Quality of Raisins Treated and Stored under Different Conditions

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Grapes treated using three different sample treatments before drying were dehydrated with hot air and stored under different conditions of temperature (14, 21, 28, and 35 °C), material packaging (oxygen barrier film or glass), and light. Samples were periodically analyzed in order to determine the evolution of various physical and chemical characteristics and sensory acceptability of raisins. Samples treated with sulfur dioxide as a preservative provided high-quality raisins that were deemed acceptable by a taste panel. A statistical study on pooled data showed that there were no differences between samples stored at 14 and 21 °C nor between samples stored in film and those stored in glass containers. Samples stored in darkness maintained better their quality. It has been proved that chitosan can be used as a food additive in grape preparation, although its addition did not increase grape quality. Results obtained by analytical techniques were consistent with those of the taste panel.

Keywords: *Storage; raisins; dehydration; quality; sulfite content; chitosan*

INTRODUCTION

Grapes (*Vitis vinifera* L.) are popular seasonal and perishable fruits. A traditional method, still commonly used throughout the Mediterranean area, to extend the storage time of the product is dehydration. This process leads to a product which is consumed without prior rehydration and which possesses organoleptic characteristics highly valued by the consumer. When the water activity of a product decreases, it becomes more stable toward degradative reactions. However, estimation of optimum storage conditions is important in order to achieve good microbiological, nutritional, and organoleptic characteristics in the product.

Treatment of grapes before drying has an important effect not only on drying rates but also on their final physical, chemical, nutritional, and organoleptic characteristics after drying and stability during the storage time as well. Before drying some biological materials, it is often useful to increase the drying rate by creating caustically fissures on their surfaces (Alvarez and Legues, 1986; Sharma et al., 1992) or applying an oil surfactant emulsion which removes most of the waxy layer and induces micropore formation in cuticle (Aguilera et al., 1987).

Dried fruits are judged largely by their color, which is affected by numerous factors, such as the treatments prior to drying, storage conditions, and illumination (Bolin and Boyle, 1972). Raisins are among the food products whose color can be easily altered, mainly due to the effect of browning reactions, both enzymic and nonenzymic. In general, since light-colored raisins are preferred by consumers, it is important to avoid browning reactions that cause darkening and undesirable flavors.

Peroxidase activity is mainly located at the level of the skin in grapes (Ros et al., 1994), which catalyzes oxidation of phenolic compounds and is responsible for enzymic browning. This kind of browning reaction can be controlled or inhibited by thermal processing or by using additives such as SO_2.

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Nonenzymic browning (Maillard reaction) is one of the most important chemical phenomena that may affect food quality in processing and storage (Roos and Himberg, 1994), which may reduce food palatability by altering flavor and color and losses in nutritional characteristics. This amino−carbonyl reaction has been considered dependent upon the storage temperature after an initial induction period and to follow either zero-order or first-order kinetics (Johnson et al., 1995).

For the purpose of reducing the fruit-darkening rate during drying and storage, sulfur dioxide treatment is widely used in the food industry (Bolin and Jackson, 1985). It acts as an antioxidant and an inhibitor of both enzymic and nonenzymic browning. Sulfur dioxide also reduces microbial spoilage and preserves the color and flavor of dried fruits (Sayavedra-Soto and Montgomery, 1988; Cañellas et al., 1993). Inhibition of browning occurs through two different types of reactions: reversible inactivation of carbonyl groups by the formation of hydroxysulfonates and irreversible sulfonation of the double bond in α,β-unsaturated carbonylic intermediates in browning (Wedzicha, 1986).

Chitosan, obtained by deacetylation of chitin, has been shown to be active against several fungi (El Ghaouth et al., 1992). Due to its polymeric nature, chitosan can form films permeable to gases (Young et al., 1982) modifying the food internal atmosphere and prevent enzymic browning (Sapers, 1992), favoring color preservation. These characteristics can be profited using chitosan as an additive in order to improve the quality and stability of dried food like raisins. Chitosan is nontoxic, and its biological safety has been demonstrated by feeding trials with domestic animals (El Ghaouth et al., 1991). In 1983 chitosan was approved as a food additive in Japan. The Food and Drug Administration (FDA) considers chitosan to be a food additive in animal feed, although it is not considered generally recognized as save (GRAS) yet (McCurdy, 1991).

Usually, grapes are often dried in the sun. This form of drying is excessively slow, requiring an extensive

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surface area for drying, and the sunlight probably promotes oxidative degradation during drying (Mínguez-Mosquera et al., 1994). Through hot air drying, sanitary characteristics are improved; a better control over the final product is attained and losses due to inadequate weather are diminished (Guerrero and Nuñez, 1992).

Traditional packaging materials such as cans and glass containers are absolute barriers to gases and water. The use of plastic packaging materials is desirable because they are cheaper and easier to handle than cans and glass containers; however, their oxygen and water permeability properties often result in reduced product shelf life (Fernandes and McLellan, 1992).

