentrations.

2.10. Accelerated storage studies

In this type of test, samples are stored at a higher temperature to accelerate reactions of interest so that their changes can be measured in a much shorter period. The method also allows the determination of a Q_{10} value for each reaction which can be used to estimate the changes with time at lower storage temperatures

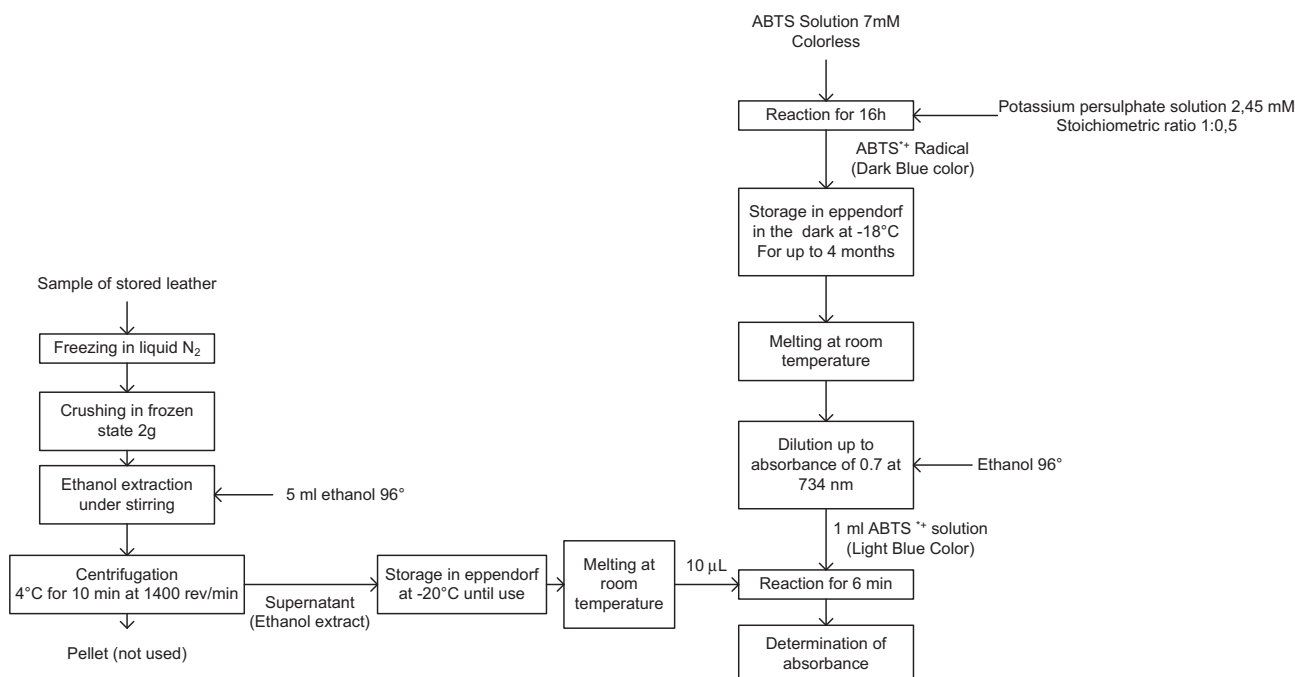


Fig. 2. Diagram showing experimental routes for the preparation of both sample and reactant (ABTS^{•+} radical) in the antioxidant activity test.

(Steele, 2004). By this method, changes in colour and antioxidant activity of apple leathers were measured during storage of packaged samples maintained at 30 °C in an air oven, over 35 days. Samples were removed for analysis every five days. Kinetic models were fitted to the experimental data thus collected as a function of time in order to determine the kinetic constants. These coefficients relate the quality parameter with its rate of change with time and enabled the calculation of the Q_{10} factors of both the browning index and antioxidant activity index.

The Q_{10} factor can be calculated as the ratio of kinetic constants (k_c) for quality changes occurring at a given (reference) temperature (T) and 10 °C above this value ($T + 10$ °C) Eq. (8).

$$Q_{10} = \frac{k_{cT+10}}{k_{cT}} \quad (8)$$

The Q_{10} concept is based on kinetic constants determined by applying models of the type

$$-\left(\frac{dC}{dt}\right) = k_c C^h \quad (9)$$

where h is the order (0,1,2,...) of the kinetic model, and C the measured quality parameter Eq. (9) (Labuza & Schmidl, 1985).

In foods, experimental quality changes can usually be modelled with zero or first order models, which allow kinetic constants to be determined for every experimental temperature. Another measure of the effect of temperature on a quality parameter, is the Arrhenius activation Energy (E_a , J mol⁻¹). This can be estimated from the value of Q_{10} Eq. (10) (Labuza & Schmidl, 1985).

$$E_a = \frac{2.303 \log_{10}(Q_{10}) R T_k (T_k + 10)}{10} \quad (10)$$

Where, T_k is the absolute temperature in K.

