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F.L. Moreno, M.X. Quintanilla-Carvajal, L.I. Sotelo, C. Osorio, M. Raventós, E. Hernández, Y. Ruiz

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Volatile compounds, sensory quality and ice morphology in falling-film and block freeze concentration of coffee extract

Moreno[a,b,d] F.L., Quintanilla-Carvajal[b] M.X., Sotelo[b]L.I., Osorio[c] C., Raventós[d] M., Hernández[b] E., Ruiz[b] Y. [*]

[a]*Biosciencies Doctoral Program, Universidad de La Sabana, Campus Universitario del Puente del Común, Km 7 Autopista Norte de Bogotá, Chía – Cundinamarca – Colombia*

[b]*Agroindustrial Process Engineering, Universidad de La Sabana, Campus Universitario del Puente del Común, Km 7 Autopista Norte de Bogotá, Chía – Cundinamarca – Colombia. e-mail: ruth.ruiz@unisabana.edu.co*

[c] *Departamento de Química, Universidad Nacional de Colombia, AA 14490, Bogotá, Colombia*

[d] *Agri-Food Engineering and Biotechnology Department, Universidad Politécnica de Cataluña (UPC) C/ Esteve Terradas, 8. 08860 Castelldefels –Barcelona, Spain.*

Abbreviated running title: Block and falling-film freeze concentration of coffee extract

* Corresponding author: Ruth Yolanda Ruiz Tel +571-8615555 Ext 25217; e-mail: ruth.ruiz@unisabana.edu.co

Abstract

Coffee extract was freeze-concentrated through block and falling-film techniques. Solute retention and concentration efficiency were determined after one stage of these processes. Ice morphology was characterized through image analysis. Preservation of volatile compounds was determined through GC-MS. The effect of coffee extract on flavour was determined after freeze concentration through sensory evaluation. Solute occlusion was higher for falling-film than for block freeze-concentration, with an average distribution coefficient of 0.45 and 0.29, respectively. The ice crystal size was lower for the falling-film technique; this explains the higher solute occlusion. The dewatering capacity was higher for the falling-film technique, as this process is faster than block freeze-concentration. The most abundant volatile compounds of the coffee extracts were preserved after freeze concentration with both techniques. In the same way, no differences were found in most of the sensory attributes of the freeze-concentrated extract obtained using both techniques. Our results confirm the benefits of the block and falling-film freeze concentration techniques in preserving the quality of coffee extracts.

Key Words:

Coffee concentration

Volatiles

Cryoconcentration

Sensory evaluation

Ice morphology

1. Introduction

Coffee is the most traded food in the world, and the preservation of its flavour is very important during processing (Caporaso et al., 2014). Freeze-dried coffee is a higher quality product than soluble coffee due to its lower processing temperatures (Fissore et al., 2014). The process of obtaining freeze-dried coffee starts with an initial stage of aqueous extraction by percolation, followed by the concentration and drying of the extract. The objective of the concentration stage is to eliminate some of the water from the extract. This stage is performed through freeze concentration. Freeze concentration (FC) is a technology used to remove water from aqueous solutions by freezing (Sánchez et al., 2009) to reduce processing times (Moreno et al., 2014c).

Three techniques of freeze concentration are recognized: suspension FC, film FC (known as progressive FC) and block freeze concentration (known as freeze- thaw FC) (Moreno at al., 2014a). The most implemented FC technique is the suspension FC. In this technique, small ice crystals are produced in a scraped heat exchanger and then removed through washing columns (Qin et al., 2009). A high separation efficiency is achieved; however, the initial and operational costs are relatively high (Petzold and Aguilera, 2013). As a result, different techniques, such as falling-film and block FC, are being developed. In block freeze-concentration the solution is completely frozen in a vessel. Then, the solution is partially thawed to recover a concentrated liquid fraction (Aider and de Halleux, 2009; Moreno et al., 2014c; Nakagawa et al., 2010). On the other hand, in falling-

film freeze concentration (FFFC), the solution is circulated through a cooling plate. An ice sheet is formed on the plate and the solution is recirculated until a desired concentration is reached in a batch operation (Hernández et al., 2010). Several researchers have established the viability of both techniques to concentrate food solutions (Aider and de Halleux, 2008; Nakagawa et al., 2010; Petzold and Aguilera, 2013; Raventós et al., 2007; Sánchez et al., 2010; Petzold et al. 2015; Benedetti et al., 2015).

The behaviour of block and falling film freeze concentration is related to some parameters such as the solute occlusion in the ice, the effect of the technique on volatile compounds and the effect on sensory quality of the product. The separation efficiency in freeze concentration (FC) is related to solid occlusion in the ice layer that can be influenced by the morphology of ice crystals created by the freezing conditions and the solution type (Ayel et al., 2006; Butler, 2002; Okawa et al., 2009; Pardo et al., 2002). Understanding the quantitative relationships between freeze concentration and ice crystal morphology is of practical importance. The physical properties of the ice layer can be considered to be the result of the characteristics (size) and spatial arrangement of the crystals (Germain and Aguilera, 2012). The freezing stage is a key step because it fixes the morphology of the frozen material, and as a result, it can affect the efficiency of the freeze concentration process, which is why it is important to evaluate the morphology generated by the processes mentioned above. It has been observed that the distribution of ice crystals of different sizes depends not only on the freezing rates but also on the sample size and freezing direction, among other variables (Hottot et al. 2007). On the other hand, the sensory attributes of the

coffee beverage is one of its most important quality parameters, consequently, sensory analysis is the most used technique to evaluate coffee quality (Cheong et al., 2013; MacLeod et al., 2006; Sopelana et al., 2013; Farah et al., 2006). However, there are few reported works on the efficacy of volatile compound preservation when using FC (Ramos et al., 2005).

