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Factors Affecting Color Formation During Storage of White Crystal Sugar

Claudio Lima de Aguiar, Ana Laura Bodoni Rocha, Jéssica Rodrigues Jambassi, Antonio Sampaio Baptista and Roberta Bergamin Lima

Universidade de São Paulo, ESALQ-USP, Departamento de Agroindústria, Alimentos e Nutrição, Setor de Açúcar e Álcool, Laboratório Hugot de Tecnologia em Sucroderivados, Piracicaba, SP., Brasil.

Abstract

There are many reports of problems caused by incorrect storage of sugar production - hardening, caking, dimming, losses and fires. Given the importance of crystal sugar, one of the main sugarcane-based products in Latin America or around the World, there is a growing realization of work to increase efficiency and avoid losses in the manufacturing. However, during sugar storage, it is known that environmental factors (temperature, humidity, light and weather) influence the quality of the final product – several types of crystal sugars, such as: very high polarization (VHP); very-very high polarization (V-VHP), and whites – Types 1, 2, 3 or 4. During storage, the temperature must be not exceed and/or sensitive to variations. The optimum relative humidity is 55-65% with the maximum equilibrium moisture at 65%. This work aimed to assess which factors are important to accentuate the color during the storage process (specially, ICUMSA color and sucrose hydrolysis) of white sugar (Type 1). The results of the amounts of reducing sugars and ICUMSA color were evaluated by the response surface. It was concluded that there were changes in the amounts of reducing sugars, sucrose and ICUMSA color in the analyzed samples, that moisture is the most decisive factor. Therefore, it became clear that you should avoid such conditions of high humidity and temperature in storage sugar, in order to preserve the quality, which is highly perishable.

Keywords

Sugar, Sucrose, Storage, Humidity, Temperature

Introduction

The importance of industry and trade balance of sugarcane and its derivatives in tropical countries, especially sugar, encourage papers addressing the export performance. This sector has direct involvement in both domestic and international markets, since sugarcane is a major crop in terms of area, production volume and cost (Alves and Bacchi, 2004). Sucrose is the carbohydrate more interested in the processing of sugarcane, which is desired in crystallized form, and it is likely that the effect of temperature, enzymes and microorganisms is more important (Mantelatto, 2005).

However, ABIA (2010) reported that during storage of crystal sugar, it is known that different environmental factors affect the quality of the finished product. These factores can be: temperature, humidity, presence of light, and the time, i.e., the period when the product is stored. According to Legendre and Clarke (Legendre and Clarke), the sugarcane juice color and therefore sugar originate from various compounds, such as flavonoids, phenolic compounds, and these pigments that react with reducing sugars, which affect directly the juice color and sugar quality. The formation of colored compounds in the process is carried out mainly by degradation of sugar (sucrose) and the formation of the monosaccharides, glucose and fructose (Mónica et al., 2004).

In general, browning reactions are detrimental to the nutritional value of the food in question, and may occur during processing and storage of foodstuffs. It is therefore necessary to find the conditions to prevent these reactions, therefore, not only to prevent any change in diet, but other changes that may cause the food unacceptable for the consumer (Eskin et al., 1971).

When related to inadequate storage, forming a darker is still a visual theme that can influence the buying decision of the consumer to opt for a sugar more white. In addition, changes in the environment cause changes into sugar, because it absorbs moisture for balance, and this moisture dissolves a small amount of crystal sugar. However, when there is a decrease in humidity, sugar becomes difficult due to water evaporation and recrystallization of the

molecular sucrose. The contact point of two crystals expands so that they hold together. Each time this process occurs, sugar turns into a hard mass that significantly affects the quality of the product (Howes, 1966). According to SRI (2007), it is generally accepted that for every 10 ºC rise in temperature the rate of colour formation increases by a factor of approximately three. According to TIS (2015), during storage, the temperature of sugars must not exceed a maximum and/or they are sensitive to temperature variations, and for the optimum relative humidity is 55-65% with the maximum equilibrium moisture at 65%.

In this context, this study was aimed at assessing the determinants that emphasize the process of color formation during storage of white crystal sugar and how the interaction between them are, allowing knowledge to adapt the warehouses currently used to maintain product quality.

Material and Methods

Sample Preparation and Experiment Design

Assays were performed at Hugot Sugar Technology Laboratory from the Department of Agri-Food and Nutrition (LAN/ESALQ) University of San Paulo and samples of high purity sucrose were used (99%; Synth Co., San Paulo, Brasil).

