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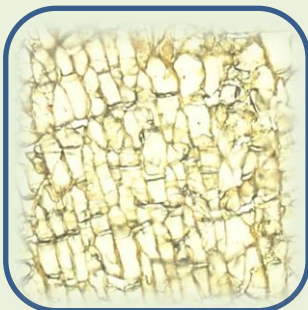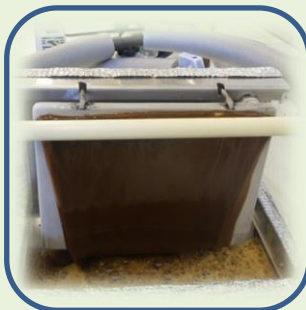UNIVERSIDAD DE LA SABANA
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FREEZE CONCENTRATION OF COFFEE EXTRACT: STUDY OF BLOCK AND FALLING-FILM TECHNIQUES

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FREEZE CONCENTRATION OF COFFEE EXTRACT: STUDY OF BLOCK AND FALLING-FILM TECHNIQUES.

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CRIOCONCENTRACIÓN DE EXTRACTO ACUOSO DE CAFÉ: ESTUDIO DE LAS TÉCNICAS DE BLOQUE TOTAL Y PELÍCULA DESCENDENTE.

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A mi esposa María Isabel y mi hija Natalia, la razón de mi vida.

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ABSTRACT

Coffee is the most traded food in the world. The coffee industry has a great economic and social relevance worldwide. The sensory and functional properties of the product are highly important for the consumers, and therefore, technologies that promote quality preservation are highly valued in coffee processing. In the production of freeze-dried coffee, freeze concentration is used to remove water from the extract. Water removal in freeze concentration is achieved by cooling the solution until ice crystals form and separate. Freeze concentration is a technology known for its ability to preserve the quality of the product thanks to low processing temperatures.

Three techniques are used according to ice crystal growth: suspension, film (progressive or falling-film) and block (total or partial). Suspension freeze concentration is the most implemented technique at the industrial level. This is an efficient technique in terms of ice purity and increased concentration; however, it requires complex systems for ice separation and many moving parts, which increases the initial and operating costs. For this reason, other freeze concentration techniques have been studied. Different techniques, such as falling-film freeze concentration, and block freeze concentration are being developed seeking to reduce operational costs.

In the present work, block and falling-film freeze concentration techniques used to concentrate aqueous coffee extract were studied. Equipment to study those techniques was designed and implemented. The effect of the operational variables of block and falling-film freeze concentration on separation efficiency was established. Preservation of bioactive compounds, volatile compounds, antioxidant activity, and sensory quality of the coffee extract when using freeze concentration was demonstrated. Finally, an operational strategy was proposed to integrate the studied techniques. Separation efficiency obtained with this process was comparable to industrial standards.

The project was developed as a doctoral thesis under joint supervision by the Ph.D. in Biosciences of the University of La Sabana in Bogotá, Colombia and the Agribusiness Technology and Biotechnology Doctorate of the Technical University of Catalonia in Barcelona, Spain. Five papers were published as a result of the present work.

RESUMEN

El café es el alimento más comercializado en el mundo y por esto es alta su importancia económica y social. En la industria del café, la calidad sensorial y funcional de la bebida es un parámetro de alta importancia, por lo cual se promueve el uso de tecnologías de proceso que permitan su preservación. En el proceso de obtención de café soluble liofilizado se utiliza la crioconcentración como una etapa para la eliminación parcial del agua del extracto.

La crioconcentración es una tecnología para la eliminación de agua de soluciones mediante su enfriamiento hasta la formación y separación de cristales de hielo. Es una técnica que puede preservar la calidad del producto debido a las bajas temperaturas que maneja.

Existen tres técnicas de crioconcentración: suspensión, película y bloque. La única técnica disponible comercialmente a nivel mundial es la crioconcentración en suspensión. Esta es una técnica que logra altas eficiencias de separación pero los equipos requieren gran número de partes móviles por lo cual es relativamente costosa. Debido a esto se busca el desarrollo de técnicas más simples que a la vez consigan una alta eficiencia en la separación. La crioconcentración en película descendente y en bloque son nuevas técnicas que se han propuesto como alternativas más simples que pueden reducir costos operacionales.