Block and falling-film FC have been studied in coffee extract concentration (Moreno et al., 2014a). However, the effect of FC on volatile compounds and the sensory quality of the beverage has not been studied in these techniques. In addition, the ice morphology achieved through these FC techniques and its relationship with solute occlusion has not been determined. Thus, the aim of the present study was to compare the solute retention, dewatering capacity per unit of time of the operation, ice morphology, volatile compound preservation, and sensory quality between falling-film freeze concentration and block freeze-concentration of a coffee extract.

2. Materials and methods

2.1. Materials

The coffee extract from roasted Colombian coffea arabica supplied by the company Buencafé Liofilizado de Colombia (Colombian Coffee Growers Federation) produced at industrial conditions was used for the FC tests. The extract was 13% w/w solids. The extract was stored at -18°C and thawed at 4°C for 8 hours prior to the tests.

2.2. Freeze concentration tests

2.2.1. Block freeze-concentration tests

One stage of block FC was tested according to the parameters reported by Moreno et al., (2014c). The block FC technique consisted of the complete freezing of the extract in a closed vessel and the subsequent partial thawing and separation of the liquid phase. The tests were performed in the device shown in Figure 1a. The coffee sample (160 g) was placed into a cylindrical double-jacketed container that was 5.2 cm in diameter and 8.5 cm in height. The internal jacket was cooled through a mixture of ethylene glycol and water (53% w/w) from a bath (Polystat, Cole Parmer, USA) with temperature control (-35 °C to 150 °C +/- 0.01 °C). The cooling fluid temperature was set at -10 °C. The cooling fluid was circulated into the internal jacket once it reached that temperature.

Ice grew from the centre to the external wall of the container. When the sample was completely frozen, it was thawed by heating the external jacket at 20°C with the fluid from the second bath. Fifty percent of the extract mass was collected and separated from the ice, according to the results proposed by Moreno et al. (2014c). The solid concentration (Cs) of the liquid and the ice fractions was measured via refractometry (Atago Pal 100, Japan). Cs is defined as the mass of coffee solids per unit of mass of coffee solution. The relationship between Brix degrees and CS is represented by the equation Cs=0.87 °Brix, as reported by Moreno et al., (2015). The two fractions were stored at 4°C for 12 hours for the analysis of volatile compounds. The tests were performed in triplicate.

2.2.2. Falling Film Freeze Concentration Tests

One stage of FFFC was tested according to the parameters reported by Moreno et al., 2014b. The FFFC remained in continuous circulation of the extract through a refrigerated plate until ice sheet formation and separation occurred. The coffee extract (800 g) was freeze-concentrated using the experimental setup outlined in Figure 1b. The coffee extract flowed through a descending film over a cooling plate that was 25 cm in width and 20 cm in height. The extract was collected in a tank and recirculated by a VGC-400 peristaltic pump (Seditesa, Spain). The cooling fluid temperature was set at -20 °C. The cooling fluid was circulated into the plate once it reached that temperature. Ice grew on the surface of the freezing plate and was removed at the end of the stage. This stage was completed after 2 hours when the ice produced was close to 50% of the initial extract. The solid concentration of the liquid fraction and the ice were measured through refractometry (Atago Pal 100, Japan). The temperature of the liquid phase was determined during the tests. The experiments were performed in triplicate.

2.2.3. Data analysis for FC tests

Solute retention in the ice produced through block and falling-film FC was analysed by comparing the solute yield, the concentration index, the partition coefficient, the ice front growth and the dewatering capacity of the operation.

Solute yield (Y) represents the amount of solute or coffee solids recovered in the liquid fraction. It was defined as the relationship between the mass of solute present in the freeze-concentrated liquid and the mass of the solute present in the

initial solution, as calculated by Eq. 1 (Moreno et al., 2014b; Nakagawa et al., 2010).

$$Y=m_{s\ liq}/m_{s\ 0} \quad (1)$$

Where *Y* is the solute yield, $m_{s\ liq}$ is the solute mass in the liquid fraction, and $m_{s\ 0}$ is the initial solute mass.

The Concentration Index (CI) was defined as the relationship between the solid concentration in the liquid freeze-concentrated fraction and the solid concentration in the initial solution (Nakagawa et al., 2009).

$$CI = C_{s\ liq}/C_{s\ 0} \quad (2)$$

Where CI is the concentration index, $C_{s\ liq}$ is the solid concentration (% m/m) in the freeze-concentrated liquid, and $C_{s\ 0}$ is the solid concentration (% m/m) in the initial solution.