2.11. Statistical analysis

Determinations on apple pectic gels were carried out in triplicate during storage. The statistical software OriginPro v 8.1 (Origin, 2009) was used for data analysis and model fitting. The statistical significance was assessed by one-way analysis of variance (ANOVA), as well as by the Tukey's test ($p < 0.05$), in order to detect significant differences of samples stored for several periods.

3. Results and discussion

3.1. Moisture and soluble solids content

The moisture content of apple leather after dehydration was 25% w/w or 0.333 kg water/kg dry matter and showed negligible change during storage. The soluble solids concentration, however, of about 75° Brix, was higher than the minimum value required for sugar-acid-high methoxyl pectin gelation (65° Brix) (Table 1.). The sum of the percentage moisture content on a wet basis and the soluble

Table 1
Average results of physicochemical parameters in pectic gels over storage of seven months for control and preservative-added formulations.

Physicochemical parameter	Control formulation	KMBS-added formulation
Moisture content, (kg water/100 kg of final product)	24.85	24.80
Soluble solids content (°Brix)	75.1	75.7
pH	3.29	3.26
Water activity (a_w)	0.70	0.71

solids content in °Brix, was almost 100% due to the extremely low proportion of low-solubility or insoluble components.

3.2. pH

The pH of the apple puree was 3.50, which dropped to 3.30 after addition of citric acid, and also showed negligible changes over the storage time.

3.3. Water activity

Water activity determinations were carried out in triplicate for each formulation and the average value for each formulation, which was substantially unaltered during storage, was 0.7. This value provides a margin of safety for the storage of acid foods at ambient temperatures (Welti-Chanes, Alzamora, López-Malo, and Tapia, 2000), because it would not only prevent growth of pathogenic microorganism but also would strongly inhibit growth of non-pathogenic fungi and yeasts as well. However, for this level of water activity, rates of non-enzymatic browning and enzymatic activity are not negligible and may even be considerable (Roos, 1995). As the PPO enzyme was inactivated in the preliminary thermal treatment, the organoleptic changes during storage would be more likely to occur due to non-enzymatic browning.

3.4. Growth of microorganisms

Despite the microbially safe characteristics of the fruit leathers (low pH and intermediate water activity), PCA counts were conducted to detect the possible presence of bacteria in the samples, for which negative results were found. In turn, yeast and mould counts were below the admissible levels in all the plates analysed during storage, being, for the control formulation, in the range of 50–100 CFU g⁻¹ for yeasts and below 10 CFU g⁻¹ for moulds. The samples with added preservative did not exhibit any detectable microbial growth over the seven-month storage period at 20 °C.

3.5. Colour changes

Measurements by the tristimulus colorimeter were conducted in triplicate. Average values of L^* , a^* and b^* for each sample were used in Eqs. (1)–(7), in order to calculate the browning index (Fig. 3). When evaluating the effect of time on each formulation separately, an ANOVA test was carried out and the results are shown in Fig. 3. Overall, the browning index increased with time (7-month storage) for both formulations. At a water activity value of 0.7 the fruit leathers were flexible, shiny and microbially stable, but led to conditions for high rates of Maillard browning (combination of reducing sugars with amino groups) and ascorbic acid oxidation reactions, both leading to the production of dark pigments (Sikorski, 2007). Browning index in the control leather was significantly higher than in the KMBS-added product ($p < 0.05$) from the first up to the fifth month of storage, though there were no differences in months 6 and 7. Various kinetic models were fitted to the experimental data of browning index as a function of time in order to describe the variation of colour: zero order (Eq. (11)), first order (Eq. (12)) and logistic models (Eq. (13)) (Vaikousi, Koutsoumanis, & Biliaderis, 2008)