En el presente proyecto se estudió la crioconcentración en bloque total y en película descendente para la obtención de extractos concentrados de café. Se realizó el diseñó de una unidad de estudios para la crioconentración. Igualmente, se estableció el efecto de las variables operativas de la crioconcentración en bloque y en película sobre la eficiencia de la separación y se demostró la preservación de los componentes bioactivos, la preservación de los componentes volátiles y de la calidad sensorial del extracto de café. Se obtuvieron modelos matemáticos para la predicción del coeficiente de distribución en el hielo que permite predecir el comportamiento de la crioconcentración. Finalmente, se propuso una estrategia operativa para integración de las técnicas estudiadas que permite obtener eficiencias de separación acordes con los estándares industriales.

El proyecto se desarrolló bajo la modalidad de Cotutela de Tesis Doctoral en forma conjunta entre el Doctorado en Biociencias de la Universidad de La Sabana en Bogotá, Colombia y el Doctorado en Tecnología Agroalimentaria y Biotecnología de la Universidad Politécnica de Cataluña en Barcelona, España. Como resultado del proyecto se publicaron cinco artículos en revistas indexadas.

RESUM

El cafè és l'aliment més comercialitzat del món i té una gran importància econòmica i social. En la indústria del cafè, la qualitat sensorial i funcional de la beguda és un paràmetre important la qual cosa incentiva l'ús de tecnologies de procés que permetin mantenir-ne la qualitat. Durant el procés d'obtenció de cafè liofilitzat s'utilitza la crioconcentració com etapa prèvia d'eliminació de part de l'aigua continguda en la solució.

La crioconcentració és una tecnologia que permet l'eliminació d'aigua d'una solució a través del seu refredament fins a la formació i la separació dels cristalls de gel. Es tracta d'una tècnica que pot preservar la qualitat del producte a causa de les baixes temperatures utilitzades.

Hi ha tres tècniques de crioconcentració: suspensió, pel·lícula i bloc. La única tècnica disponible comercialment arreu del món és la crioconcentració en suspensió. Aquesta és una tècnica que aconsegueix una gran eficiència en la separació, però és relativament cara per la qual cosa es busca el desenvolupament de tècniques més senzilles que al mateix temps aconsegueixin una alta eficiència de separació. La crioconcentració de pel·lícula descendent i en bloc es mostren com a alternatives.

En aquest projecte hem estudiat la crioconcentració en bloc total i en pel·lícula descendent per a la producció d'extractes concentrats de cafè. S'ha dissenyat una unitat d'estudi per a la crioconcentracio. També s'ha establert l'efecte de les variables operatives de la crioconcentració en bloc i pel·lícula sobre l'eficàcia de la separació i s'ha demostrat la preservació de compostos bioactius, la preservació dels components volàtils i de la qualitat sensorial de l'extracte de cafè. S'han obtingut models matemàtics per a la predicció del coeficient de distribució en el gel que li permeten predir el comportament de la crioconcentració. Finalment, es proposa una estratègia operativa per a la integració de les tècniques estudiades permetent obtenir eficiències de separació coherents amb estàndards de la indústria.

El projecte s'ha desenvolupat en forma de tesi cotutelada conjuntament entre el doctorat en Biociències de la Universidad de La Sabana de Bogotà, Colòmbia i el doctorat en Tecnologia dels aliments i Biotecnologia de la Universitat Politècnica de Catalunya a Barcelona, Espanya. Arran del projecte hi ha cinc articles publicats en revistes indexades.

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1. INTRODUCTION

This chapter offers a brief introduction of this thesis. The chapter describes the state of the art of freeze concentration research, the motivations of conducting this study and the research question. Then the objectives of the study are presented. Finally, the chapter introduces the overall structure of the document.