The ice fraction (f ice) was defined as the ratio between the ice mass and the mass of the original solution as calculated by Eq. 3 (Miyawaki et al., 2012; Nakagawa et al., 2010):

$$f = m_{ice}/m_0 \quad (3)$$

The average distribution coefficient was defined as the ratio between the solid concentration in the ice ($C_{s\ ice}$) and the solid concentration in the freeze-concentrated liquid ($C_{s\ liq}$), as shown in Eq. 4 (Chen and Chen, 2000).

$$K = \frac{C_{s\ ice}}{C_{s\ liq}} \quad (4)$$

The average ice growth rate was calculated by Eq. 5 (Chen, Chen, & Free, 1999), where V_{ice} is the ice growth rate, m_{ice} is the ice mass, $C_{s\ ice}$ is the coffee

concentration in the ice, t is the total freezing time, A is the heat transfer area, and ρ_{ice} is the density of ice.

$$\bar{v}_{ice} = \frac{m_{ice}(1-C_{s\ ice}/100)}{t\ A\ \rho_{ice}} \cdot 10^6\ \ (\mu m\ s^{-1})\ \ (5)$$

Finally, the dewatering capacity was calculated as the relationship of the mass of water removed from the solution per unit of mass of initial extract and per unit of time (t), Eq. 6.

$$Dewatering\ capacity = m_{ice} \cdot (1 - (C_{s\ ice}/100))/(m_0 \cdot t)\ (6)$$

2.3. Image analysis of the morphological structure of the ice crystals

Ice samples from block and falling-film freeze concentration were characterized by microscopic analysis. In every experiment, ice was removed from the equipment. Then, a portion of the frozen sample was transferred to a cryomicrotome CM1850 (Leica, Germany) with a chamber temperature set at -20°C. The ice crystals produced were observed with a Nikon Eclipse Ti microscope (Nikon, United States) using transmitted light and a 10X Nikon DS-Fi1 objective. To avoid thawing of the frozen samples, the microscope was fitted with a PE120 Peltier-based cooling stage coupled to a PE 94 temperature control system (Linkam Scientific Instruments, United Kingdom), allowing temperature control down to −20 °C. This cooling stage and all of the materials employed for sample manipulation (spatula, coverslip glasses, tweezers and so on) were previously tempered to the freezing point of the freeze-concentrated sample (-21°C).

The images of the ice crystals formed in the samples were 20148 x 1536 pixels and were captured using a Nikon microscope camera (Nikon, United States) fitted to the microscope by means of the NIS-elements F V2.30 software interfaced to a personal computer. These images were converted to grey scale (8 bits) maps and then to binary images (black and white) using ImageJ v.5.1 (National Institutes of Health, Unites States) as the image analysis software. A threshold was applied to each image by using the default settings. Spatial measurements, originally expressed as the number of pixels, were calibrated using a micrograph taken from a 1-mm stage micrometer placed on the microscope stage.

The hydraulic diameter, area, and circularity values were estimated using the ImageJ v.5.1 software. More than 30 images were analysed at the top, at the middle, and at the bottom of the sample to obtain a good reproducibility of the parameters of the ice crystals.

2.4. Volatile compound analysis

The volatile compounds of the initial extract, the liquid, and the ice fractions of block FC and FFFC were obtained by HS-SPME (Headspace-Solid Phase Microextraction) and analysed by gas chromatography coupled to mass spectrometry (GC-MS) according to the method reported by Ribeiro et al., (2010) with some modifications. Each sample (2 g) was equilibrated for 1 h in a 40-mL sealed vial at 18 °C using a magnetic stirrer. The volatile compounds released from the headspace of each sample was collected on a DVB/PDMS fibre (75 μm

thickness, Supelco Inc., Bellefonte, PA, USA) for 1 h at 18 °C and then directly injected (the desorption time was set at 5 min) into a gas chromatograph Shimadzu GC-17A coupled to a mass selective detector QP5050 and operated in splitless mode. The mass spectra were recorded in electronic impact (EI) ionization mode at 70 eV and were scanned in the range m/z 40-350 µ. An RTX-5 fused silica column (Restek, Bellefonte, PA, USA, 30 m x 0.32 mm i.d., 0.25 µm film thickness) was used. The column oven was programmed from 40 (after 2 min) to 250 °C at 5 °C/min, and the final temperature was held for 5 min. The injector temperature was maintained at 250 °C; the carrier gas was 1.5 mL of He/min. All of the measurements were performed in triplicate. Structural assignments of volatile compounds were performed by comparison of analytical (retention index and mass spectra) data of each analyte with the commercial mass spectral databases WILEY and EPA/NIH and by comparison with published data by Sanz et al. (2002). Linear retention indices were calculated according to the Kovats method using a mixture of normal paraffin C_6-C_{28} as external references. Data were processed by Class 5000 v 2.2 MS-Workstation software.

The relative ice loss percentage from each FC technique was calculated by Eq. 7. modified from Ramos et al., (2005), where RPA is the relative percent area in the ice fraction and liquid fractions.

Relative ice loss percentage= RPA ice/(RPA ice + RPA liq)*100 Eq. (7)

2.5. Sensory analysis

A discriminant sensory evaluation was performed on the liquid and ice fractions obtained from the two methods (block and falling-film FC) in comparison to the initial extract. The sensory panel was composed from seven to nine trained judges recruited from the staff of the “Laboratorio de Análisis Sensorial de Alimentos, Universidad de Antioquia (Medellín, Colombia)”, who were trained in several sessions prior to analysis. The coffee descriptors, including aroma, acidity, bitterness, sweetness, tobacco, fruity, floral, aftertaste, body, and global impact, were evaluated according to the National standard NTC 4883 (Icontec, 2000). The panellists evaluated the four coffee samples (1.5% solid content in water at 90°C solid), which were randomly served in white cups coded with random numbers. The panellists were instructed to rank the samples from ten (10) to zero (0) according to the intensity, with 10 being a very strong attribute intensity. The results were averaged for each of the descriptive attributes and plotted in a web diagram.