$$BI = BI_{i0} + k_{c0}t \quad (11)$$

$$BI = BI_{i1} \exp(k_{c1}t) \quad (12)$$

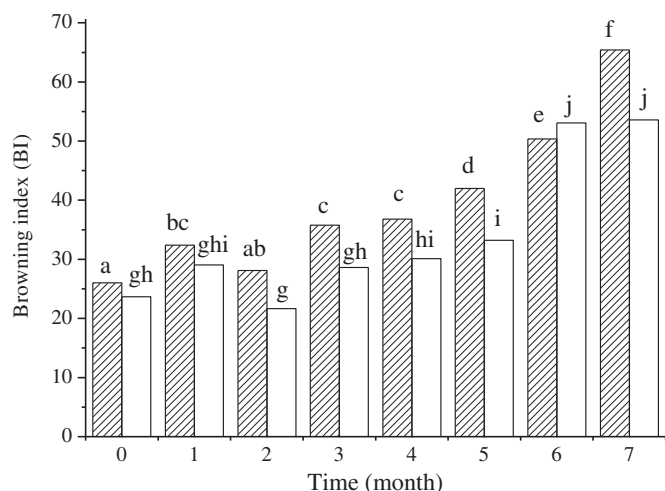


Fig. 3. Colour variation in apple leathers represented by the browning index (BI) as a function of time during 7 months of storage at 20 °C, bars represent experimental data for control (▨) and KMBS-added (□) formulations. The means with the same letter are not significantly different ($p < 0.05$).

$$BI = \frac{BI_{iL} - BI_{as}}{1 + (t/t_m)^p} + BI_{as} \quad (13)$$

Where, for these three equations, BI_{i0} , BI_{i1} , BI_{iL} are fitting parameters, related to the initial browning index in Eqs. (11)–(13), respectively. In turn, k_{c0} (Browning index units month⁻¹) is the kinetic constant of the zero-order model, and k_{c1} (month⁻¹) the corresponding value for the first-order model. Concerning the logistic model, BI_{as} represents the asymptotic browning index or value for long times, p is a phenomenological fitting coefficient and t_m is the time in month required to reach a browning index of $(BI_{iL} + BI_{as})/2$, i.e., the average of initial and asymptotic values.

Table 2 lists the parameters thus determined and the indices of goodness of fit.

According with the results of Table 2, the logistic model provided the best description of experimental results for both control and preservative-added formulations (Fig. 4).

In order to compare the change in colour determined in our work with literature data, results by Picouet, Landl, Abadías, Castellari, and Viñas (2009) were analysed for Granny Smith apple puree added with lemon juice (which contains citric acid), glucose-fructose syrup and acerola extract (rich in vitamin C). The formulation of this product was relatively similar to that of apple leather, though it was treated by microwave energy, and process conditions as well as storage time were different. The change in colour of the microwave-treated puree, measured by the authors as L^* , a^* and b^* , was recomputed here in the form of a browning index

to find an increase of 49.3% over a 14 day-storage at 5 °C. The change in browning index for the KMBS-added apple leather in this study was not significant ($p < 0.05$), essentially negligible over the first four months of the storage trial.

Therefore, browning development was considerably faster in the work by Picouet et al. (2009), possibly because of the higher concentration of reducing sugars in their sample which facilitated the development of Maillard reactions. Its higher vitamin C content may have also contributed, by undergoing oxidative browning. Furthermore, the higher initial browning index calculated for the samples studied by Picouet et al. (2009), may have contributed through a first-order kinetic mechanism, to a faster browning development.

3.6. Variations in antioxidant activity

Reduction of the ABTS^{•+} radical was between 20 and 80% in all cases, so dilution or concentration of the extracts was unnecessary. A linear expression was fitted to the calibration curve data with $r^2 = 0.991$. By rearranging the equation, the Chlorogenic acid equivalents (CAE) were expressed as a function of the percentage reduction of ABTS^{•+} absorbance (Eq. (14)).

$$CAE = \frac{\%Reduction\ of\ ABTS^{•+} - 2.685}{2436.8} \quad (14)$$

The results calculated as CAE can also be expressed as $\mu\text{mol g}^{-1}$, by knowing the amount of dry matter necessary to prepare the ethanolic extract of the leather.

With regard to the preservative-added apple leather, the initial antioxidant activity was 0.0159 $\mu\text{mol chlorogenic acid/g dry matter}$, which decreased by 15.9% over the entire storage period. However, results of the ANOVA statistical test with a confidence level of 95%, indicate that the variation was not significant. On the other hand, the antioxidant capacity of the control formulation (starting value of: 0.0162 $\mu\text{mol chlorogenic acid/g dry matter}$) diminished by 47% over the storage period, being this decrease statistically significant. The results, normalised with the corresponding initial concentrations were plotted in Fig. 5 together with the corresponding predictions by a first-order model (Eq. (15)), which again proved to be more accurate than a zero order model.

$$\frac{CAE}{CAE_i} = \exp(-k_c t) \quad (15)$$

where CAE is the chlorogenic acid equivalent at time t , while CAE_i is the initial value. The resulting fitting parameters are listed in Table 3.

Concerning the preservative-added formulation, the scarce variation in antioxidant activity demonstrates the suitability of KMBS for protecting these micronutrients in the pectic gel. This effect was achieved with 100 mg/kg final product SO_2 , which

Table 2

Fitting parameters for the three kinetic models used to describe the evolution of the browning index over the 7 month storage at 20 °C.

