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FULL PAPER

Isothermal Thermogravimetry and Factorial Design Applied to Development and Validation of an Oven Drying Method for Cane Syrups

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Abstract:

A new and green loss drying method in conventional oven for moisture analysis in cane syrup was developed and in house validated at the first time in this work. According factorial design results, the best conditions of drying in oven were the use of fiber glass paper discs, drying temperature of 70 °C and drying time of 90 min. In-house validation study demonstrated that the developed drying method presents performance comparable to that of Karl Fischer titration in terms of precision and accuracy as verified by results of F-test of variances comparison and of paired t-test. This loss drying method is advantageous because it uses low cost instrumentation, is environmentally friendly since it does not use toxic solvents and it could be applied in quality control laboratories, by supervisory bodies or by small industries.

Keywords: cane syrup, factorial design, loss drying, moisture analysis, method validation, thermogravimetry

1. Introduction

Cane syrup, according [1], is a "syrupy liquid obtained by the evaporation of sugarcane juice (*Saccharum officinarum* L.) or from of the rapadura by appropriate technological processes. This food is considered a food of great importance in several regions of the Brazil. Each 100 g of the product provides 300 calories, in addition to enclosing also a significant amount of minerals and vitamins. Its use in human food is diversified and varies between regions. It is consumed pure and in mixtures with other foods such as cheeses, flour, biscuits, cake, yam and cassava. In addition, cane syrup is also used as an ingredient in the confectionery industry, beverages, candies, and even as a substitute for corn syrup in the packaging of some types of canned fruit [2, 3]. Because of its properties, in the interior regions, it is recommended medicinally in cases of anemia and constipation. It has laxative action and favors the growth of bones and teeth [3].

In order to be considered a quality product and not to pose a risk to the consumer's health, cane syrups must have the following physicochemical characteristics: maximum moisture of 25% (w/w), acidity in normal solution of maximum 10 % (w/v), total sugars of at least 50 % (w/w), maximum mineral residue of 6 % (w/w) and a sugar concentration around 65° to 74° Brix [4]. It should also present sensorial characteristics such as syrupy liquid and dense (viscous), amber yellow color, sweet taste and from the microscopic point of view it should have absence of dirt, parasites, larvae and insects and their fragments [2]. Among the physical-chemical parameters adopted in the quality control of cane syrups, moisture is one of the most critical, since their contents directly affect

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the development of microorganisms and therefore their stability and shelf life [5]. In view of this, the development and validation of new analytical methods, which besides present good performance (in terms of precision and accuracy), are environmentally friendly and low cost, enabling their implementation in laboratories of quality control and inspection is very interesting.

The determination of moisture in foods containing high sugars such as cane syrup is usually carried out by vacuum loss drying in which the drying temperature is reduced by the application of vacuum at 60 or 70 ºC as an alternative to minimize the impact of decomposition reactions in the results. However, this is a relatively time-consuming method (analysis time > 6.0 h) and does not guarantee that all the water contained in the food will be removed [6, 7].

Recently, in the literature, loss drying and thermogravimetric methods have not been recommended for the drying of foods containing high sugars contents due to the release of volatiles from decomposition reactions together with the water contained in the sample. However, some authors have demonstrated that with the use of fiberglass paper it is possible to minimize the decomposition reactions of sugars present in the food and to develop methods of drying in oven and thermogravimetric that produce results comparable to those of official methods such as the Karl Fischer titration [8, 9].

With this objective, in this work a conventional oven drying method was developed by applying a factorial design in two levels and by the application of thermogravimetry on isothermal mode. The optimal conditions of the factorial design were used in the *in-house* validation of the drying method by application of different statistical techniques.

2. Material and Methods

2.1. Sampling

Six Brazilian cane syrups samples coded by letters and numbers (CS1 to CS6) were purchased in commercial establishments and stored in their original containers at room temperature until the analyzes were carried out. The CS1 sample was used in the studies of isothermal thermogravimetry and development of the drying methodology and the samples CS1 to CS6 in the *in house* validation study.

2.2. Methods

2.2.1 Isothermal Thermogravimetry

Thermogravimetry on isothermal mode was realized using a simultaneous TG/DTA system from Seiko, Exstar 6000 series model. Isothermal thermogravimetric tests were performed at temperatures of 70 °C and 105 °C until 240 minutes, with a heating rate of 25 °C min^{-1} until the isotherm temperatures (70 and 105 °C) were reached. The isothermal curves were obtained in a dynamic air atmosphere (50 mL min^{-1}), with sample masses of approximately 5.0 mg, in alumina sample port (50 μL) containing a fiberglass paper disk (Celm) (diameter = 5.0 mm).