2.6. Statistical analysis

All of the tests were performed in triplicate. The data included the mean and standard deviation. One-way analysis of variance (ANOVA) was applied to the results with a level of significance of 95% to evaluate the significance of the differences. For the sensory evaluation, a Dunnett test was applied to establish the significance of the difference. The statistical analysis was performed using the SAS 9.2 software package.

3. Results and discussion

3.1. Freeze concentration tests

The results regarding the concentration of coffee solids in the liquid (C liq) and ice (C ice) fractions achieved through block and falling-film FC are shown in Table 1. The concentration index (CI) achieved through the block technique was significantly higher than the CI obtained through the FFFC. The concentration increased 1.5 times to 20.8% with the block technique. On the other hand, the FFFC increased the concentration 1.3 times and reached a value of 17.8%. The solute yield (Y) for the block technique was higher than for the FFFC technique, but the difference was not statistically significant. This value is affected by the ice fraction. Solute occlusion in the ice, expressed by the average partition coefficient, was significantly higher in FFFC than in block FC.

The best result of the block technique in terms of the lowest solute retention can be explained by the difference in the ice front rate, which was higher for FFFC. At a higher freezing rate, a higher amount of solute can be retained in the ice (Caretta et al., 2006). When the heat transfer rate is higher than the mass transfer rate, solute elution cannot exceed the ice front growth rate and the solute is trapped in the ice. In addition, the difference in the freezing point produced by the concentration gradient in the liquid around the ice front produces a zone where ice growth is unstable (Petzold and Aguilera, 2009). The ice growth is trapped in the portions of concentrated liquid; this phenomenon is known as constitutional supercooling and it can affect concentration efficiency (Butler, 2001; Rodrigues et

al., 2011; Ruiz et al., 2010; Sánchez et al., 2010). This effect was reported in block freeze-concentration (Moreno, et al., 2014c; Nakagawa et al., 2010) and in falling-film FC (Chen and Chen, 2000; Gulfo et al., 2013). The ice growth rate depends on the cooling temperature and the heat transfer area. These design parameters are very important in the design of FC equipment.

The lowest solute occlusion obtained through the block technique contrasted with the result of the dewatering capacity per unit of time for both techniques. The dewatering capacity was significantly higher for the falling-film FC. This technique produced a value of 0.28 kg of water per kg of coffee extract per hour, 3.6 times the dewatering capacity of the block technique. Block FC can employ a high freezing time, and if the freezing rate is increased to reduce the process time, the ice growth would be more occluded and the concentration index would be lower in the concentration of coffee extract (Moreno et al., 2014b). FFFC allowed high freezing rates with relatively low solute occlusion due to the solute dragging that was produced for the falling-film of the fluid. Both techniques can be developed in successive stages to increase the concentration index. These results suggest that FFFC is a good alternative to concentrate the extract with low processing time, and the block technique is appropriate for obtaining ice with high purity.

3.2. Image analysis of the morphological structure of the ice crystals

The images of ice crystals obtained during block and falling-film FC are shown in Fig. 2. Ice crystals were present as cells with similar shapes of solid prisms or plate ice morphologies, a behaviour that was observed in both techniques. This

morphology depends on the cooling rate, the supercooling, and the presence of solutes (Petzold and Aguilera, 2009). Channels of concentrated coffee extract were observed between the ice crystals, verifying the freeze concentration phenomenon. These channels of concentrated liquid determine the level of solute occlusion inside the ice layer. The level of solute occlusion is related to ice morphology, which depends on the shape and size of the ice crystals. Differences in these parameters were observed between each FC technique among the distance measured from the cooling surface. Morphometric parameters were calculated to quantify these differences.

The morphological characteristics of ice crystals were determined through image analysis in block and falling-film FC (Table 2). In general, the size of ice crystals was higher for block FC than for FFFC. The area and diameter were statistically equal in the first position located close to the cooling surface; however, the diameter and area were higher for the block technique than for FFFC in subsequent positions. The size of ice crystals increased with the distance from the cooling position. This result is explained by the decrease in the heat transfer rate due to the thermal resistance produced by the growing ice layer. The average distribution coefficient and the ice growth rate were higher for the FFFC than for Block FC, as shown in Table 1. Fast ice growth produces a crystal of small size. The highest K obtained in the FFFC can be explained by the lowest diameter of ice crystals. The smaller the ice crystal, the larger the amount of liquid trapped in the channels. This result confirms that solute occlusion is higher when ice growth is faster.

The circularity of the ice crystals decreased with the ice front position; however, the difference was not statistically significant. Morphometric parameters, such as size and circularity, can be important in the thawing step of block FC, where a low tortuosity of the channels is desirable to recover the liquid fraction. In the same way, solutes can be recovered by the partial thawing of the ice layer produced in FFFC (Moreno et al., 2014a), and the shape of ice crystals can play an important role in this step. The morphometric parameters of ice crystals affect solute retention in the ice layer. These parameters could be an interesting topic of research to increase the separation efficiency of block and falling-film freeze concentration.