To evaluate color changes in the crystal sugar samples, the samples were placed in sealed desiccators, where the relative humidity was controlled within the vessel via saturated solutions of: magnesium chloride ($MgCl_2.6H_2O$) to obtain equal to 30% moisture; magnesium nitrate ($MgN_2O_6.6\ H_2O$) for humidity equal to 50%; and sodium chloride (NaCl) for humidity equal to 70% (Rockland, 1960). The assembled group was taken to a furnace with controlled temperature at 30, 40 and 50°C for 6, 12 and 24 hours for accompanying factors potentially affecting the formation of color during storage, being the factors studied: temperature and humidity, both factors associated with increasing intervals of time.

For a full factorial experimental design used 2^3 experiments with 3 at the center point replicates, with a total of 11 trials (Table 1).

The results evaluated the factors that influence ICUMSA color formation in crystals by the response surface methodology with all analytical data evaluated in statistical package StatSoft (2001), and the data were subjected to analysis of variance (ANOVA) using the F-test and the averages compared by Tukey test at 5% probability ($p < 0.05$).

TABLE 1. FACTORS (IN PARENTHESES) AND FULL FACTORIAL EXPERIMENTAL DESIGN DOMAIN 2^3 FOR EVALUATING FACTORS THAT AFFECT THE SUGAR STORAGE.

Runs	factors		
	x1: humidity (%)	x2: temperature (°C)	x3: time (hours)
1	(-) 30	(-) 30	(-) 6
2	(+) 70	(-) 30	(-) 6
3	(-) 30	(+) 50	(-) 6
4	(+) 70	(+) 50	(-) 6
5	(-) 30	(-) 30	(+) 24
6	(+) 70	(-) 30	(+) 24
7	(-) 30	(+) 50	(+) 24
8	(+) 70	(+) 50	(+) 24
9	(0) 50	(0) 40	(0) 12
10	(0) 50	(0) 40	(0) 12
11	(0) 50	(0) 40	(0) 12

Evaluation of Reducing Sugars and ICUMSA Color into Crystal Sugar Samples

The parameters examined were:

(1) Reducing sugars (RS) by the Somogyi-Nelson (Nelson, 1960) colorimetric method, in which the reading was taken transmittance (T%) at 520 nm in spectrophotometer UV Mini 1240 (Shimadzu Co., Kyoto, Japón). Reducing sugars (mg g^{-1}) were calculated by the following equation of the standard curve of glucose:

$$RS = \frac{\left[\frac{(T\%+0.015)}{0.043}\right]}{0.00157}$$

(2) ICUMSA color: the method described by Lopes (1985), in which the samples were read in spectrophotometer UV Mini 1240 (Shimadzu Co., Kyoto, Japón) at 420 nm. Distilled water was used as control solution to evaluate the device. The color index was calculated according to the following equation:

$$Color = \frac{1000 * (-\log T)}{\mathrm{bc}}$$

T = solution transmittance (%); b = measure of the cell (cm); c = solution concentration (g mL^{-1});

Analysis of Sugars Using Ultra Fast Liquid Chromatograph (UFLC)

The method employing an UFLC chromatographic system (Shimadzu Co.; Kyoto, Japan) equipped with ELS-LT (evaporative light scattering at low temperature) detector was carried out at 35ºC using isocratic elution of acetonitrile (HPLC grade; Tedia Co., Farfield, USA) and water (deionized; Millipore, France) at a flow rate of 1.0 mL min^{-1}. Isocratic elution was employed for 12 min with a mixture of 70:30 (v/v) acetonitrile-water. Nitrogen (≥99.0%; Air Liquide, São Paulo, Brazil) at 350 kPa was used to nebulize the effluent coming from the column NH_2P-50 4E (250 mm x 4.6 mm) Shodex Packed (Shodex Group, Kawasaki, Japan) at 30ºC, and the evaporation temperature of the chromatographic eluent was 30°C. Before the injection (sample volume = 10 μL), the samples were clarified with lead subacetate, diluted to 1/10 (v/v), and filtered through Durapore filters 0.45 μm and 13 mm (Millipore-Merck, São Paulo, Brazil). All sugars (sucrose – Gain at 3; and glucose and fructose – Gain at 7) were analyzed against known standards purchased by Sigma-Aldrich (≥99.0%, MS grade).