This study was designed to assess the suitability of various sample treatments before grape dehydration and to determine the effect of storage time, temperature, packaging material, and presence of light on various physical and chemical characteristics and sensory acceptability of raisins.

MATERIALS AND METHODS

Seedless grapes (Flame variety) from the island of Mallorca were the raw material used in all the experiments. Fruits were washed, and different treatments before drying were applied (A−C), those treatments were set up according to literature (Cañellas et al., 1993) and preliminary experiments.

A: subsequent dipping in NaOH (6 g/L) solution at 100 °C for 20 s, distilled water at 25 °C for 5 min, a 40 g/L $Na_2S_2O_5$ solution for 5 min, and finally a 10 mL/L acetic acid solution for 5 min.

B: subsequent dipping in NaOH (6 g/L) solution at 100 °C for 20 s, distilled water at 25 °C for 5 min, a 40 g/L $Na_2S_2O_5$ solution for 5 min, and finally a 10 g/L chitosan solution in 10 mL/L acetic acid solution for 5 min.

C: immersion in 6 g/L NaOH solution at 100 °C for 20 s.

Drying. Grapes were dehydrated in a pilot scale hot air drier to a final moisture content of ca. 17% (g of water/100 g of raisins). Drying air temperature was 40 °C. These three different sample treatments before drying provided grapes with similar drying curves (Simal et al., 1996). During drying experiments room air moisture and temperature were 65−70% and 22−24 °C, respectively. A monolayer loading was used.

The drier basically consisted of an aluminum structure with three main parts: a heating system, equipped with four 750 W oil electric resistances serially connected, the inside chamber temperature could be varied between 30 and 70°C; a drying chamber with a capacity for a pile of nine perforated trays of 1 m^2, 68 holes/m of 4 mm diameter; a system including a 0.75 CV driver and a 1500 rpm low-pressure fan impelling the air parallel through the bed. An automated system built in the drier allows the continuous weighing of the samples by a METTLER multirange KC120 balance. The balance is connected to a ID1 terminal which transfers the weights measured to a Hewlett Packard PCs Vectra QS/20 computer. A general layout of the unit is shown in Figure 1.

Storage. Raisins were stored in glass twist-off containers of 125 mL capacity and oxygen barrier film bags of $10^{-1} \times 10^{-1}$ m thermally sealed. The film used for packaging shows an O_2 transmission rate of 14.39 ± 0.88 mL/m^2/day. In each container samples of ca. 120 g were placed.

To cover the room temperature storage attainable in a country like Spain four storage temperatures were chosen of 14, 21, 28, and 35 °C. The effects of the treatment (A, B or C), packaging, and absence or presence of artificial light (15 W 900 lumen) uniformly applied were evaluated. Raisin storage conditions are shown in Table 1.

Initial characterization of the three samples (A−C) was carried out before storage. Different physical and chemical parameters were evaluated (color, texture, water activity, moisture content, and sugar and SO_2 contents) at different storage times (10, 21, 35, 50, 72, 106, and 173 days).

Analytical Methods. All measurements except color were performed in triplicate. Color measurements were carried out three times on 20 different raisins in a CR300 colorimeter (MINOLTA), with specular component included, C illuminant, and an observer with an angle of 0°. Results were expressed as L^*, a^*, and b^* values (CIELab coordinates).

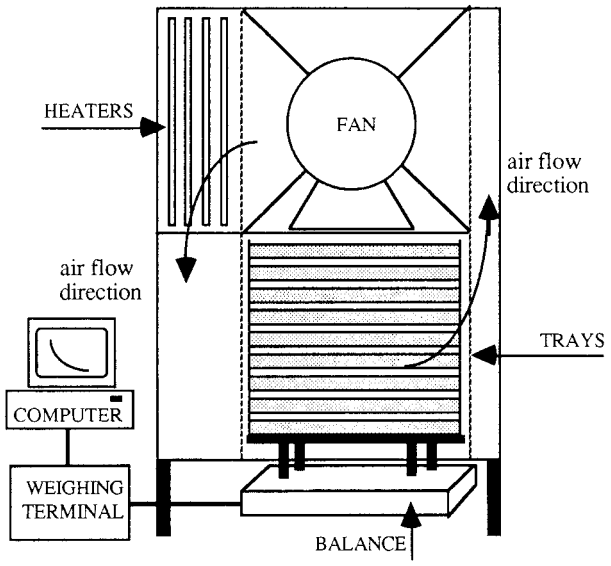

Figure 1. Pilot scale drier.

Table 1. Raisins Storage Conditions

sample	treatment	temp (°C)	package material	light presence
14A	A	14	film	no
14B	B	14	film	no
21A	A	21	film	no
21AL	A	21	film	yes
21B	B	21	film	no
28C	C	28	film	no
28A	A	28	film	no
28AG	A	28	glass	no
28B	B	28	film	no
35A	A	35	film	no
35B	B	35	film	no

Texture was evaluated by a compression assay in a LLOYD press L1000R model, with a Kramer cell, using 5000 N head at a rate of 50 mm/min, on ca. 20 g of raisins.