3.3. Volatile compound analysis

The most abundant volatile compounds of the initial extract, the liquid, and the ice fractions of block FC and FFFC were identified and quantified through GC-MS (Fig. 3). It is evident that all of the profiles were qualitatively and quantitatively (relation among volatile compounds determined by area percentage in GC analysis) similar, showing that the volatile compounds were retained in the samples after freeze concentration. The eight most abundant volatile compounds were identified in the coffee extract and the freeze-concentrated samples (Table 3), which represent approximately 70% of the volatile compounds detected. These volatiles were mainly furfural, furfuryl derivatives, pyrazines, and aldehydes. The furan concentration in coffee drink depends on its content in coffee powder as well as the brewing procedure (Petisca et al, 2013). Pentanal has been identified in

coffee beverages (Toci & Farah, 2008) and is associated with vanilla, fruity, and nutty odour notes (Flament, 2002). Furans, such as furfural, furfuryl alcohol, and furfuryl acetate, are responsible for toasted odour notes, such as burnt, caramel-like, and smoke (Cheong et al., 2013; Roldán et al., 2003; Toci and Farah, 2008; Caporaso et al., 2014; Piccino et al. 2014). Pirazines are a dominant group of volatile compounds in coffee aroma that are associated with roast and earth odour notes (Budryn et al., 2011; Cheong et al., 2013; Korhonová et al., 2009; Sopelana et al., 2013; Sunarharum et al., 2014).

In general, the relative concentration of volatile compounds was preserved in the freeze-concentrated liquids obtained from both techniques. Differences were found only in furfural, the concentration of which was slightly decreased in the liquid fractions of both techniques. Furfuryl alcohol was better preserved in FFC than in Block FC; in contrast, 2-ethyl-3,5-dimethylpyrazine preservation was higher in block FC than in FFFC.

The relative ice loss percentage of volatile compounds after processing is reported in Table 3. A relative ice loss percentage of 50% indicates that the volatile compound is distributed equally in the liquid and ice fractions, a percentage higher than 50% indicates a higher retention in ice than in the liquid fraction, and a value lower than 50% indicates a higher presence of the volatile compound in the liquid freeze concentrated fraction. For most cases, the relative ice loss percentage of volatile compounds was approximately 50%, indicating that there was not a selective loss of volatile compounds in the ice or the liquid fraction (ice fraction was 50% in mass for block FC and 54% for FFFC). A comparable result was reported

by Gunathilake et al. (2014) for progressive freeze concentration of coffee extract, where the incorporation of components into the ice phase was nonselective.

Volatile compounds were preserved in the freeze concentrated liquid, and the ice loss percentage indicated that the retention of volatile compounds is not preferential in one of the phases. However, the sensory profile and the intensity of the flavour has to be evaluated. These results are presented in the sensory analysis in the section 3.4.

3.4. Sensory analysis

Coffee cup analyses were performed before and after freeze concentration to evaluate if this process affects the nonvolatile composition of coffee extract, which is directly related to taste properties. Fig. 4 shows the results of the sensory analysis in a spider web diagram. Samples were characterized by the highest scores in aroma, acidity, bitterness, body, and global impact. The lowest scores were obtained for sweetness, tobacco, fruity, floral, and aftertaste.

The ice and liquid fractions of Block FC and FFFC were compared with the initial extract. Most of the sensory parameters evaluated in the liquid and ice fractions were not significantly different from those evaluated in the initial extract, as shown in Table 4. In block freeze-concentration, eight of ten attributes were statistically equal to the initial extract. A slight difference in body and global impact was found. In falling-film freeze concentration, seven of the ten attributes were equal to the initial extract. The aroma profiles of the freeze-concentrated samples

and the initial extract were similar. These results show that freeze concentration is an effective technique to preserve the sensory quality of coffee extract.

A slight difference in body and global impact was found. A difference in the floral note was detected in the falling-film technique. Fluid motion in this technique may cause a small loss of some minor volatile compounds responsible for this note. No differences were found between the liquid and ice fractions in both techniques. This result suggests that compounds responsible for aroma or flavour were equally distributed in the ice and the liquid fractions. A comparable result was reported for progressive freeze concentration of fruit pulps (Ramos et al., 2005).

The differences in global impact can be explained by the different residual notes identified by the panel associated with the handling of the extract during processing or by the slight differences found in pentanal, furfural, 2-furanmethanol acetate, 2-ethyl-3,5-dimethylpyrazine, and nonenal. The differences in the floral note can be attributed to the minor volatile compound loss associated with this note. The differences in the body attribute can be explained by the production of sediments in the coffee extract. When coffee solutions are cooled, gelation is still in the solution (Delgado et al., 2008; Thaler, 1978). Cryogels could be the result of freezing and thawing (Doyle et al., 2006) considering the galactomannan content in the coffee extract. Gel presence depends on the type of coffee and the roasting method (Navarini et. al. 1999). More research is needed to identify the influence of cryogels on the quality of freeze-concentrated coffee.

A comparable result for the preservation of quality with freeze concentration was reported for the preservation of functional quality by Moreno et al. (2014c). The concentration of bioactive compounds and the antioxidant activity of coffee

extract were preserved when using freeze concentration. In the present work, volatile compounds and sensory quality were also preserved. In both results, volatile and bioactive compounds were equally distributed in the ice and the liquid fractions, which indicates that the increase in the total solid concentration produces a concentration of the compounds responsible for sensory and functional properties without a selectivity of the compounds retained in the ice. These results confirmed the benefits of implementing freeze concentration to preserve the quality of the extract.