UV-visible Spectrophotometric Analysis of the Crystal Sugar Samples

Samples were conditioned in desiccators with relative humidity controlled, such as 30, 50, and 70%, such as temperatures of 30, 40, and 50ºC. The storage time was 6, 12, and 24 h, according to Table 1. To evaluating the spectra of maximum absorption (scanning), the samples were added 12.5 g of sugar and then diluted in distilled water (25 mL). The spectra were obtained by UV Mini-1240 spectrophotometer (Shimadzu Co., Kyoto, Japan) between 250 and 470 nm at different time intervals, being: 0, 24, and 96 h after storage. The samples were examined under UV-visible light for proximate analysis. For UV-VIS spectrophotometer analysis, crystal sugars were conditioned in desiccators with relative humidity controlled, such as 30, 50, and 70%, such as temperatures of 30, 40, and 50ºC. The storage time was 6, 12, and 24 h, according to Table 1. To evaluating the spectra of maximum absorption (scanning), the samples were added 12.5 g of sugar and then diluted in distilled water (25 mL). The solutions were scanned in the wavelength ranging from 200-1100 nm using UV Mini-1240 spectrophotometer (Shimadzu Co., Kyoto, Japan) and the characteristic peaks were detected. The peak values of the UV-VIS were recorded in triplicate.

Results and Discussion

By Fig. 1a, it can be inferred that there is a progressive increase in the levels of reducing sugars with temperature change. This may be related to temperature increase, contributing to the process of inversion of sucrose into glucose and fructose (evaluated as reducing sugars by Somogyi-Nelson method).Fig. 1b analysis allowed verifying that, since there is no increase in relative humidity, obtained higher concentrations of the reducing sugars, thus the reaction is catalyzed as a higher water content available in the environment (desiccators). In this experiment, the levels of reducing sugars increased as temperature also increased.

Rodrigues et al. (2000) in studies of catalytic hydrolysis of sucrose found that the most influential factor is the temperature, and that this increase was directly proportional to the inversion (or hydrolysis) of sucrose to glucose and fructose.

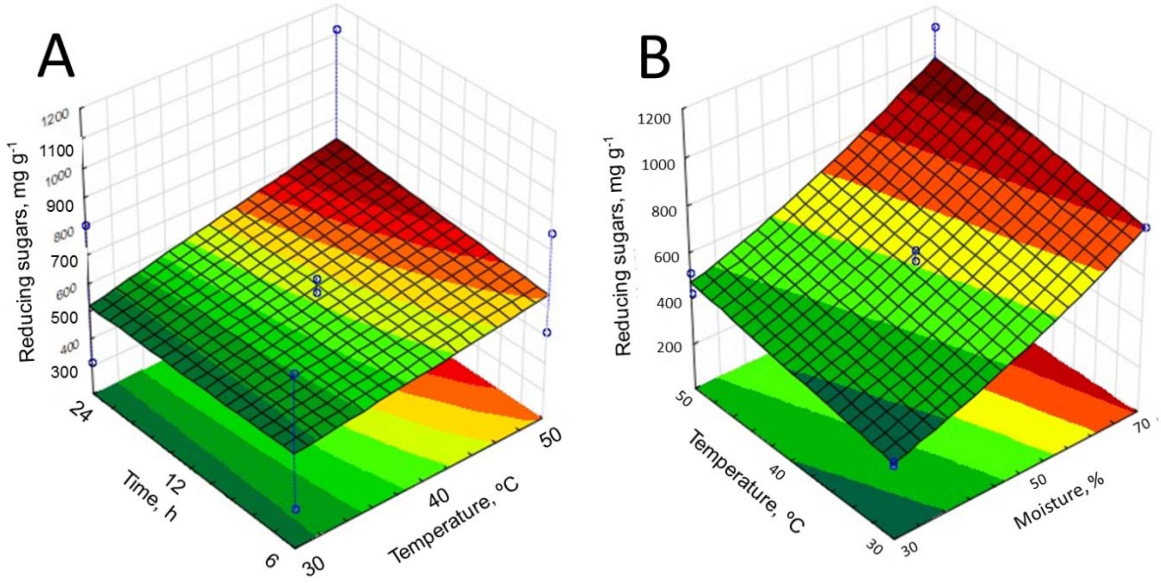

FIG. 1. RESPONSE SURFACE GENERATED BY THE INTERACTION FROM THE VARIABLES (A) TEMPERATURE (°C) AND TIME (H) AND FOR INTERACTION FROM THE VARIABLES (B) MOISTURE (%) AND TEMPERATURE (°C) TO OBTAIN VALUES REDUCING SUGARS (RS) (mg g^{-1}).