Water activity was measured at 25 °C by refractometry, according to the method proposed by Steele (1987) using glycerol as the hygroscopic liquid. Moisture content was measured by drying samples to a constant weight (AOAC, 1990).

Sugar composition was determined by gas−liquid chromatography. Water was removed using a TELSTAR CRYODOS freeze-drier. The procedures described by Laker (1980) and Zweig and Sherma (1982) were used to prepare trimethylsilyl derivatives. Identifications were carried out by comparing the retention time of samples and standards. Quantitative analyses were performed by comparing the peak-corrected areas. Gas chromatography was performed on a 5890A gas chromatograph HP using a stainless steel column packed with 3% SE-30 on Supelcoport 80/100. Experimental conditions: temperature at 190 °C, carrier gas flow at 25 mL of He/min, and injector and detector temperatures at 290 °C.

Protein content was determined by Kjeldhal method (N × 6.25), and oils were extracted in a Soxhlet apparatus with ether.

Fiber content was determined by the detergent method (Robertson and Van Soest, 1981). Samples were treated with neutral and acid detergent solutions, respectively, to determine NDF and ADF contents. The hemicellulose content was determined as the weight loss of the NDF when treated with acid detergent.

Table 2. Initial Characterization of Raisins

	sample A	sample B	sample C
L^*	27.5 ± 4.2	26.1 ± 4.2	23.6 ± 2.2
a^*	12.2 ± 2.5	12.7 ± 3.4	9.0 ± 3.3
b^*	7.1 ± 3.6	6.1 ± 2.6	3.3 ± 1.9
F_{max}/m (N/g)	23.5 ± 0.6	21.3 ± 0.5	22.0 ± 1.1
moisture content (g/100 g)	17.4 ± 0.4	17.4 ± 0.2	17.0 ± 0.3
water activity	0.59 ± 0.02	0.60 ± 0.01	0.60 ± 0.01
energy (kJ/100 g of dm)	1360 ± 65	1321 ± 72	1336 ± 72
ppm SO_2 (wm)	567 ± 15	445 ± 14	
glucose (g/100 g of dm)	43.0 ± 1.6	39.2 ± 1.2	40.2 ± 1.8
fructose (g/100 g of dm)	40.6 ± 1.9	38.0 ± 2.4	38.5 ± 2.4
% protein (g/100 g of dm)	3.0 ± 0.1	3.2 ± 0.1	2.7 ± 0.1
% oil (g/100 g of dm)	0.19 ± 0.01	0.19 ± 0.01	0.19 ± 0.01
NDF (g/100 g of dm)	3.13 ± 0.17	2.96 ± 0.18	3.30 ± 0.23
ADF (g/100 g of dm)	1.29 ± 0.12	1.04 ± 0.12	1.01 ± 0.14
hemicellulose (g/100 g of dm)	1.84 ± 0.29	1.93 ± 0.29	2.29 ± 0.37
cellulose (g/100 g of dm)	1.23 ± 0.22	0.99 ± 0.19	0.90 ± 0.24
lignin (g/100 g of dm)	traces	traces	traces
soluble pectic substances (g/100 g of dm)	0.73 ± 0.12	0.82 ± 0.11	0.89 ± 0.11
soluble pectic substances HCl dil (g/100 g of dm)	1.26 ± 0.07	1.44 ± 0.07	1.58 ± 0.16
Mg, ppm (d.m)	204 ± 5	207 ± 7	207 ± 2
Ca, ppm (dm)	366 ± 7	369 ± 4	383 ± 4
K, ppm (dm)	5904 ± 68	5840 ± 72	6087 ± 87
Fe, ppm (dm)	11.5 ± 0.1	9.8 ± 0.1	9.0 ± 0.1
P, ppm (dm)	1141 ± 6	1162 ± 20	1091 ± 16

Soluble in water and soluble in 0.05 M HCl (at 80 °C) pectic substance determinations were performed spectrophotometrically using carbazole as a reactant, according to the method proposed by McComb and McReady (1952), measuring absorbance at 520 nm against a galacturonic acid standard.

Ash contents were determined by overnight heating at 550 °C (AOAC, 1980). Determination of Mg, Ca, K, Fe, and P was carried out by plasma atomic emission spectroscopy inductively coupled (ICP/AES) by the use of a calibration curve.

The sulfur dioxide content was determined by using the method proposed by DeVries et al. (1986) by distillation in acid media and titration with iodine.

Sensorial Analysis. Members of the ad hoc panel were experienced in judging food quality. Three tests were performed after 75 days of storage. In the first test, the panel had to put the 11 samples in order by color gradation and color preferences, pointing out which samples were visually unacceptable.

The second test consisted of putting in order by preference, two sets of samples: on the one hand, samples stored at 21 °C (21A, 21AL, and 21B) and on the other hand, samples stored at 28 °C (28A, 28AG, 28B, and 28C). The variables considered were apperance, taste, and flavor.