1.1. State of the art

1.1.1. Coffee

Coffee is the second most traded commodity in the world after petroleum and the most traded food worldwide (Esquivel and Jiménez, 2012; Vignoli et al., 2011). Current competition in the coffee industry focuses on product quality. Soluble coffee is a processed product created to facilitate beverage preparation, while preserving product quality (Cheong et al., 2013; Farah et al., 2006).

Two value parameters are recognized in soluble coffee: sensory quality and functional quality. Coffee has more than 800 compounds responsible for its aroma, but few impact compounds are particularly important (Franca et al., 2005; Sarrazin and Que, 2000). The sensory evaluation and volatile compounds determinations are parameters of sensory quality evaluation (Farah et al., 2006). On the other hand, several studies report the health benefits of consuming coffee beverages. Compounds with antioxidant activity have been identified in coffee extract, including those of the chlorogenic acid group: chlorogenic acid (CGA) (3-caffeoylquinic acid), crypto-chlorogenic acid (cCGA) (4-caffeoylquinic acid), neo chlorogenic acid (n-CGA) (5-caffeoylquinic acid), and caffeine (Fujioka and Shibamoto, 2008; Sopelana et al., 2013; Vignoli et al., 2011). Functional quality and organoleptic quality are common parameters used in the evaluation of soluble coffee production.

Fig. 1.1 shows the process used to obtain soluble coffee. The process begins with the roasting and grinding of green coffee beans. After that, the soluble fraction is extracted by percolation. Finally, the extract has to be dried. Two technologies can be used for this purpose: spray-drying and freeze-drying. A previous stage of concentration is needed to reduce the amount of water in the extract before the drying stage in order to reduce processing costs and time (Boss et al., 2004). This concentration stage can be performed by evaporation, microfiltration, or freeze concentration. When freeze-drying is used, the concentration stage is achieved by freeze concentration.

Figure 1.1. Process used to obtain soluble coffee

1.1.1. Freeze Concentration

Freeze Concentration (FC) is a technology used to remove water at low temperatures, preserving the quality of the original material. Water removal in FC is achieved by cooling the solution until ice crystals form and separate, producing a more concentrated fluid (Sánchez et al., 2009). Several industries use freeze concentration technology, including the food industry −fruit juices, dairy products, wine, and beer−, biotechnology and waste water treatment (Aider and de Halleux, 2009b; Sánchez et al., 2009).

Two phases are obtained when the temperature of an aqueous solution is decreased below the freezing point: a liquid phase with higher solute concentration than the initial solution, and a solid phase composed by pure ice in the ideal situation or ice with trapped solutes in the practical situation (Rahman, 2006). This phenomenon is known as solute occlusion (Aider and de Halleux, 2009b; Sánchez et al., 2009). Heat and mass transfer are implied in this phenomenon (Petzold and Aguilera, 2009).

The freezing process involves the crystallization of water contained in the solution. Crystallization is the formation of solid particles from a homogenous phase (Chen et al., 1998). This process involves three steps. First, the solution must be subjected to supersaturation or supercooling. Second, a nucleation or production of the first stable particles is needed. Finally, crystal particles grow to their final size depending on temperature conditions (Sánchez et al., 2009). Primary heterogeneous nucleation occurs on surfaces different than the crystal itself, such as the container wall or impurities (Mullin, 2001). Once the ice seeds are produced, they grow through a process known as Ostwald ripening (Aider et al., 2009a). Crystallization plays an important role on the behaviour of freeze concentration technology. Separation is determined by freezing and thawing stages. Research usually focuses on these stages, as well as on the type of solution and the operational variables that have an effect on separation.