After the melting, sucrose loses water and glucose and fructose anhydrides or glucosans and levulosans become. The reaction is self-catalyzed water formed as a function of accelerating the reaction. The anhydrides formed combine with water to produce acid derivatives and hydrolyze the remaining sucrose, fructose and glucose. The glucosans and levulosans formed also can be combined with water and reappear fructose and glucose (Oetterer et al., 2006).

According to Araujo (1995), sugars at temperatures above described 120°C are pyrolized at various degradation products and high molecular weight called dark caramel. This reaction involves the sugar degradation in the absence of amino acids or proteins.

During the whole time of dehydration and hydrolysis reactions occurring, with predominance of acids such as acetic and formic, or aldehydes such as formaldehyde and 5-hydroxymethylfurfural, diacetyl, carbonyl and enol groups. These compounds are responsible for the aroma and color , which recombine and form polymers called melanoidins (Oetterer et al., 2006).

Evaluating the trend of increasing ICUMSA color (Fig. 2), it appears that under high relative humidity, regardless of the temperature in question, there was an increase in color, with the fact that storage process of sugar was unwanted.

Fig. 2c shows the response surface for ICUMSA color from interaction between humidity and time. It was noted that, regardless of the time in experimental design, ICUMSA color was more pronounced in the maximum relative humidity used. ICUMSA color results presented an inverse behavior, and several authors (Arena et al., 2001; Ibarz et al., 2000; Sapers and Hicks, 1989; Namiki, 1988) have shown that the time-temperature relationship is markedly important for the hydrolysis of sucrose. However, the formation of pigmented compounds promotessugar's color. By analyzing response surfaces, one can observe a general trend of increasing ICUMSA color, and reducing sugars according to progressive increases in relative humidity of the environment, regardless of the temperatures and times used.