Formulation	Model	Fitting parameters ^a					r^2
		BI_i	BI_{as}	k_c	t_m (month)	p	
Control	Zero-order	22.6 ± 3.6	–	4.86 ± 0.85 ^c	–	–	0.815
	First-order	23.6 ± 2.1	–	0.13 ± 0.02 ^b	–	–	0.897
	Logistic	29.3 ± 2.2	64.5 ± 9.7	–	5.68 ± 2.18	2.86 ± 2.25	0.941
Added with KMBS	Zero-order	18.9 ± 4.4	–	4.35 ± 1.05 ^c	–	–	0.697
	First-order	19.6 ± 2.9	–	0.14 ± 0.03 ^b	–	–	0.789
	Logistic	26.6 ± 1.7	53.8 ± 3.9	–	5.23 ± 0.37	24.7 ± 33.5	0.910

^a value ± standard deviation.

^b units (month⁻¹).

^c units (browning index units month⁻¹).

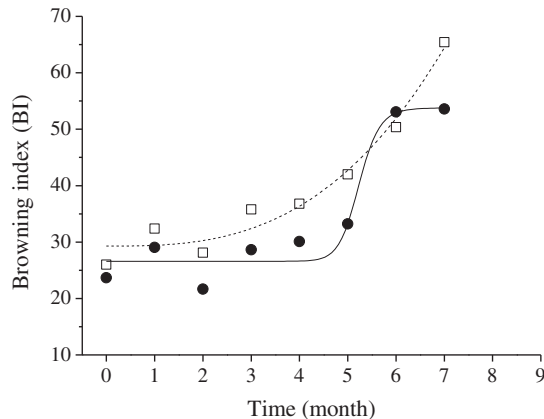


Fig. 4. Colour variation in apple leathers represented by the browning index (BI) as a function of time during storage at 20 °C for control (□) and KMBS-added (●) formulations. Symbols represent experimental data, while lines are the corresponding predictions by the logistic model.

represents only one tenth of the maximum admissible in dehydrated fruits (FAO-WHO, 2010). No published data for the storage of a similar food matrix (i.e., dehydrated apple leather) was found which could enable a comparison with the evolution of antioxidant activity measured here.

3.7. Accelerated storage studies

As indicated in materials and methods, accelerated studies allow the effect of storage temperature to be determined using a reference value T and a higher value, $T + 10$ °C. By assuming that the effect is similar between T and $T + 10$ and between T and $T - 10$ °C, an extrapolation can be carried out to estimate the deteriorative change that would occur over a longer period at a lower temperature, which, as such, is more difficult to assess experimentally. This procedure was employed both for browning index and antioxidant activity.

3.7.1. Colour changes (Browning Index, BI)

The change in colour was expressed as a browning index and plotted in Fig. 6 as a function of time during storage at 20 and 30 °C. A zero-order, first-order and logistic kinetic models were fitted to

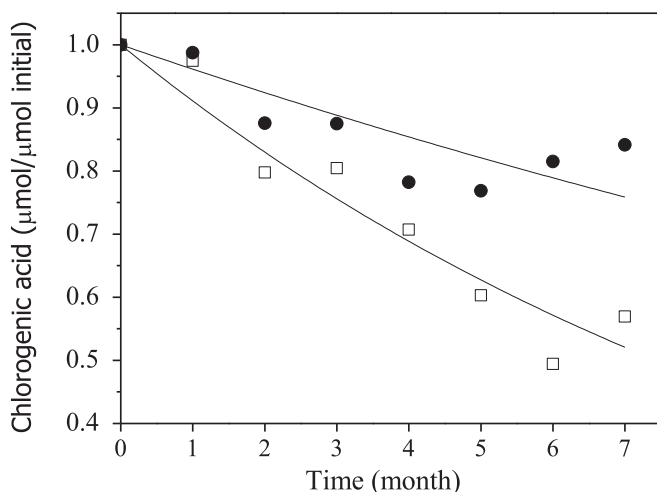


Fig. 5. Normalised antioxidant activities (values at time = t /values at time = 0) as a function of time during storage at 20 °C. Results were plotted for control (□) and KMBS-added (●) apple leathers. Corresponding predicted trends (---- and —) represent the corresponding calculations by a first-order model.

Table 3

Fitting parameters of the first-order model describing the evolution of normalised antioxidant activity over 7 months of storage at 20 °C.