As shown in Fig. 1.2, there are three freeze concentration techniques according to ice crystal growth: suspension FC, film FC (progressive or falling-film FC) and block FC (total or partial) (Aider & de Halleux, 2009b; Sánchez et al., 2009). A brief description of each technique is presented in the following paragraphs.
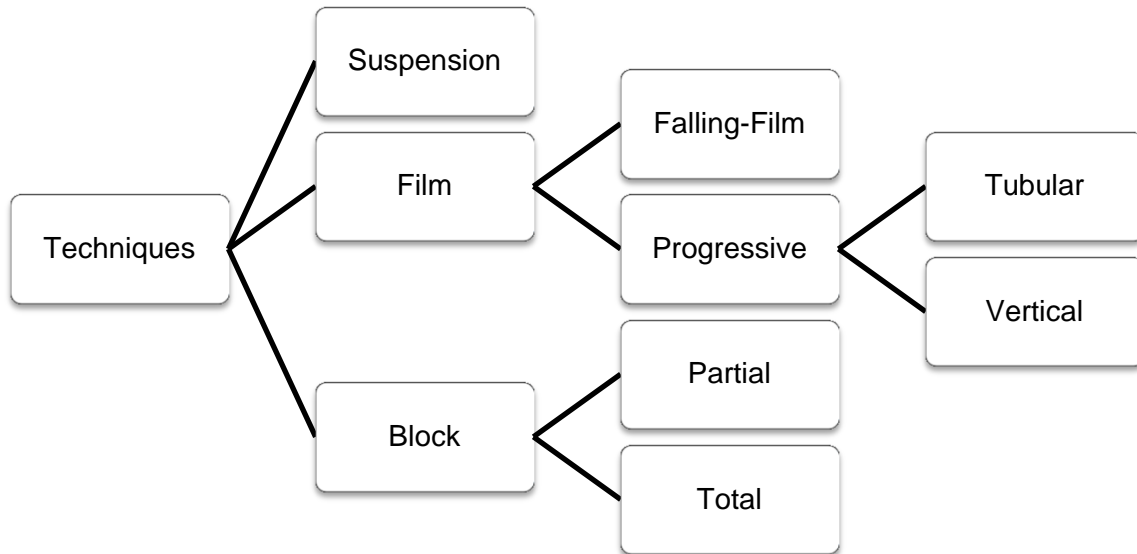
Figure 1.2. Freeze concentration techniques. Source: The author.

1.1.1. Suspension Freeze Concentration

Suspension FC is the most implemented technique at the industrial level. This technique was developed by Niro Process Technology B.V. It comprises three stages (Sánchez et al., 2009): crystallization, ripening, and separation of ice crystals. First, the solution enters into a scraped surface heat exchanger. Then, small crystals are used to form a suspension and these crystals grow in the ripening stage. Finally, ice crystals are separated through filtrating and washing columns.

This technique was first studied by Huige and Thijssen (1972). Production of ice crystals was studied and the freeze concentration technique was subsequently developed and patented. There has been extensive research on the nucleation mechanism (Shirai et al., 1987), washing columns (Quin et al, 2008), and the scraped heat exchanger (Habib and Farid, 2006).

Suspension freeze concentration is an efficient technique in terms of ice purity and increased concentration (Qin et al., 2007, 2006; van der Ham et al., 2004). This technique allows to concentrate coffee extract up to 32–35% solids and to obtain a high-purity effluent with 0.1% solids (Van Mil and Bouman, 1990; Van Pelt and Bassoli, 1990). However, this technique requires complex systems for ice separation and many moving parts, which increases the initial and operating costs (Aider and de Halleux, 2009b; Miyawaki et al., 2005; Sánchez et al., 2009). Recent developments have focused on minimizing moving parts, replacing the scrapped surface heat exchanger, and improving washing columns (Petzold and Aguilera, 2013; Sánchez et al., 2009; Van der Ham et al., 2004).

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1.1.1. Film Freeze Concentration

Film freeze concentration consists in the formation of a single ice film on a cooling surface. Separation of the ice is easier than in the suspension technique as the film remains adhered to the surface. Ice growing and separation stages are carried out using the same equipment. Heat transfer is achieved across the ice layer. Two different options have been developed for film freeze concentration: falling-film freeze concentration and progressive freeze concentration.

Progressive Freeze Concentration

In progressive freeze concentration, an ice film is produced on a cooling surface while the fluid is moving on the growing ice layer (Miyawaki et al., 2005). Progressive freeze concentration can be performed in vertical or tubular equipment.