2.2.2. Oven Drying

Drying of the cane syrup samples was performed in a Odontobrás 1.4 oven on a Celm glass fiber disc (diameter = 70 mm) inserted in an aluminum capsule (diameter = 70 mm) for a period of 90 minutes at temperature of 70 °C and using masses of approximately 1.0 g.

2.2.3. Karl Fischer Titration

Water content of cane syrups was measured by a volumetric Karl Fischer titration with titrator Q349-1 from Quimis using Karl Fischer reagent without pyridine (Biotec, Brazil) and anhydrous methanol (J.T. Baker, USA) according to the method 014/IV of the Physicochemical Methods for the Food Analyses [10]. All measurements were carried out in duplicate.

2.2.4. Oven Drying Optimization by Factorial Design

For optimization of the drying methodology in oven, the influence of the variables drying temperature (70 and 105 °C), drying time (90 and 150 min) and glass fiber paper disk utilization (without and with paper) in the moisture contents of cane syrups was investigated by application of a 2^3 factorial design (Table 1).

The significance of factorial design effects was verified by standard error analysis and by Pareto graph at 95 % confidence level. All statistical analyses were carried out by software *Minitab for Windows versão 16*.

Table 1. Variables and levels of 2^3 factorial design applied for moisture analysis from cane syrup by oven drying.

Variables	Level (-)	Level (+)
Drying temperature (°C)	70	105
Drying time (min)	90	150
Glass fiber paper disk	without	with

2.2.5. Oven Drying Validation

For the validation study of the oven drying method, two parameters were calculated: accuracy and precision according to the AOAC guidelines [11, 12]. Both were determined by comparing the method developed for oven drying with the Karl Fischer titration method, which was adopted as reference method in this work. In order to evaluate the accuracy of oven drying methodology, a paired *t*-test was applied for the mean differences in moisture/water contents obtained for the two analytical methods [11,13,14]. To evaluate the accuracy of the developed method the pooled variances (Sp^2) of each of the analytical methods were compared by applying an appropriate *F*-test and by calculating confidence intervals for the ratio between the variances and the pooled standard deviations (Sp). All statistical analyzes were performed at 95.0% confidence level using software *Minitab for Windows v. 16*.

3. Results and Discussion

3.1. Isothermal Thermogravimetry

For the optimization study of a conventional oven drying method, thermogravimetric data in isothermal mode of CS1 cane syrup sample were used. Figure 1 shows the isothermal thermogravimetric curves at temperatures of 70 and 105 °C. These temperatures were chosen because they are the temperatures usually adopted in the vacuum oven drying and conventional oven drying methods, respectively, for the analysis of moisture in foods [10].

The analysis of isothermal TG curves (Figure 1) indicates a strong influence of drying temperature on the complete removal of water from the cane syrup sample (CS1). It is observed that at 105 °C, higher moisture contents (21.80%) are obtained than those determined by the Karl Fischer titration (20.52%) when the mass losses become approximately constant in 180 minutes. Another interesting result that can be seen in Figure 1-b is that the moisture contents already exceeded the value determined by the reference method before the isothermal temperature was reached. This behavior can be explained by the fact that at higher temperatures crust formation can occur [7] and the degradation reactions of the cane syrup are favored, introducing systematic errors in moisture analysis. On the other hand, the isothermal curves performed at 70 °C (Figure 1-a) showed that moisture contents (20.47%) comparable to those of Karl Fischer titration (20.52%) were obtained with 90 minutes of heating. However, longer heating times at this temperature may favor the sugar decomposition reactions or Maillard reactions [15] and interfere also in this type of determination.