4. Conclusions

Block and falling-film freeze concentration techniques were tested to compare the solute retention in ice, ice morphology, volatile compounds, and preservation of sensory quality in both techniques. The freezing rate affects the average distribution coefficient. Block FC produces ice with less solute retention and a higher concentration index in one stage than falling-film FC due to its low freezing rates. Falling-film FC is a faster technique and has a higher dewatering capacity than block FC.

The morphology of the ice is related to the freezing rate. For a high freezing rate, small ice crystals and high solute retention in the ice were obtained. The diameter and area of the ice crystals produced through block FC were higher than those of ice crystals obtained from FFFC due to the freezing rate. The size of the

ice crystals defines the space where the concentrated liquid is retained, and its control is important to increase the concentration efficiency.

The most abundant volatile compounds of coffee extract were preserved in both techniques of freeze concentration. The sensory quality of the extract was preserved by freeze concentration. Our results indicate that falling-film freeze concentration can be used as a fast technique to concentrate coffee extract, and block freeze-concentration is effective for producing ice with a low solid retention. Both techniques are useful to preserve the sensory quality of the beverage.

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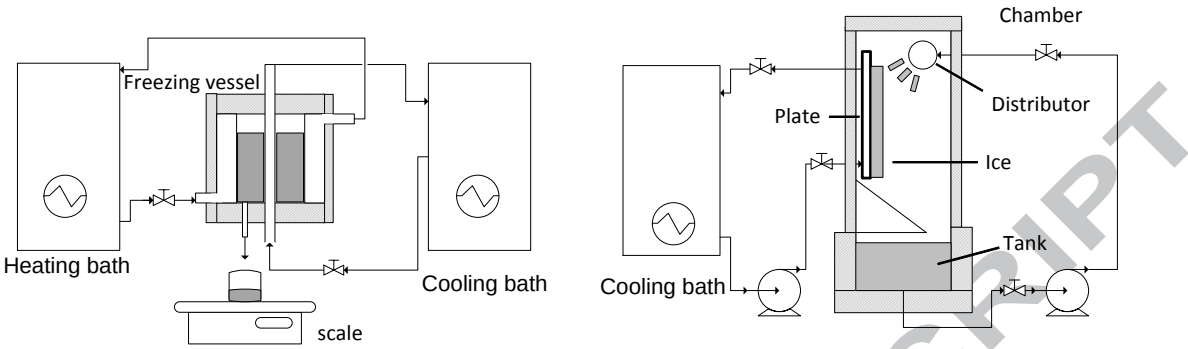

(a) (b)

Fig. 1. Experimental setup. (a) Block freeze concentrator; (b) falling-film freeze concentrator.

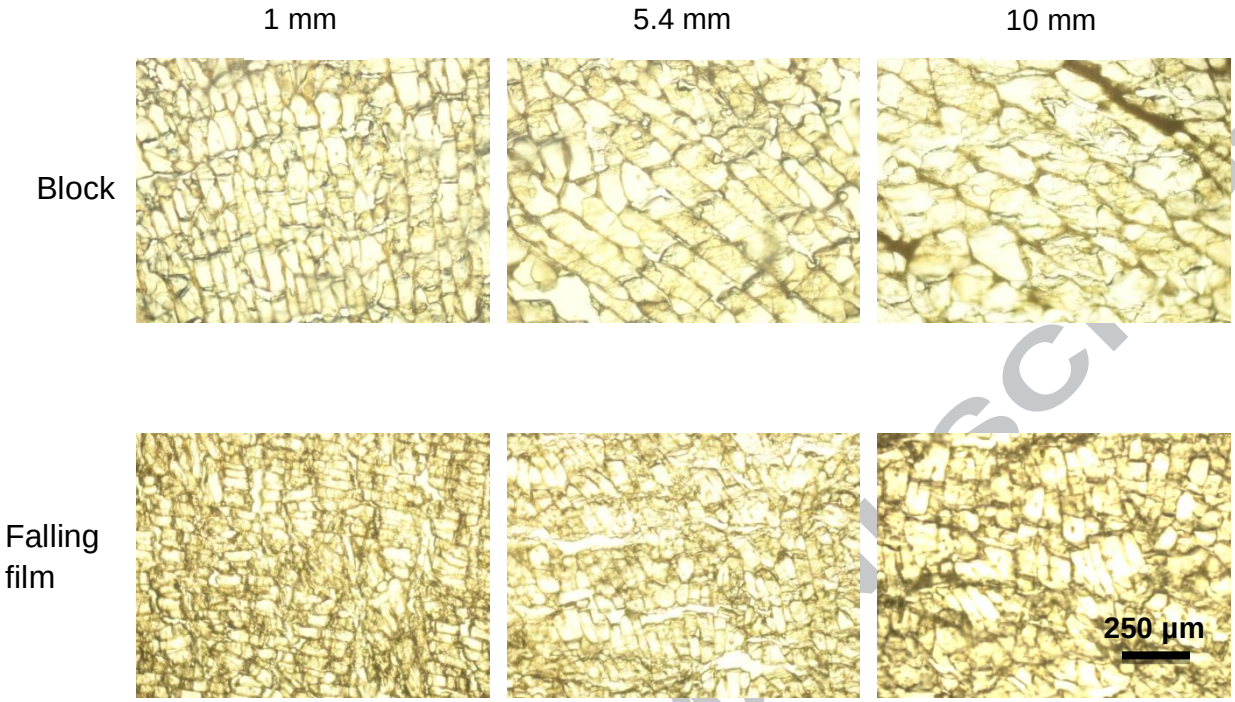

Fig. 2. Microphotographs of the ice crystals of block and falling film-freeze concentration at three positions from the cooling surface (10X).