Formulation	k_c^a (month ⁻¹)	r^2
Control	$0.09324 \pm 6.83 \times 10^{-3}$	0.9302
Added with KMBS	$0.03947 \pm 5.41 \times 10^{-3}$	0.646

^a Values \pm standard deviation.

the experimental data by the least square method (Fig. 6). The most accurate was the logistic model (Table 4), which agrees with the results found for storage at 20 °C. Although the logistic model would be preferred for simulating the variation of quality parameters with time for each storage temperature, the effect of temperature was evaluated by coefficient Q_{10} which needs to be calculated as the ratio of kinetic constants of n-order type models, provided the n-order is the same for each quality parameter at the two temperatures (Vaikousi et al., 2008). On these grounds, the first-order kinetic model was chosen as it fitted the experimental data of browning index better (higher r^2) than the zero-order model both at 20 and at 30 °C. Values of both kinetic constants are listed in Table 4. By using Eq. (8) and data of Table 5, the Q_{10} coefficient was calculated for the colour change in apple leathers to be 2.55. In turn, Eq. (10) was employed to estimate the Arrhenius activation energy, which resulted in $E_a = 68.9$ kJ mol⁻¹. This preliminary value was within the published range of activation energies for colour changes of 68.0–80.8 kJ mol⁻¹ by Toribio and Lozano (1984) for concentrated apple juice, and is also close to the value of 75.0 kJ mol⁻¹ determined for colour variations in apple puree by Ibarz, Pagán, and Garza (2000). The value of activation energy is a measure of the intensity of the temperature effect on a given parameter. Therefore, comparable values may indicate comparable quality decay mechanisms.

3.7.2. Antioxidant activity

The evolution of the normalised antioxidant activity with time for the KMBS added leather at storage temperatures of 20 and 30 °C was plotted in Fig. 7. In order to evaluate the effect of temperature, a first-order kinetic model (Eq. (15)), was also fitted to the normalised data of the KMBS-added formulation stored at 30 °C. The results of the fitting at 20 °C and 30 °C for both quality parameters were grouped together in Table 5. Oszmianski, Wolniak, Wojdyło, and Wawer (2008) worked with a red apple cultivar which was sliced and exposed to several alternative treatments. The sample, conventionally heated for 4 min at 90 °C without ascorbic acid

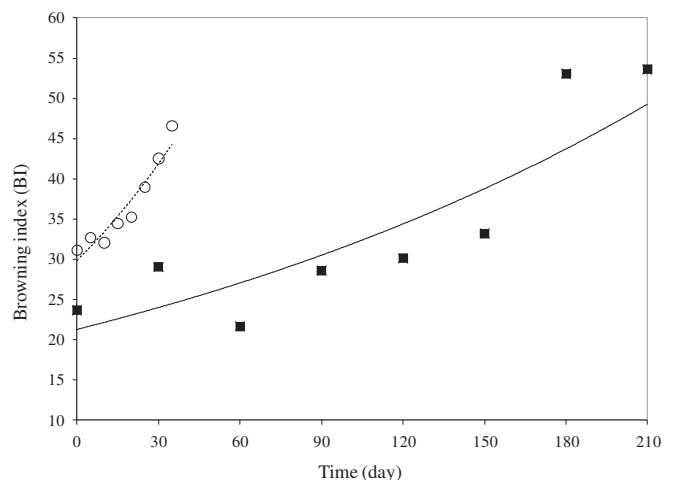


Fig. 6. Colour change in KMBS-added leather, expressed as browning index, as function of time for storage at 20 °C (■) and 30 °C (○). Corresponding trends (— and ----) were predicted by first-order models.

Table 4

Results of the fitting of zero-order, first-order and logistic models to experimental data of browning index as a function of time for storage at 30 °C.

Model	Fitting coefficients ^a					r^2	s_y
	Bl_i	Bl_{as}	k_c (month ⁻¹)	t_m (month)	p		
Zero-order	29.3 ± 1.2	—	0.43 ± 0.08	—	—	0.878	1.92
First-order	29.5 ± 0.9	—	0.012 ± 0.001	—	—	0.915	1.60
Logistic	30.7 ± 0.5	46.7 ± 1.7	—	26.5 ± 0.18	2.44 ± 0.97	0.982	0.72

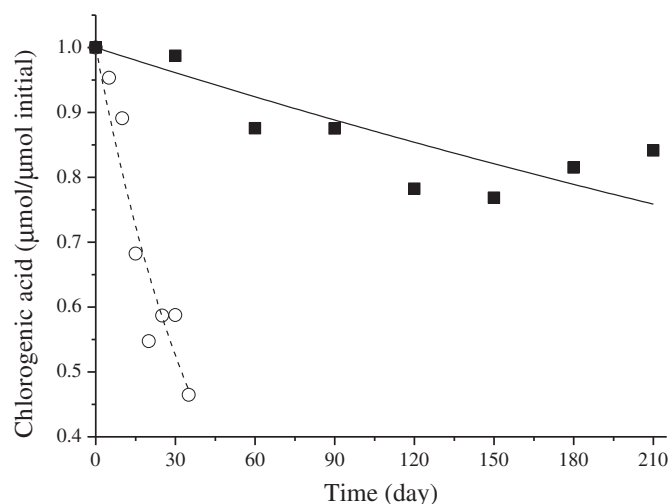
^a Values ± standard deviation.**Table 5**

First order kinetic constants for the variation of browning index and normalised antioxidant activity as a function of time during storage of KMBS-added product at 20 and 30 °C.