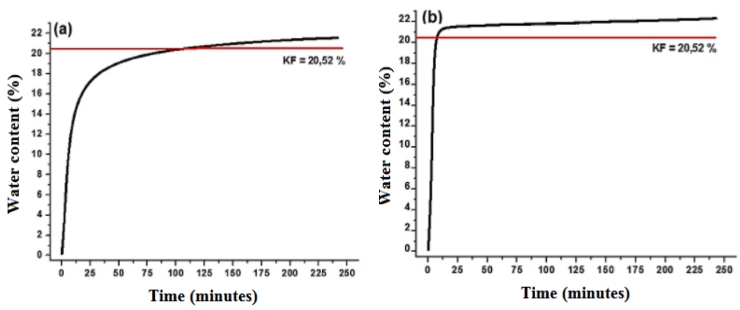


Figure 1. Isothermal TG curves of the CS1 sample performed at temperatures of (a) 70 °C and (b) 105 °C for 240 minutes in a dynamic air atmosphere, with mass of 5.0 mg and in alumina sample port containing a fiber glass paper disc (diameter = 5.0 mm). The red line represents the water content determined by the Karl Fischer titration method (reference method).

3.2. Optimization of a New Oven Drying Method

To optimize an oven drying method for cane syrup samples considering the results of isothermal thermogravimetric analysis, a 2^3 factorial design was applied to determine the best conditions of drying temperature, drying time and use of fiber glass paper discs. The results and calculated effects are presented in Tables 2 and 3.

Table 2. Matrix of 2^3 factorial design applied for the moisture analysis in cane syrups by oven drying.

Tests	Drying Temperature (°C)	Drying Time (min)	Fiber glass paper	Moisture content averages (g 100 g^{-1}) ± SD*
1	70	90	without	20.52 ± 0.16
2	105	90	without	22.36 ± 0.03
3	70	150	without	21.16 ± 0.40
4	105	150	without	24.27 ± 0.06
5	70	90	with	20.65 ± 0.10
6	105	90	with	23.46 ± 0.60
7	70	150	with	21.93 ± 0.30
8	105	150	with	24.68 ± 0.24

*standard deviations were calculated using replicates for each test (n = 3).

The results of the factorial design (Table 3, Figure 2) suggest that all variables investigated (drying temperature, drying time and glass fiber paper) are significant as well as the interaction effects between drying temperature and drying time and between drying temperature, drying time and fiber glass paper at the 95.0% confidence level. The increase of the drying temperature and of the drying time as well as the use of fiber glass paper resulted in higher moisture contents. These facts suggest that during drying occurs the release of volatiles from the degradation of sugars in cane syrup along with the removal of water. These results are in agreement with those obtained in the isothermal thermogravimetric study (Figure 1).

Table 3. Effects and standard errors calculated of the 2^3 factorial design applied to moisture analysis in cane syrups by oven drying.

Effects	Estimates ± Standard Error*
Mean	*22.35 ± 0.03*
Main Effects:	
Drying Temperature (1)	*2.69 ± 0.06*
Drying Time (2)	*1.20 ± 0.06*
Glass Fiber Paper (3)	*0.67 ± 0.06*
Interaction Effects:	
(1)X (2)	*0.37 ± 0.06*
(1)X(3)	*0.09 ± 0.06*
(2)X(3)	*0.05 ± 0.06*
(1)X(2)X(3)	*- 0.40 ± 0.06*

*standard errors were calculated using triplicates of oven drying tests

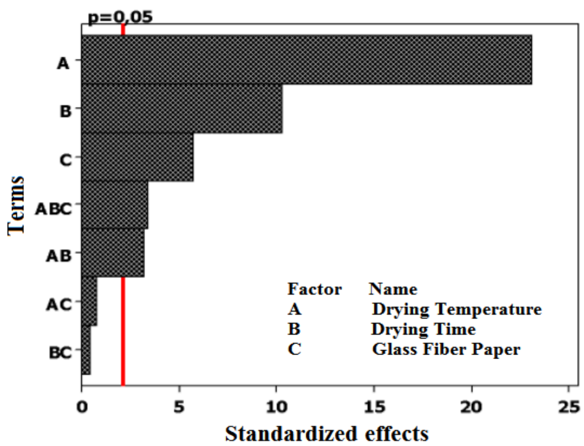


Figure 2. Pareto graph for standardized effects of 2^3 factorial design at 95.0 % confidence level.