In the third test, the panel had to put in order, by preference, samples treated with the same methodology but stored at different temperatures: on the one hand, 14A, 21A, 28A, and 35A and on the other hand, 14B, 21B, 28B, and 35B.

Statistical Analysis. Varianza (ANOVA) and multiple range analysis (Bisquerra, 1989; Best, 1990) were performed using statgraphics statistic software. The analysis was carried out on pooled data for the independent variables, storage time and temperature, as well as light, sample treatments used before drying, and material used for packaging (film or glass), evaluating their effects on the chemical and physical parameters measured and sensorial preferences.

RESULTS AND DISCUSSION

Initial Characterization. Initial characterization of the three samples of raisins is shown in Table 2. The product obtained after dehydration presented an important energetic content (nearly 1300 kJ/100 g of dm) mainly due to the high sugar content. It also seems important to point out that samples presented a high fiber content (cellulose and hemicellulose) of almost 3%. This figure increases to 6% when soluble fiber, of the cellulosic polysaccharides type, is taken into account. Mineral content is important especially in K and P. Similar results were found by Lagrange et al. (1994) for Thompson raisins.

Table 3. Evolution of the Quality Parameters in Raisins during Storage (Samples A)

time (days)	14A	21A	21AL	28A	35A
			L^*		
10	27.9 ± 3.0	31.7 ± 2.9	30.4 ± 2.8	29.5 ± 3.1	27.7 ± 2.5
21	30.5 ± 2.7	30.7 ± 3.2	28.5 ± 3.4	31.4 ± 2.2	26.8 ± 2.1
35	29.5 ± 2.8	32.1 ± 3.9	29.9 ± 3.4	28.8 ± 3.1	25.6 ± 2.2
50	30.6 ± 2.4	28.6 ± 3.4	26.0 ± 2.4	28.6 ± 2.8	23.3 ± 0.8
72	31.4 ± 2.8	30.9 ± 3.7	26.3 ± 2.8	26.7 ± 2.7	23.4 ± 1.9
106	30.0 ± 2.4	29.4 ± 3.4	27.1 ± 3.1	26.9 ± 2.1	23.9 ± 1.5
173	31.5 ± 2.5	28.0 ± 2.9	26.9 ± 2.8	25.4 ± 2.0	23.4 ± 2.3
			a^*		
10	12.5 ± 1.7	11.4 ± 1.9	12.5 ± 1.1	11.2 ± 1.6	12.4 ± 1.7
21	11.5 ± 1.2	12.5 ± 1.8	12.0 ± 1.5	12.0 ± 1.2	10.2 ± 1.4
35	12.8 ± 1.8	12.6 ± 1.9	11.4 ± 1.5	12.4 ± 1.7	9.2 ± 0.5
50	12.7 ± 1.5	11.2 ± 2.4	11.1 ± 2.2	11.6 ± 1.9	10.0 ± 0.8
72	12.3 ± 1.7	10.8 ± 1.5	11.2 ± 1.8	11.7 ± 1.9	6.7 ± 0.7
106	11.6 ± 1.3	12.1 ± 1.7	11.1 ± 0.7	10.2 ± 1.5	5.9 ± 1.0
173	11.3 ± 1.3	9.9 ± 1.2	10.2 ± 1.5	7.8 ± 1.7	5.5 ± 0.8
			b^*		
10	8.6 ± 2.4	11.6 ± 3.0	9.3 ± 2.3	9.4 ± 3.1	8.0 ± 2.1
21	11.7 ± 3.0	12.3 ± 3.0	8.1 ± 2.5	11.5 ± 2.0	6.4 ± 1.9
35	11.9 ± 2.7	12.0 ± 2.0	7.2 ± 3.0	9.1 ± 2.2	4.2 ± 1.6
50	11.8 ± 3.0	8.9 ± 2.8	4.8 ± 1.6	8.0 ± 3.1	3.5 ± 1.1
72	11.6 ± 2.7	11.6 ± 3.0	5.5 ± 1.9	6.2 ± 2.0	3.9 ± 1.5
106	10.4 ± 2.4	10.2 ± 2.0	5.6 ± 1.4	6.4 ± 1.6	3.9 ± 1.3
173	11.5 ± 1.9	8.7 ± 1.8	4.8 ± 1.3	5.6 ± 1.0	5.1 ± 1.5
			F_{max}/m (N/g)		
10	24.0 ± 1.0	22.8 ± 0.7	23.1 ± 1.0	24.3 ± 1.1	23.3 ± 1.0
21	26.6 ± 1.1	25.0 ± 1.4	24.5 ± 0.8	25.4 ± 1.4	23.5 ± 1.3
35	24.7 ± 1.1	23.8 ± 1.2	25.0 ± 0.6	24.3 ± 0.7	23.7 ± 1.0
50	24.4 ± 0.4	23.7 ± 2.0	25.0 ± 0.5	25.2 ± 0.5	24.9 ± 2.0
72	25.3 ± 1.5	23.0 ± 1.9	26.1 ± 1.0	25.2 ± 1.9	25.5 ± 1.6
106	27.5 ± 2.0		27.3 ± 0.7	26.5 ± 1.3	27.0 ± 1.2
173	27.2 ± 0.7	27.8 ± 0.7	26.4 ± 1.4	29.3 ± 0.1	28.8 ± 0.9
			Glucose (mg/g of dm)		
21	44.8 ± 0.9	41.1 ± 4.0	38.4 ± 1.0	37.4 ± 1.0	36.6 ± 1.9
35	40.6 ± 1.0	29.9 ± 1.6	35.7 ± 3.8	35.7 ± 1.4	31.8 ± 1.6
50	38.7 ± 1.4	28.8 ± 1.8	44.7 ± 3.6	32.0 ± 0.9	29.6 ± 1.4
106	37.0 ± 0.8		42.2 ± 2.4	36.3 ± 2.0	32.5 ± 1.0
173	35.0 ± 1.2	32.0 ± 1.6	29.0 ± 3.2	35.1 ± 1.0	31.5 ± 0.6
			Fructose (mg/g of dm)		
21	40.6 ± 2.2	36.9 ± 2.2	34.0 ± 1.6	36.1 ± 3.1	35.0 ± 2.4
35	37.9 ± 2.2	40.2 ± 3.0	30.7 ± 1.5	38.2 ± 1.2	34.5 ± 0.6
50	34.9 ± 1.6	40.0 ± 1.9		38.7 ± 1.5	33.4 ± 1.8
106	35.5 ± 2.4		37.5 ± 3.0	31.8 ± 1.9	31.0 ± 0.6
173	36.8 ± 2.0	35.9 ± 1.4	34.7 ± 1.9	28.8 ± 1.0	30.2 ± 1.8