Quality parameter	Storage temperature	k_c^a (day ⁻¹)	r^2	s_y
Browning index	20 °C	0.00473 ± 9.27 × 10 ⁻⁴	0.789	5.69
	30 °C	0.012 ± 0.001	0.915	1.60
Antioxidant activity	20 °C	0.00132 ± 1.81 × 10 ⁻⁴	0.645	0.06
	30 °C	0.02146 ± 1.85 × 10 ⁻²	0.910	0.05

^a Values ± standard deviation.

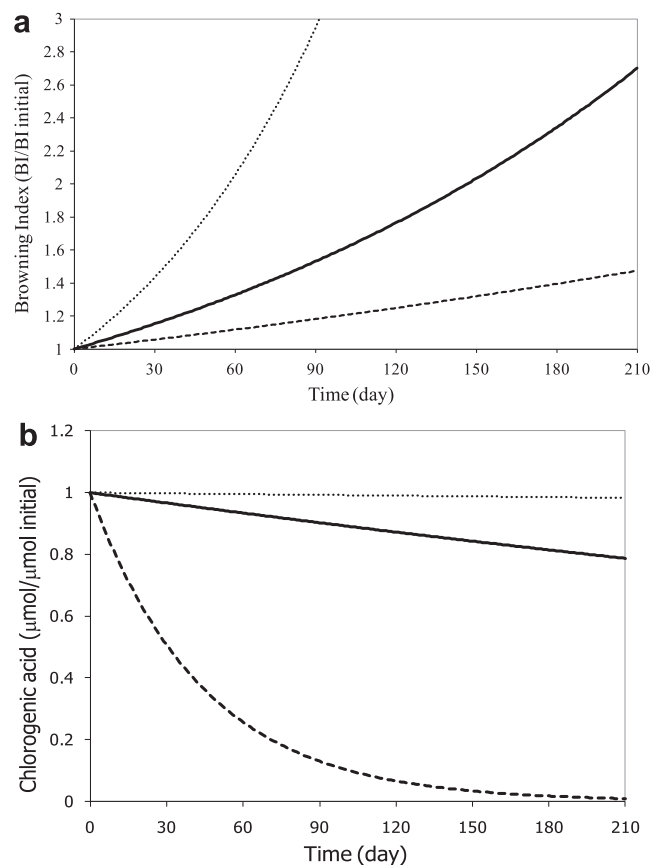
addition (control), was then pureed, packaged and pasteurised at 90 °C for 20 min, then immediately cooled and placed in storage at 30 °C. Starting with a chlorogenic acid equivalent value of 1.77 × 10⁻³ μmol Chlorogenic acid/g dry matter, its antioxidant activity at 6 months of storage was decreased by 63%. Returning to the results of the present work on apple leather, samples having 173.7 mg/kg final product KMBS experienced lower losses of antioxidant activity at 20 °C compared with the published results, but the rate of loss at 30 °C was faster, i.e., 53.5% over 35 days, possibly due to a higher (1.25 × 10⁻² μmol Chlorogenic acid/g dry matter) initial antioxidant activity. The value of Q_{10} for antioxidant activity of apple leathers, calculated with the kinetic constants listed in Table 5 was 16.3, suggesting a strong sensitivity to temperature. The corresponding estimation of the activation energy was $E_a = 206.1$ kJ mol⁻¹. Giner, Lupano, and Añon (1991), in a study of the effect of hot-air drying on wheat viability, found an Arrhenius activation energy of 339.6 kJ mol⁻¹ for this extremely sensitive quality parameter. With regard to changes in total antioxidant activities of freeze dried apple puree with $a_w = 0.7$ during storage, Lavelli (2009) presented sufficient data to allow us to estimate an E_a of 116.7 kJ mol⁻¹ which, even if lower than the estimated value

**Fig. 7.** Normalised antioxidant activity of KMBS-added apple leather during storage at 20 °C (■) and 30 °C (○). Corresponding predicted trends (— and - - -) represent calculations by first-order model.

found for apple leather in this work, shows the considerable influence of temperature, nature of the food matrix and the type of process on quality retention.