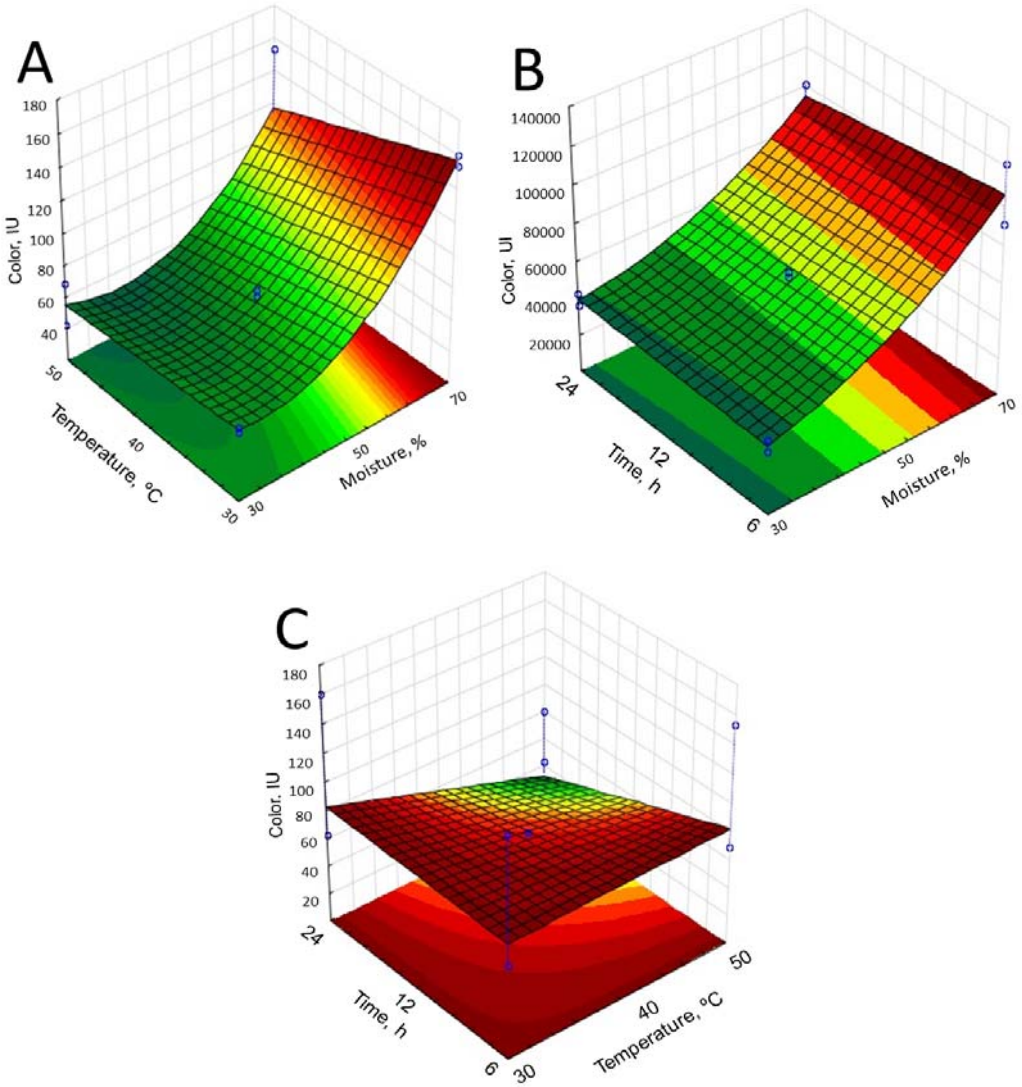

FIG.2. RESPONSE SURFACE GENERATED BY THE INTERACTION FROM THE VARIABLES (A) TEMPERATURE (°C) AND HUMIDITY (%); FOR INTERACTION FROM THE VARIABLES (B) MOISTURE (%) AND TIME (H); AND FOR INTERACTION FROM THE VARIABLES (C) TEMPERATURE (ºC) AND TIME (H) TO OBTAIN VALUES ICUMSA COLOR.

Below related tables of analysis of variance (ANOVA) for treatments performed in the samples. In Table 2, we can observe the data for analysis of ICUMSA color and Table 3 observes the data for analysis of reducing sugars.

TABLE2.RESULTS OF ANALYSIS OF VARIANCE FOR ICUMSA COLOR.

	SS	df	MS	F	p
Regression	16579,1268	6	2763,188	6,34749	0,047578
Residual	1741,2789	4	435,3197		
Total	18320,4057	10	1832,041		
		R^2	0,904954		

TABLE3.RESULTS OF ANALYSIS OF VARIANCE FOR REDUCING SUGARS.

	SS	df	MS	F	p
Regression	573980,97	6,00	95663,49	14,9087	0,010375
Residual	25666,49	4,00	6416,621		
Total	599647,45	10,00	59964,75		
		R^2	0,957197		

As shown in Tables 2 and 3, R^2 values were significant at the 5% level of confidence for all analyses. Therefore, the response surface results are presented below. Through data analysis, it can be inferred that there is a progressive increase in the reducing sugar contents with increasing of temperature. This fact has been related to the trend of increasing temperature, which contributed to the process of inversion of sucrose to glucose and fructose. Echavarria et al. (2013), in studies of non-enzymatic browning in potatos, reported a trend in reduction of sucrose levels for increasing temperature.

According to Tomasik et al. (1989) and Suarez-Pereira et al. (2010), in the oligomerization reaction, there is a formation of brown and the change in material texture is more viscous. First, the individual sugars react to form a molecule containing a new form of two rings connected by a third central ring. This compound can also react by three ways. At first, water-losing molecules form a composite structure called caramelans ($C_{12}H_{12}O_9$), adding to form small dark particles of the size 0.46 μm. The second type of molecule can form, is caramelens ($C_{36}H_{18}O_{24}$), which aggregate to form molecules with 0.95 μm. Finally, it is possible to form the caramelins ($C_{24}H_{26}O_{13}$), the combination of two fructose dianhydrides and the elimination of 27 water molecules. These caramelins are generally aggregates with a size of 4.33 μm.

Fig. 3 (adapted from Tomasik et al., 1989) shows the decomposition reaction of sucrose (see Fig. 4) and the oligomerization of glucose and fructose formed after induction by temperature and humidity.

The analysis of the chromatograms (Fig. 4) shows that they are consistent with the characteristic sucrose profiles, and the variation in the glucose and fructose contents results from the hydrolysis of sucrose. The degradation of sucrose was represented in Fig. 4.8. Samples were prepared at concentrations of 1g mL^{-1} and subjected to chromatographic analysis showing reduced levels of sucrose.