As can be observed in Table 2, similar results were obtained in all chemical and physical measurements for the three samples except for color and SO_2 content. The lowest figures for L^*, a^*, and b^* coordinates measured in sample C could be due to the fact that this sample was not treated with SO_2. L^* figures were lower than that proposed by Cañellas et al. (1993) for grapes with a initial SO_2 content of 640 ppm; meanwhile a^* and b^* values were higher in this study.

Evolution of Control Parameters. Results obtained in the measurements of the different physical and chemical parameters during storage time are shown in Tables 3 (for sample A) and 4 (for samples B and C) and Figure 2 for SO_2 changes with regard to the initial SO_2 contents in samples A and B. In these results no differences were found between samples 28A and 28AG. Therefore, in Table 3 and Figure 2, results of sample 28AG have been omitted because of their similarity with sample 28A results.

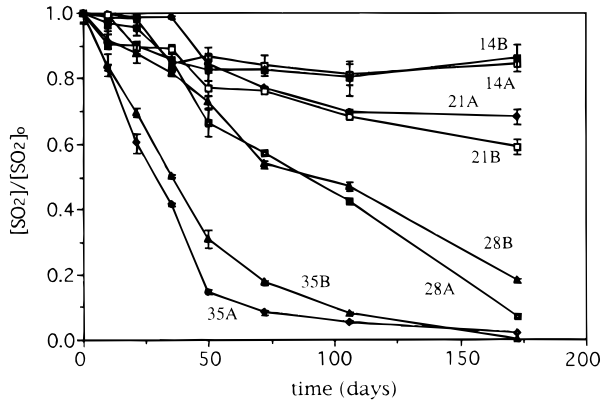

Figure 2. SO_2 losses in raisin samples A and B.

Table 4. Evolution of the Quality Parameters in Raisins during Storage (Samples B and C)