3.7.3. Estimation of the behaviour at a lower storage temperature

Labuza and Schmidl (1985) considered two reactions with different Q_{10} values that cause quality losses in a given food. They indicated that the reaction with the higher Q_{10} would be the most damaging at high temperatures, while that with the lower Q_{10} would cause higher quality losses at lower temperatures. Results of the coefficient Q_{10} for browning index and antioxidant activity calculated between 20 °C and 30 °C were employed to estimate the corresponding kinetic constants at a lower temperature of 10 °C. With them, the predicted behaviour of normalised browning index as a function of time for the three temperatures was calculated and plotted in Fig. 8. The corresponding results for the normalized antioxidant activity as a function of time are exhibited in Fig. 8. For the apple leathers, cautious quality limits were considered, in view of the experimental results determined in this work, so as to have

**Fig. 8.** Predicted values as a function of time for storage of apple leather for (a) Normalised browning index at 10 °C (···), 20 °C (solid line) and 30 °C (—) and (b) Normalised antioxidant activity at 10 °C (···), 20 °C (solid line) and 30 °C (—).

a preliminary estimation of the allowable storage time. They are a normalised browning index = 2 (increase of the browning index by 100%) and a normalized antioxidant activity of 0.8 (decrease of the antioxidant activity by 20%). In Fig. 8, for temperatures of 10 and 20 °C, colour changes reach the limit faster than variations in antioxidant activity, while the opposite behaviour is predicted at 30 °C. For that reason, as far as the determination of shelf life of apple leathers is concerned, antioxidant activity should be chosen as the quality-determining parameter for temperatures above 20 °C, while the browning index should be the parameter to monitor in refrigerated storage.

If considered a functional food, apple leathers should be stored under refrigeration so as to minimize antioxidant activity losses.

4. Conclusions

A potassium metabisulphite (KMBS)-added formulation, satisfactorily maintained the quality characteristics of apple leathers without microbial development over a 7 month storage period.

The browning index, was observed to increase during storage at 20 °C. This increase was especially moderate in the KMBS-added leather. Zero- and first-order kinetic models were fitted to the data, as well as a three-parameter logistic model. The last provided the best fit, because it accounted better for the initial delay of the curve.

The antioxidant activity (AA), determined over storage and expressed as chlorogenic acid equivalents, decreased by 47% during the 7-month period at 20 °C in the control formulation, while losses in the KMBS-added formulation were considerably lower, 15.9% of the initial value.

An accelerated storage experiment of the KMBS-added formulation at 30 °C, allowed the estimation of the effect of storage temperature using a Q_{10} coefficient of 2.55 for browning index and of Q_{10} of 16.3 for antioxidant activity. According to these respective values for Q_{10} browning would be the storage-limiting parameter at or below 20 °C, while at higher temperatures, antioxidant activity would control the allowable storage time, especially if the product is to be commercialised as a functional food. In this regard, if the product functional characteristics are to be preserved, leathers should be stored under refrigeration.

Acknowledgements

To Agencia Nacional de Promoción Científica y Tecnológica, Argentina, for funding provided to project PICT 2007-01088.

To Consejo Nacional de Investigaciones Científicas y Técnicas (Conicet), Comisión de Investigaciones Científicas (CIC PBA) and Universidad Nacional de La Plata, for permanent support