The drying temperature change from 70 to 105 °C and the change in drying time from 90 to 150 minutes produced a increase of 2.69 % and 1.20 %, respectively on moisture contents (Table 3, Figures 2, 3 and 4). The increase in drying temperature and drying time favors the reactions of degradation of sugars that insert systematic errors in the moisture analysis. An example of this is the formation of HMF, an intermediate of the Maillard reaction, due to high concentrations of reducing sugars in acid medium, application of high temperatures during processing or storage and long periods of storage [16,17,18] . According to Nielsen (1994), the sugars begin to deteriorate at temperatures above 100 °C, so the moisture contents are high when using the temperature of 105 ºC when compared to the value obtained at 70 ºC [7]. In addition, with the increase in drying temperature, volatile compounds are released from the reactions of degradation of sugars. Besides this, prolonged heating of sugars may cause the extent of degradation reactions with releasing of volatiles, resulting in increased moisture contents [19-21].

The use of glass fiber paper in the oven drying provided an increase in the moisture contents of 0.67 % (Table 3, Figures 2, 3 and 4). It can be seen in Figure 5 that without the use of glass fiber paper in the oven drying occurs to the formation of a crust which prevents the complete removal of water in the cane syrup. As the sample film formed in the aluminum capsule is thin, together with the water elimination occurs also releasing of volatiles from degradation reactions during oven drying. With the use of glass fiber paper (Figure 5), it is observed that the cane syrup sample is homogeneously distributed in the paper and that the crust formation is minimized. However, with the use of glass fiber paper in all factorial design tests, higher moisture contents were obtained when compared with those determined without glass fiber paper. This can be explained by considering that with the use of fiber glass paper the heat transfer between the sample and the sample holder is better favoring drying. Thus, drying times and temperatures need to be optimized to avoid that high temperatures or long exposure times of the sample to heat favor sugars degradation reactions and interfere in the moisture analysis [19-21].

In addition to the main effects were also observed interaction effects between drying temperature and drying time and between drying temperature, drying time and fiberglass paper (Figure 3) which suggests that the variables can not be optimized independently. The analysis of Figure 4a suggests that lower temperatures (70 ºC) and shorter drying times (90 minutes) are more recommended for the analysis of moisture in cane syrup with or without the use of fiberglass paper. As can be observed in Figure 5 with the use of fiberglass paper there is no crust formation and the heat transfer between the capsule and the sample is more homogeneous, thus favoring drying. Without the use of fiberglass paper, the effect of *case hardening* or crust formation and surface degradation reactions with volatiles release are accentuated [22]. At higher drying temperatures and drying times (105 ºC and 150 minutes) and with the use of fiberglass paper, higher moisture content can be observed (Figure 1), indicating that in addition to the water contained in the sample, other volatiles due to degradation reactions on surface sample are being eliminated during drying. As previously described, the increase in temperature and drying time favors the degradation of sugars with elimination of volatiles along with the water contained in the sample (Figure 4b) [19, 20, 21]. This behavior is consistent with the results obtained in the isothermal thermogravimetric study.

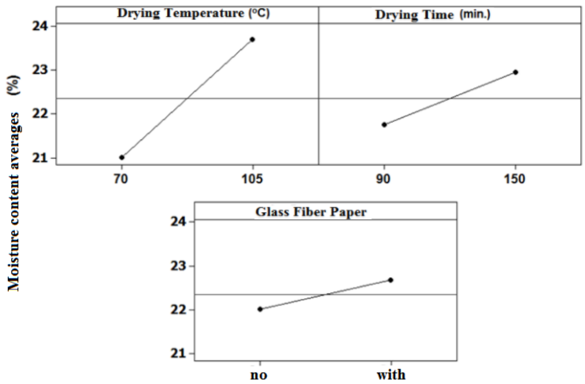


Figure 3. Main effects graph of 2^3 factorial design applied to optimization of oven drying of cane syrups.