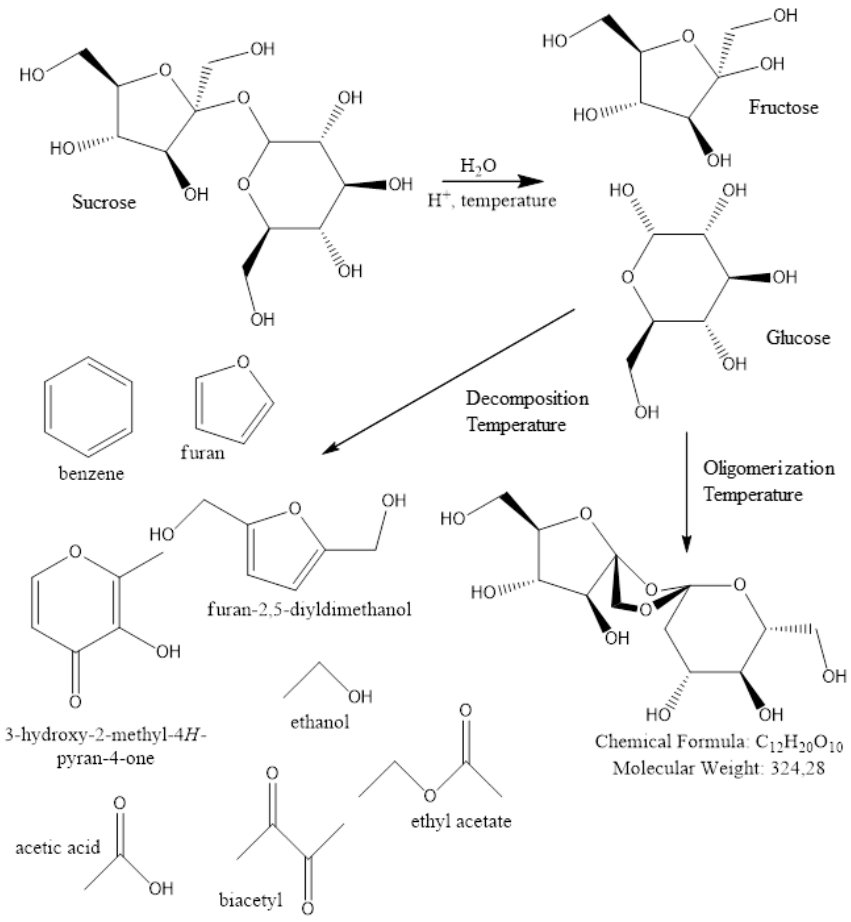

FIG. 3. CARAMELIZATION REACTION CAUSED BY THE SUCROSE DECOMPOSITION AND OLIGOMERIZATION OF THE GLUCOSE AND FRUCTOSE (ADAPTED FROM 20).