time (days)	14B	21B	28B	35B	28C
			*L**		
10	29.6 ± 2.7	27.6 ± 2.6	27.5 ± 2.6	25.6 ± 1.8	24.1 ± 1.6
21	29.8 ± 2.9	26.4 ± 2.4	26.5 ± 2.9	25.7 ± 1.6	23.5 ± 1.5
35	29.6 ± 3.1	30.0 ± 3.3	27.3 ± 2.7	25.8 ± 1.6	24.5 ± 1.4
50	28.7 ± 2.7	28.5 ± 2.8	26.8 ± 1.2	22.8 ± 0.9	23.4 ± 1.9
72	28.9 ± 2.4	29.6 ± 3.3	25.9 ± 2.6	23.1 ± 1.2	21.9 ± 2.1
106	28.9 ± 2.8	30.1 ± 2.6	26.2 ± 2.7	22.9 ± 0.8	23.2 ± 1.5
173	31.9 ± 2.6	28.1 ± 3.0	25.7 ± 2.0	23.4 ± 1.4	23.7 ± 1.9
			*a**		
10	14.4 ± 2.4	12.6 ± 2.1	11.7 ± 1.9	10.7 ± 2.1	7.3 ± 1.7
21	13.4 ± 1.9	13.4 ± 1.7	11.3 ± 2.0	10.6 ± 2.1	6.9 ± 1.8
35	13.8 ± 1.9	13.2 ± 1.9	12.1 ± 2.2	9.4 ± 0.5	7.5 ± 1.5
50	14.1 ± 2.3	13.3 ± 1.9	11.7 ± 0.3	10.1 ± 0.5	7.2 ± 1.6
72	13.9 ± 1.7	12.7 ± 1.4	10.8 ± 1.9	7.4 ± 0.6	6.3 ± 1.6
106	14.1 ± 1.7	14.6 ± 1.1	11.3 ± 1.4	7.6 ± 0.6	6.0 ± 1.3
173	14.3 ± 1.8	12.2 ± 1.4	9.4 ± 1.4	6.9 ± 1.1	5.9 ± 1.6
			*b**		
10	8.2 ± 2.4	5.9 ± 2.9	5.8 ± 2.1	4.2 ± 1.8	2.3 ± 1.3
21	9.3 ± 2.0	6.6 ± 1.8	5.6 ± 1.7	4.4 ± 1.2	2.4 ± 1.2
35	7.2 ± 1.9	7.4 ± 1.9	5.1 ± 1.8	3.5 ± 1.0	3.2 ± 1.1
50	7.7 ± 1.8	6.0 ± 1.9	4.8 ± 0.9	3.0 ± 0.7	4.4 ± 1.4
72	7.9 ± 1.9	7.7 ± 2.1	4.6 ± 1.4	2.6 ± 0.6	3.2 ± 1.5
106	7.2 ± 1.5	7.7 ± 1.8	4.6 ± 1.2	2.7 ± 0.6	2.7 ± 0.7
173	8.2 ± 2.2	6.3 ± 2.0	4.6 ± 1.1	3.9 ± 0.9	3.4 ± 1.1
			F_{max}/m (N/g)		
10	21.5 ± 1.4	20.8 ± 0.7	20.9 ± 1.2	21.8 ± 1.3	22.0 ± 1.1
21	22.5 ± 2.1	20.9 ± 1.0	22.2 ± 0.8	21.1 ± 1.6	22.9 ± 1.3
35	21.8 ± 0.4	22.1 ± 1.2	22.6 ± 1.3	20.5 ± 1.1	22.5 ± 1.4
50	21.6 ± 0.5	22.7 ± 0.5	22.1 ± 1.3	21.5 ± 0.3	24.0 ± 1.2
72	21.8 ± 1.9	20.9 ± 1.1	22.0 ± 1.2	22.8 ± 0.9	25.8 ± 1.4
106	23.5 ± 2.0	22.8 ± 0.5	23.2 ± 0.3	25.8 ± 2.1	25.5 ± 1.5
173	27.2 ± 0.6	26.3 ± 1.3	25.5 ± 0.9	24.9 ± 1.0	27.2 ± 2.5
			Glucose (mg/g of dm)		
21	38.8 ± 1.0	42.2 ± 1.6	36.0 ± 0.7	39.6 ± 1.1	40.2 ± 0.7
35	38.9 ± 1.9	42.8 ± 1.7	34.2 ± 1.2	34.1 ± 0.8	36.5 ± 1.3
50	39.5 ± 1.6	36.7 ± 2.0	37.0 ± 1.7	32.1 ± 1.2	35.6 ± 1.2
106	40.5 ± 1.6	33.6 ± 1.1	32.8 ± 1.0	32.8 ± 1.9	36.5 ± 1.3
173	36.7 ± 1.6	33.3 ± 1.4	33.8 ± 1.4	31.8 ± 1.3	33.0 ± 1.2
			Fructose (mg/g of dm)		
21	35.7 ± 2.0	35.7 ± 2.5	37.1 ± 1.5	34.1 ± 1.5	35.8 ± 1.7
35	37.5 ± 1.0	36.3 ± 1.4	3.5 ± 1.0		
50	38.1 ± 1.7	38.2 ± 1.5	32.7 ± 1.9	33.5 ± 0.6	
106	34.8 ± 0.8	35.3 ± 1.0	35.4 ± 2.0	34.4 ± 0.9	39.9 ± 2.6
173	36.6 ± 2.6	35.0 ± 1.3	31.0 ± 1.1	31.2 ± 1.0	32.5 ± 1.9

Water activity and moisture content remained almost constant during the storage time. *L**, *a**, and *b** decreased in samples stored at 28 and 35 °C and in sample 21AL (Tables 3 and 4). Texture figures increased during storage time in all samples, mainly in the last 2 months of storage. As can be observed in Figure 2, storage temperature had a great influence on the rate of SO_2 losses that were similar in both sample treatments A and B.