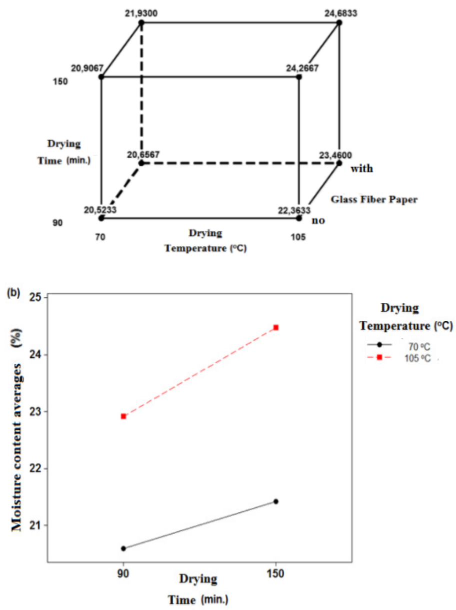
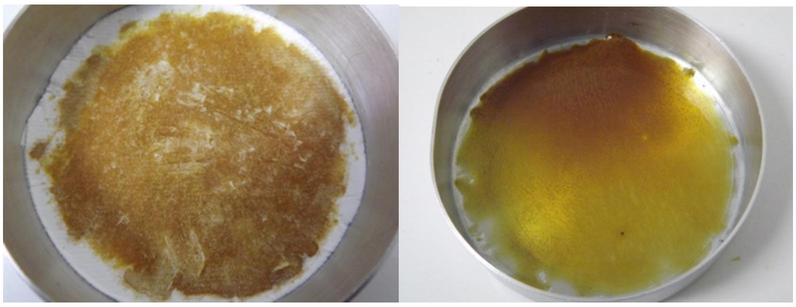


Figure 4. (a) Interaction effect graph between drying temperature, drying time and glassfiber paper (b) interaction effect graph between drying temperature and drying time.



(a) (b)

Figure 5. Photos of cane syrup samples after drying in an oven (a) with the use of fiberglass paper at 70 °C during 90 min and (b) without the use of fiberglass paper at 105 °C during 150 min.

When the moisture contents obtained in the factorial design are compared to the value determined by the Karl Fischer titration (20.52% ± 0.08), it is observed that the best analysis conditions for conventional oven drying are those presented in experiments 1 and 5 of Table 2, i.e., drying temperature and drying time of 70 °C and 90 min respectively, with or without the use of fiberglass paper. As a better sample distribution was observed on the paper that does not favor crust formation during conventional oven drying (Figure 5), the following analysis conditions were considered as optimized: drying temperature of 70 ° C, drying time of 90 minutes, sample mass of 1.0 g and aluminum caps with lid containing fiberglass paper disks.

3.3. Validation Study

The validation study of the proposed analytical methodology was performed by comparing the measurement of water/moisture contents between the conventional oven drying method and Karl Fischer titration (Table 4). The accuracy of the drying method was assessed through a paired *t-test* at the 95% confidence level for the differences between the water/moisture contents determined by the two analytical methods. Results (t_{obs} = -0.33, p = 0.747) suggest that there are not significant differences in the water/moisture contents determined by the analytical methods for this food matrix. Thus, the new drying method presents adequate accuracy for moisture analysis in cane syrup samples.

To evaluate the precision of the oven drying method an *F-test* was applied, which considers the ratio between the variances of the drying method and of the Karl Fischer titration. The confidence intervals for the ratio between variances and ratio between standard deviations were calculated at 95.0 % confidence interval. Analysis of the *F-test* results (F_{obs} = 3.23, p = 0.224) suggests that oven drying and the Karl Fischer methods have similar precision for the determination of moisture contents in cane syrup samples. These results are confirmed by the calculation of the confidence interval for the ratio between the variances (0.453 - 23.112), which has a lower limit of less than 1.0. This indicates that there are no significant differences in the precision of the oven drying method optimized in relation to Karl Fischer titration (reference method). The calculations confirm that the conventional oven drying technique developed has adequate precision for the determination of moisture in cane syrup samples.

Table 4. Average water/moisture contents determined by Karl Fischer titration and conventional oven drying for cane syrup samples.

Samples	Water/moisture contents (g 100g^{-1}) ± SD*	
	Karl Fischer	Oven Drying
CS1	20.52 ± 0.08	20.59 ± 0.18
CS2	18.60 ± 0.04	18.69 ± 0.21
CS3	14.01 ± 0.06	13.91 ± 0.06
CS4	17.41 ± 0.02	17.29 ± 0.26
CS5	16.73 ± 0.06	16.67 ± 0.18
CS6	18.83 ± 0.09	18.87 ± 0.19

*standard deviations calculated desvios padrão from duplicates of the tests

4. Conclusions

The results of the optimization study by isothermal thermogravimetry and factorial design suggested that it is possible to apply a conventional oven drying method for the analysis of moisture in cane syrup. The results of the validation study of the new conventional oven drying method demonstrated by statistical techniques that it presents adequate accuracy and precision when compared to the Karl Fischer titration method. This method of drying is advantageous, since it uses instruments and inputs of low cost and by this reason it could be applied in quality control laboratories, in inspection bodies laboratories or by small industries.

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