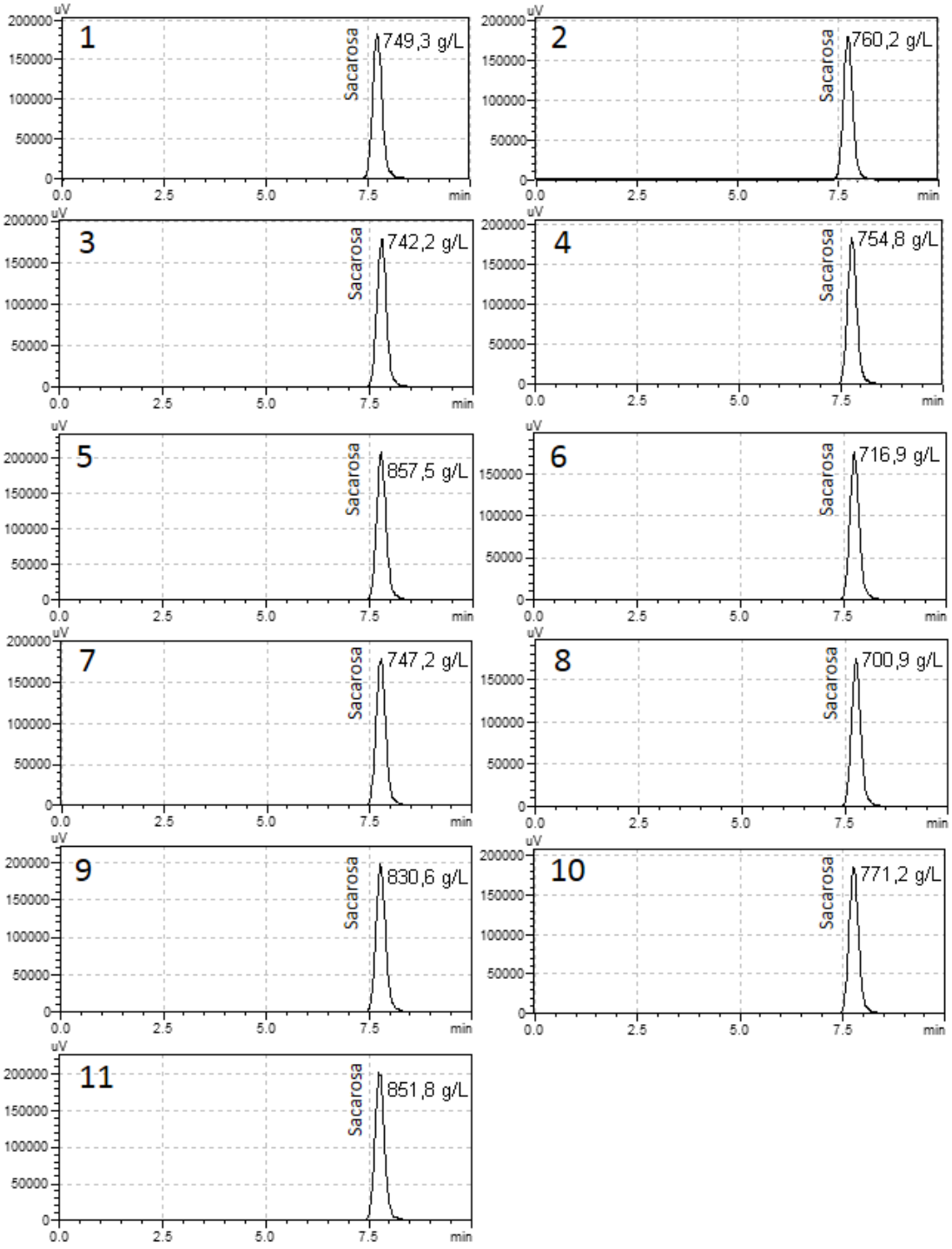

FIG. 4. CHROMATOGRAMS PROFILES OF SUCROSE SUBMMITED TO DIFFERENT TREATMENTS (TABLE 1) OF CRYSTAL SUGAR SAMPLES.

According to Palashudin-Sket al. (2012), in studies with caramels, it was observed that the sucrose profile when subjected to the maximum absorption spectrum was found to be consistent with results obtained in this experiment, which demonstrates that changes in the curves are related with formation of other compounds formed during the treatment and the greater the time was, the larger these changes also are. That is, samples for the change in the profile of the maximum absorption spectrum between 250 and 470 nm for different temperatures and time intervals are shown in Fig. 5 (to 30%, 50%, and 70% humidity).