Table 5. ANOVA and Multiple Range Test Analysis of Control Parameters vs Storage Time

	time (days)									
	0	10	21	5	50	72	106	173	*F*	*p*[a]
*L**	b	a	a	a	b	b	b	b	3.2	**
*a**	a	ab	ab	ab	bc	c	c	d	7.3	***
*b**	a	bc	c	abc	ab	ab	a	a	2.9	**
F_{max}/m	a	a	b	b	b	b	c	d	37.7	***
glucose	a		a	b	b		b	b	7.1	***
fructose	a		b	b	b		bc	c	7.1	***
SO_2	a	ab	bc	cd	de	ef	f	g	24.9	***

[a] *p > 95%; **p > 99%; ***p > 99.9%.

The statistical study was carried out on the pooled data for the independent variables (time, storage temperature, treatment before drying, light exposition, and material used for packaging) over the physical and chemical parameters. Results from ANOVA and multiple range test analysis are shown, summarized in Tables 5 and 6 including *F*-ratio figures and the significance levels.

Time, temperature, and treatment variables showed a significant influence on the three color coordinates (p > 99% for time variable and p > 99.9% for temperature and treatment variables). Light presence showed a significant influence on the *L** (p > 99%) and *b** (p > 99.9%) coordinates but not on the *a** coordinate.

Throughout the multiple range analysis it can be deduced that according to the influence of the storage temperature on the color coordinates, samples could be grouped in three well-differentiated clusters. The first includes samples stored at 14 and 21 °C, which maintained their color characteristics during the storage time and with no significant differences between them, the second, samples at 28 °C, and the third, those at 35 °C. Both last samples (stored at 28 and 35 °C) showed important decreases in *L** as well as in *a** and *b**. Sample C was an exception; this sample was dark due to the absence of treatment with SO_2.

With regard to the influence of sample treatments on color coordinates, A−C samples were significantly different (p > 99.9%). Sample A showed the highest *L**, *a**, and *b** values during the storage time, being slightly higher than those showed by sample B.

Material used for packaging, film or glass, had no influence on the color parameters at the storage temperature investigated (28 °C). No significant differences were found on the color coordinates between 28A (stored in film bags) and 28AG (stored in glass containers) samples. From these results, it could be concluded that there was not any influence of the material used, at least at temperatures lower than 28 °C.

At short times the decrease in color parameters was low at the different temperatures examined. Nevertheless, the greatest losses of sulfur dioxide (Figure 2) were found in this period giving rise to sulfate ions and organic sulfonates inhibiting browning through this process. At higher times when the SO_2 content had decreased considerably, color parameters *L** and *b** vary exponentially with temperature showing correlation coefficients greater than 0.99 at 173 days of storage time.

The variable of time showed a significant influence on textural properties of the samples (p > 99.9%), as can be observed in Tables 3 and 4, and there was an increase in textural properties during the last months of storage. This conclusion was corroborated through

Table 6. ANOVA and Multiple Range Test Analysis of Control Parameters vs Storage Temperature, Treatment, Light Presence, and Package Material

	temperature (°C)						treatment					light presence				package material			
	14	21	28	35	*F*	*p*[a]	A	B	C	*F*	*p*	yes	no	*F*	*p*	glass	film	*F*	*p*
*L**	a	a	b	c	38.3	***	a	b	c	26.0	***	a	b	8.7	**			0.0	
*a**	a	a	b	c	38.1	***	a	b	c	49.5	***			0.6				0.1	
*b**	a	a	b	c	48.2	***	a	b	c	40.0	***	a	b	29.3	***			0.0	
F_{max}/m	a	b	a	ab	3.5	*	a	b	a	86.2	***			2.4	-			0.2	
glucose	a	b	b	b	5.9	**				0.6		a	b	11.6	**			0.6	
fructose	a	a	b	b	5.5	**				1.7				3.9	-			1.0	
SO_2	a	a	b	c	33.2	***	a	b	c	19.1	***	a	b	15.1	***			0.2	

[a] *p > 95%; **p > 99%; ***p > 99.9%.

Table 7. ANOVA and Multiple Range Test Analysis of Sensorial Parameters vs Storage Temperature, Treatment, Light Presence, and Package Material

	temperature (°C)						treatment					light presence				package material			
	14	21	28	35	*F*	*p*[a]	A	B	C	*F*	*p*	yes	no	*F*	*p*	glass	film	*F*	*p*
color gradation	a	a	b	c	171.9	***	a	b	c	58.3	***	a	b	12.6	***			3.4	
appearance preferences	a	ab	ab	b	15.3	***				3.2				1.0				1.9	
flavor/taste preferences	a	a	b	b	5.6	**	ab	ab	b	1.1	*			1.9				0.6	

[a] *p > 95%; **p > 99%; ***p > 99.9%.

multiple range analysis (Table 5). The different samples constituted an homogeneous group during the first 10 days of storage and from 21 to 72 days of storage.

There were significant differences between the F_{max}/ weight of samples according to the treatment used before drying (p > 99.9%). Treatment A provided raisins with slightly high textural values. The influence of storage temperature on texture samples was less significant (p > 95%) than time and pretreatment. The kind of package used and exposure also had no significant influence.