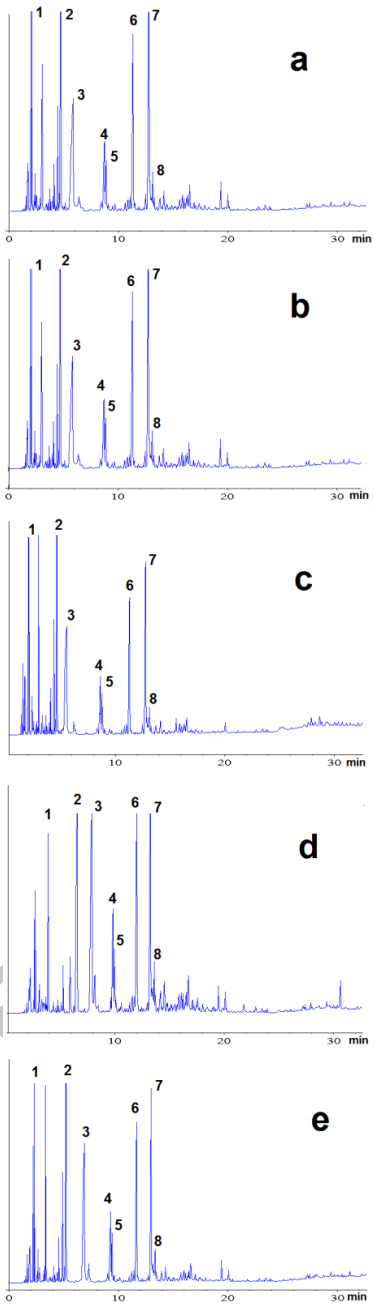

Fig. 3. GCMS analyses of volatile compounds from the a) initial extract, b) block FC liquid fraction, c) block FC ice faction, d) falling-film FC liquid fraction, and e) balling-film FC ice fraction obtained by HS-SPME. The numbers correspond to Table 3

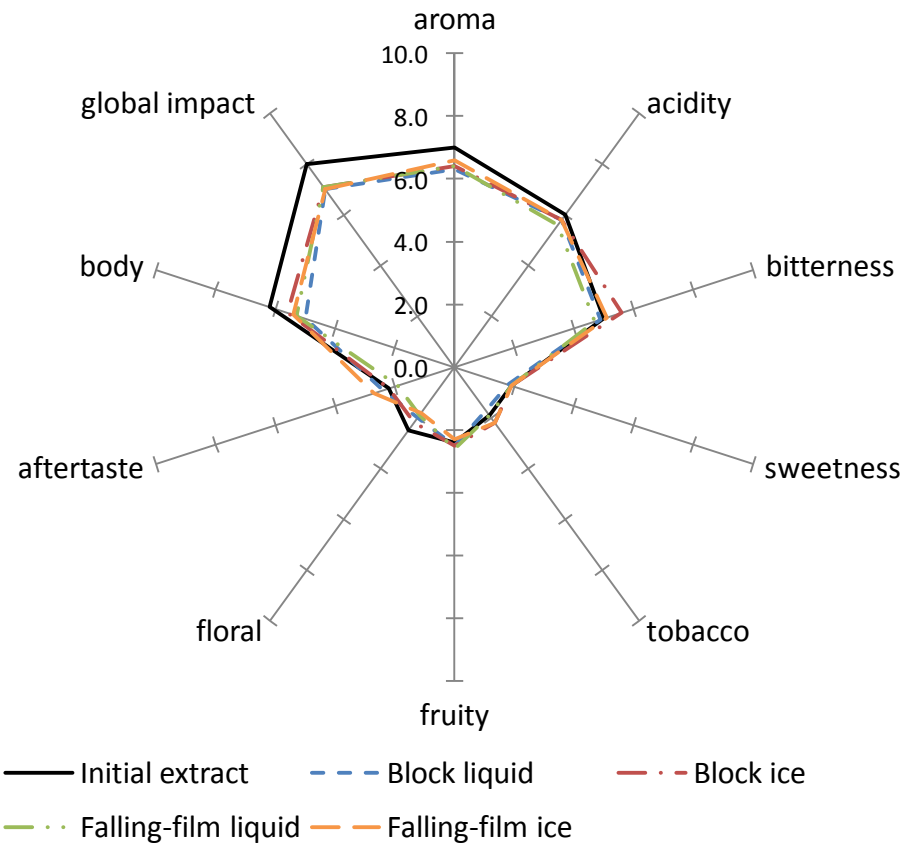

Fig. 4. Comparative sensory analysis of the initial coffee extract and freeze-concentrated samples

Table 1. Results of freeze concentration tests.