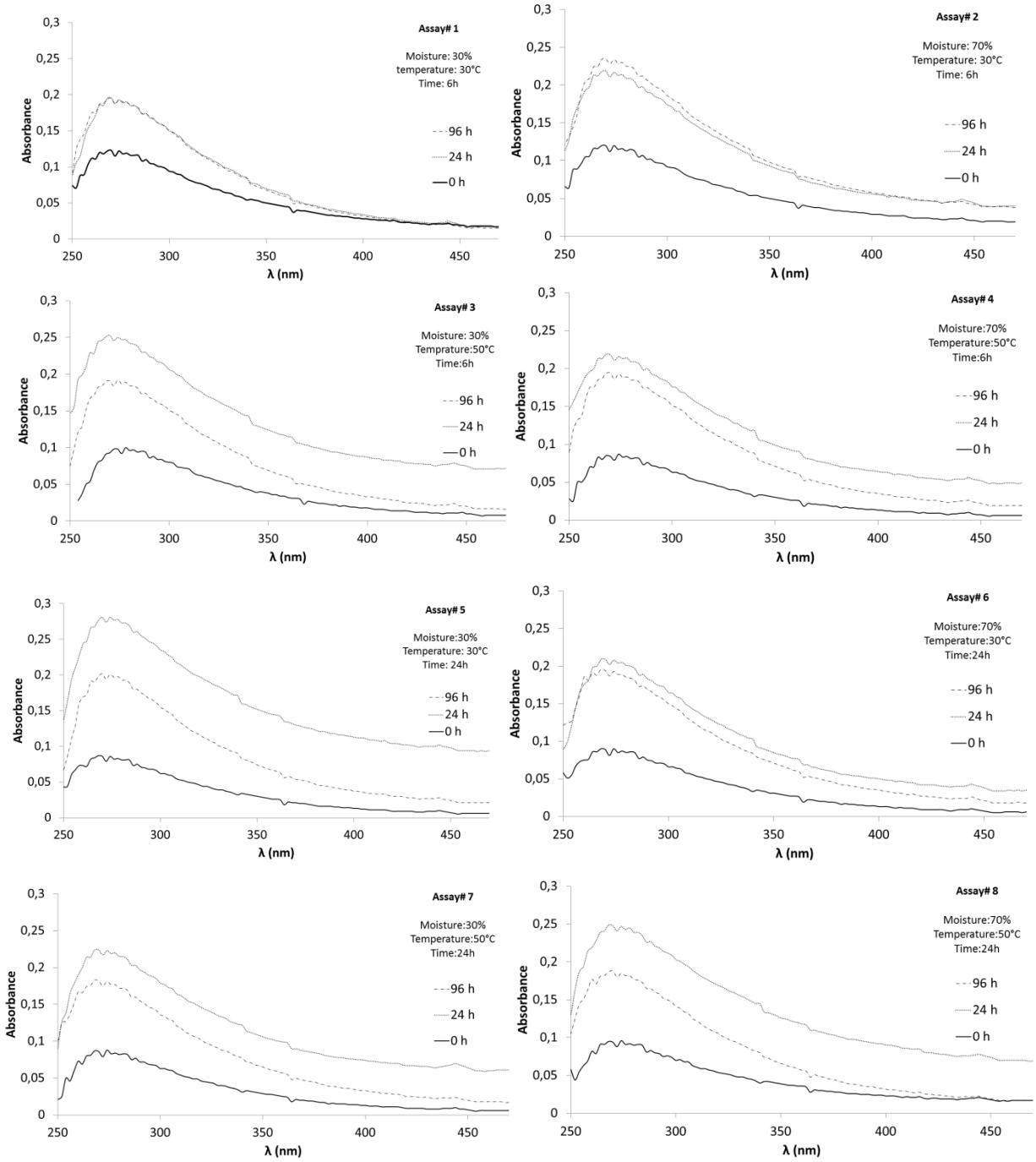

FIG. 5. SPECTRA SCANNING BETWEEN 250 TO 470 nm OF THE SUGAR SAMPLES UNDER DIFFERENT STORAGE CONDITIONS.

Analyzing Fig. 5, it is possible to observe changes in absorption profiles of the scan spectrum samples, and it has been associated by other compounds such as quinones, caramelans, caramelens and caramelins (Palashudin-Sk et al., 2012; Zhang et al., 2015; Golon and Kuhnert, 2013; Golon and Kuhnert, 2012), which also change the color of the samples and are responsible for the characteristic caramel. There is a clear observation that the higher the reaction time in this case was analyzed in time 0, 24 and 96 h, the greater the change into spectra profiles; and the higher the temperature was, which was the formation of pigmented compounds,the more samples were marked,.

Caramelization, according to Araujo (1995), requires neither oxygen nor nitrogen compounds, occurring at the optimum pH of 3.0 and 9.0, the production of caramels. Nonenzymatic browning may also be the oxidation reaction of ascorbic acid which requires oxygen, but does not require nitrogen compounds produced between pH 3.0 and 5.0 to produce melanoidins. The mechanism of this browning reaction, according to Seravalli and Ribeiro

(2007), is still unknown. According to the authors, it is known that heating causes breakage of glycosidic bonds, and formation of new glycosidic bonds, and the formation of unsaturated polymers - caramels.

More specifically, Evangelista (2005) reports that the browning is the result of the reaction between sugars containing hydroxyl and carbonyl groups. This reaction takes place at high temperatures with sugar dehydration and formation of very aldehydes such as 5-hydroxy-methylfurfural (5-HMF) responsible for the characteristic odor of caramelized sugar.

Conclusion

The analysis of the effects of different sugar storage conditions shows that there are consistent alterations in the profile of sucrose, glucose and fructose contents, and there is color formation during the storage. By the maximum absorption spectra it was possible to observe changes in absorption profiles of the samples subjected to high temperatures and humidity, thus being the binomial temperature-time associated with moisture, important factors in maintaining the quality of sugar white stored.

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