References

- AOAC. (1998). *Official methods of analysis* (16th ed.). Gaithersburg, USA: AOAC International.
- Bains, M. S., Ramaswamy, H. S., & Lo, K. V. (1989). Tray drying of apple puree. *Journal of Food Engineering*, 9(3), 195–201.
- Buera, M.d. P., Lozano, R. D., & Petriella, C. (1985\1986). Definition of color in the non-enzymatic browning process. *Die Farbe*, 32/33, 316–326.
- Camacho, A., Giles, M., Ortegón, A., Palao, M., Serrano, B., & Velázquez, O. (2009). *Técnicas para el análisis microbiológico de alimentos* (Segunda ed.). Mexico D.F.: Facultad de Química, UNAM.
- Chan, H. T., & Cavaletto, C. G. (1978). Dehydration and storage stability of papaya leather. *Journal of Food Science*, 43(6), 1723–1725.
- FAO-WHO. (2010). *Codex alimentarius*. Retrieved 18.04.10, from <http://www.codexalimentarius.net/gsaonline/foods/details.html?id=61>.
- Fiorentini, C., Leiva Diaz, E., & Giner, S. A. (2008). A mass-transfer model for the drying of an innovative tomato gel. *Food Science and Technology International*, 14(1), 39–46.
- Giner, S. A., Lupano, C. E., & Añón, M. C. (1991). A model for estimating loss of wheat seed viability during hot-air drying. *Cereal Chemistry*, 68(1), 77–80.
- Gonzales, A. P., Burin, L., & Buera, M.d. P. (1999). Color changes during storage of honeys in relation to their composition and initial color. *Food Research International*, 32(3), 185–191.
- Greensmith, M. (1998). *Practical dehydration* (Segunda ed.). Cambridge, UK: Woodhead Publishing Limited.
- Gujral, H. S., & Khanna, G. (2002). Effect of skim milk powder, soy protein concentrate and sucrose on the dehydration behaviour, texture, color and acceptability of mango leather. *Journal of Food Engineering*, 55(4), 343–348.
- Ibarz, A., Pagán, J., & Garza, S. (2000). Kinetic models of non-enzymatic browning in apple puree. *Journal of the Science of Food and Agriculture*, 80(8), 1162–1168.
- Jaturonglumert, S., & Kiatsiriroat, T. (2010). Heat and mass transfer in combined convective and far-infrared drying of fruit leather. *Journal of Food Engineering*, 100(2), 254–260.
- Kang, H. R. (2006). *Computational color technology*. Bellingham, USA: SPIE, The International Society for Optical Engineering.
- Labuza, L. P., & Riboh, D. (1982). Theory and application of arrhenius kinetics to the prediction of nutrient losses in foods. *Food Technology*, 36(10), 66–74.
- Labuza, L. P., & Schmidl, M. P. (1985). Accelerated shelf-life testing of foods. *Food Technology*, 39(9), 57–64.
- Lavelli, V. (2009). Combined effect of storage temperature and water activity on the antglycoxidative properties and color of dehydrated apples. *Journal of Agricultural and Food Chemistry*, 57(24), 11491–11497.
- Leiva Diaz, E., Giannuzzi, L., & Giner, S. (2009). Apple pectic gel produced by dehydration. *Food and Bioprocess Technology*, 2(2), 194–207.
- Miller, N. J., Rice-Evans, C., Davies, M. J., Gopinathan, V., & Milner, A. (1993). A novel method for measuring antioxidant capacity and its application to monitoring the antioxidant status in premature neonates. *Clinical Science*, 84, 407–412.
- Moyls, A. L. (1981). Drying of apple purees. *Journal of Food Science*, 46(3), 939–942.
- Origin. (2009). *OriginPro 8.1 (Version 8.1)*. Northampton, USA: Originlab Corporation.
- Oszmianski, J., Wolniak, M., Wojdylo, A., & Wawer, I. (2008). Influence of apple purée preparation and storage on polyphenol contents and antioxidant activity. *Food Chemistry*, 107(4), 1473–1484.
- Picouet, P. A., Landl, A., Abadias, M., Castellari, M., & Viñas, I. (2009). Minimal processing of a Granny Smith apple purée by microwave heating. *Innovative Food Science & Emerging Technologies*, 10(4), 545–550.
- Raab, C., & Oehler, N. (1976). *Making dried fruit leather* (Technical Report). Oregon State University Extension Service.
- Re, R., Pellegrini, N., Proteggente, A., Pannala, A., Yang, M., & Rice-Evans, C. (1999). Antioxidant activity applying an improved ABTS radical cation decolorization assay. *Free Radical Biology and Medicine*, 26(9–10), 1231–1237.
- Roos, Y. H. (1995). *Phase transitions in food*. San Diego: Academic Press, Inc.
- Sikorski, Z. E. (2007). *Chemical and functional properties of food components* (tercera ed.). Londres, UK: CRC Press.
- Steele, R. (2004). *Understanding and measuring the shelf-life of food*. Cambridge, UK: Woodhead Publishing Limited.
- Toribio, J. L., & Lozano, J. E. (1984). Nonenzymatic browning in apple juice concentrate during storage. *Journal of Food Science*, 49(3), 889–892.
- Vaikousi, H., Koutsoumanis, K., & Biliaderis, C. G. (2008). Kinetic modelling of non-enzymatic browning of apple juice concentrates differing in water activity under isothermal and dynamic heating conditions. *Food Chemistry*, 107(2), 785–796.
- Vijayanand, P., Yadav, A. R., Balasubramanyam, N., & Narasimham, P. (2000). Storage stability of guava fruit bar prepared using a new process. *Lebensmittel-Wissenschaft und-Technologie*, 33(2), 132–137.
- Welti-Chanes, J., Alzamora, S. M., López-Malo, A., & Tapia, M. S. (2000). Minimally processed fruits using hurdle technology. In G. V. Barbosa-Cánovas, & G. W. Gould (Eds.), *Innovations in food processing* (pp. 123–140). Technomic Pub. Co.
- Wu, J., Gao, H., Zhao, L., Liao, X., Chen, F., & Wang, Z. (2007). Chemical compositional characterization of some apple cultivars. *Food Chemistry*, 103(1), 88–93.