Technique	Block	Falling Film
C_0 (%m/m)	13.4 ± 0.1	13.4 ± 0.1
C_{liq} (%m/m)	20.8 ± 0.9 [a]	17.8 ± 0.3 [b]
C_{ice} (%m/m)	6.0 ± 0.9 [c]	8.0 ± 0.6 [d]
CI	1.55 ± 0.03 [e]	1.33 ± 0.03 [f]
Y	0.77 ± 0.03 [g]	0.72 ± 0.05 [g]
K	0.29 ± 0.05 [h]	0.45 ± 0.03 [i]
f	0.50 ± 0.00 [j]	0.46 ± 0.04 [j]
Average ice growth rate (μ s^{-1})	0.85 ± 0.02 [k]	1.37 ± 0.12 [l]
Dewatering Capacity (kg water / (kg extract · h))	0.08 ± 0.01 [m]	0.28 ± 0.02 [n]

Different letters indicate statistically significant differences ($p < 0.05$).

Table 2. Morphometric parameters of ice crystals produced in block and falling-film freeze concentration.

Position (mm)		Area (mm^2)	Hydraulic Diameter (mm)	Circularity	K	Average ice growth rate (μ s^{-1})
Block	1	0.008 ± 0.001[a]	0.064 ± 0.001[f]	0.440 ± 0.007[k]	0.29 ± 0.05 [m]	0.85 ± 0.02 [p]
	5.4	0.030 ± 0.001[b]	0.124 ± 0.001[g]	0.421 ± 0.007[l,]		
	10	0.080 ± 0.002[c]	0.196 ± 0.003[h]	0.415 ± 0.006[l]		
Falling film	1	0.008 ± 0.001[a]	0.065 ± 0.001[f]	0.449 ± 0.008[k]	0.45 ± 0.03 [n]	1.37 ± 0.12 [q]
	5.4	0.013 ± 0.001[d]	0.080 ± 0.001[i]	0.431 ± 0.007[k,l]		
	10	0.020 ± 0.001[e]	0.100 ± 0.001[J]	0.422 ± 0.007[l]		

Different letters indicate statistically significant differences ($p < 0.05$).

Table 3. Volatile compounds identified in coffee extract before and after freeze concentration.

Peak	Compound	IK[a]	Sample[b]					Relative ice loss percentage after freeze concentration	
			Initial	Block Liq	Block ice	Falling film liq	Falling film ice	Block	Falling film
1	Pentanal	<800	+	+	+	+	+	63.2	68.1
2	Furfural	809	++++	+++	++++	+++	++++	60.1	58.1
3	Furfuryl alcohol	850	++++	+++	++++	++++	++++	53.5	49.9
4	2,6-Dimethyl pyrazine	949	+	+	+	+	+	53.0	51.4
5	5-Methyl-2-furfural	954	+	+	+	+	+	50.6	52.2
6	Furfuryl acetate	1032	++	++	++	+++	++	47.1	46.8
7	2-Ethyl-3,5-dimethylpyrazine	1074	++++	++++	++	+++	+++	40.5	46.6
8	2-Nonenal	1085	+	+	+	+	+	47.5	49.6

[a]Kovats index (RTX-5)

[b]Volatile relative amount expressed as relative area in GC analyses: + < 6%, ++ 6-10%, +++10-15%, ++++ >15%.

Table 4. Significance of differences of quantitative descriptive analysis among freeze concentration techniques.

	Initial extract	Block liquid	Block ice	Falling-film liquid	Falling-film ice
aroma	7.0 ± 0.6 [a]	6.3 ± 1.4 [a]	6.4 ± 1.1 [a]	6.4 ± 0.9 [a]	6.6 ± 0.6 [a]
acidity	6.0 ± 0.7 [b]	5.8 ± 1.0 [b]	5.8 ± 1.0 [b]	5.6 ± 1.2 [b]	5.8 ± 1.1 [b]
bitterness	5.0 ± 0.6 [c]	4.9 ± 0.9 [c]	5.6 ± 0.8 [c]	4.7 ± 0.8 [c]	5.1 ± 0.9 [c]
sweetness	1.9 ± 0.4 [d]	1.8 ± 0.4 [d]	1.9 ± 0.6 [d]	1.9 ± 0.6 [d]	1.9 ± 0.7 [d]
tobacco	1.9 ± 0.9 [e]	1.7 ± 0.6 [e]	2.2 ± 0.7 [e]	1.9 ± 0.5 [e]	2.2 ± 0.5 [e]
Fruity	2.4 ± 0.7 [f]	2.5 ± 1.2 [f]	2.5 ± 0.7 [f]	2.6 ± 0.7 [f]	2.3 ± 0.8 [f]
Floral	2.5 ± 0.7 [g]	2.0 ± 0.9 [g]	2.2 ± 0.6 [g]	1.9 ± 0.7 [h]	1.8 ± 0.5 [h]
aftertaste	2.2 ± 0.6 [i]	2.4 ± 0.9 [i]	2.2 ± 0.6 [i]	1.9 ± 0.4 [i]	2.7 ± 0.8 [i]
Body	6.2 ± 0.5 [J]	5.0 ± 1.0 [k]	5.6 ± 0.7 [k]	5.3 ± 1.0 [k]	5.4 ± 0.9 [k]
global impact	8.0 ± 0.4 [l]	7.0 ± 0.8 [m]	7.1 ± 1.0 [m]	7.1 ± 1.0 [m]	7.0 ± 0.8 [m]

Different letters indicate statistically significant differences ($p < 0.05$).

Highlights

Block and falling film freeze concentration of coffee extract were compared
The major volatile compounds of the coffee extracts were preserved
The sensory attributes of the freeze-concentrated extract were preserved
Falling film technique produced high solute occlusion and small ice crystals
The dewatering capacity was higher for the falling-film technique