All variables except packaging material (time, temperature, light, and treatment) showed a significant influence on SO_2 content (p > 99.9%), this parameter being the one showing the most important variations during storage time. Throughout multiple range analysis, it was concluded that samples stored at 14 and 21°C showed no significant differences between them with regard to the SO_2 content until 106 days of storage. Samples at 35 °C showed the highest losses during storage time, with the final SO_2 content being negligible in these samples. Due to the fact that there were no differences between 28A and 28AG with regard to the SO_2 evolution, it could be concluded that SO_2 losses were due mainly to its role in blocking reactions between carbonyl and amino groups responsible for darkening (Cañellas et al., 1993). The disappearance of sulfur dioxide was influenced by temperature. This loss of the additive appeared to vary according to an overall first-order kinetics; the constant term varied according to the Arrhenius law (r^2 = 0.996 in samples A and 0.999 in samples B) as can be observed in Figure 3. It can be observed in that figure that the temperature influence was similar in both samples A and B. As a consequence, the activation energies were similar in both samples A and B, 26.3 and 27.6 kcal/mol, respectively, and higher than those proposed by Cañellas et al. (1993) for grapes with 640 ppm of SO_2 at the beginning of storage (12.1 kcal/mol).

Sugar content variations could not be attributed to any independent variable, due to the high deviations in the measurements. The only variable that showed a significant influence was storage time, and significant losses between the first and the last periods (p > 99.9%) in both glucose and fructose contents were found.

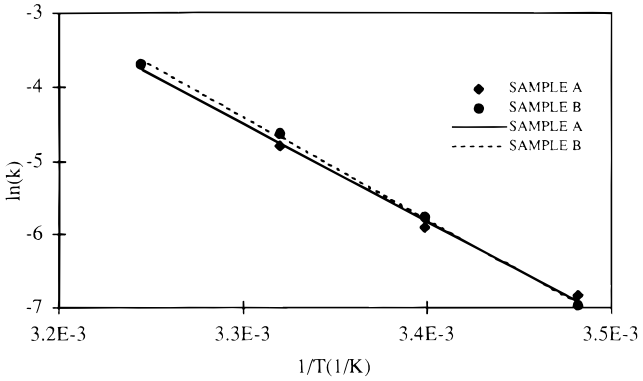

Figure 3. Influence of the storage temperature on SO_2 losses in samples A and B.

Sensorial Analysis. Results from ANOVA and multiple range test analysis are shown, summarized, in Table 7 including *F*-ratio figures and the significance levels. In the ranking test of the 11 samples color, treatment, storage temperature, and light were significant variables (p > 99.9%), although the nature of the packaging material had no significant influence. No differences were found between samples 28A and samples 28AG and between samples stored at 14 and 21 °C. These results are in agreement with physical color measurements. Correlations between sample ranking done through sensory analysis and color coordinates *b** (0.85), *L** (0.80), and *a** (0.61) were observed.

In the ranking of samples by apperance preferences only the storage temperature showed a significant influence (p > 99.9%). It is important to point out that two different preferences were found in the panel: One group of samplers preferred lighter grapes, while the other group chose the browner ones. This could be due to the fact that these two different kinds of grapes are in market, and although the darker samples had this color due to browning Maillard reactions, visually this kind of grape could be more attractive for some samplers.

Due to this finding on criteria disparity, it was considered necessary to carry out the study among a large consumer group because important commercial consequences could be derived. The results obtained through this investigation suggested that bigger-sized

raisins are preferred brown (60%) and smaller-sized raisins should be light-colored (85%).

Statistically, no differences in color, taste and flavor preferences were found between samples stored at 21 °C (21A, 21AL, and 21B). Slightly higher differences were found in samples stored at 28 °C (28A, 28AG, 28B, and 28C), mainly in color preferences ($p > 95\%$). In general, samples A were the most preferred for its taste among samples stored at 28 °C and samples C the less preferred. ANOVA analysis showed that samples stored at 28 and 35 °C were less acceptable for taste and flavor than those stored at 14 and 21 °C for both A and B treatments.

CONCLUSIONS

There were significant influences of storage temperature, time and treatment on physical and sensory sample color, taste, and flavor preferences and SO_2 content, although time and treatment were the most important variables for texture, and only the time variable showed a significant influence on sugar content.

Both treatments A and B provided high-quality raisins that were acceptable to the taste panel. Moreover, due to the fact that there were no differences between samples stored at 14 and 21°C, refrigeration is unnecessary up to those limits for the periods of time considered (less than 173 days). Higher temperatures cause important nutritional and sensory losses.

There were no significant differences between samples stored in film and those stored in glass containers. This result is of interest due to the lower cost of packaging films and ease of handling. Nevertheless samples stored in darkness maintained their quality better than those stored in light.

Agreement between sensory and instrumental results was high. It is noteworthy that for big raisins a significantly greater number of people (consumer panel) preferred darker samples, probably because of cultural factors; in fact, traditional raisins came from sun-dried grapes with big berries. It was found that chitosan could be used as a food additive in raisins although its addition showed no significant increase in the grape quality.

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