Tubular progressive freeze concentration was proposed by Shirai et al. (1998) and it consists of two concentric tubes that are connected. The solution to be concentrated and the refrigerant fluid circulate through the inner and the external tube, respectively. Ice is produced on the internal wall of the inner tube. The velocity of the fluid reduces solute occlusion on the ice layer. Relevant operational variables include initial concentration and type of solution, cooling temperature, and flow rate of the solution (Miyawaki et al., 2005; Shirai et al., 1998; Wakisaka et al., 2001).

On the other hand, the vertical system is composed by a cylindrical agitated tank equipped with a cooling jacket. Ice grows on the cooling wall. Agitation is applied to reduce solute occlusion. Operational variables in this technique are cooling rate, agitation rate, and type and initial concentration of the solution. (Liu et al., 1998)

Falling-Film Freeze Concentration

Falling-film freeze concentration is carried out in a plate equipment. In this technique, the solution to be concentrated re-circulates on a cooled vertical plate. Fluid descends down a film, and an ice sheet is produced by freezing. Ice forms a single layer on the cold surface. The solution is collected and re-circulated continuously (Sánchez et al., 2011b). The process is performed in batch operation. The simplicity of ice separation is an advantage of this technique. Current studies of this technique focus on how to increase the concentration level of the solution and the purity of ice. Table 1.1 shows the main research on falling-film freeze concentration.

Table 1.1. Main researches on falling-film freeze concentration

Author, year	Fluid	Main results
(Chen et al., 1998)	Sucrose solutions	Solute occlusion on the ice depends on freezing rate, fluid velocity and concentration of the fluid.
(Chen and Chen, 2000)	Sucrose solutions, milk	A general correlation to predict the distribution coefficient of falling-film freeze concentration was generated.
(Peters-Erjawetz et al., 2007)	Milk	Concentrated milk fat was obtained through falling-film freeze concentration with the same characteristics of the suspension technique. A method to improve nucleation through the formation of a primary layer was identified.
(Raventós et al., 2007)	Sugar solutions	The greatest purity level of the ice was found at low initial solute concentration. A better result was achieved for sucrose solutions than fructose and glucose solutions.
(Hernández et al., 2009)	Apple and pear juices	Fruit juices were freeze-concentrated in a pilot. Concentration rates of 1.4°Brix each hour were obtained. The ice production rate decreased with juice concentration.
(Hernández et al., 2010)	Must	Concentrated grape must was obtained in a multiplate freeze concentrator. A must with 30 °Brix was obtained.
(Sánchez et al., 2010)	Orange juice	Juice concentration was increased to 28 °Brix. Solute occlusion in the ice increased exponentially.
(Auleda et al., 2011)	Sugar solutions, and fruit juices	A calculation method for designing and sizing equipment for falling-film freeze concentration of fruit juices was developed.
(Sánchez et al., 2011a)	Whey	Whey concentration increased linearly in multiple stages of falling-film freeze concentration. Concentration efficiency decreased, and protein and carbohydrates concentration increased with the concentration stages.
(Belen et al, 2012)	Tofu whey	Tofu whey concentration was increased eight times in eight stages of falling-film freeze concentration. Isoflavon concentration was increased 1.5 times.

1.1.1. Block Freeze Concentration

The block freeze concentration method, also known as freeze-thaw concentration, can be performed through partial or total freezing. In the total block freeze concentration technique, the solution to be concentrated is completely frozen and then partially thawed to recover a fraction of liquid with a higher concentration (Aider & de Halleux, 2009; Nakagawa et al., 2010b). In the partial technique, ice grows partially and it is then separated from the remaining liquid. Block freeze concentration consists of three stages: freezing, thawing, and separation of the concentrated liquid fraction. These stages define separation efficiency (Nakagawa et al., 2009). Additionally, and the process can be repeated in successive cycles to increase the concentration index (Aider & Ounis, 2012).

The advantage of this technique is that the fluid remains static, and consequently there is no need for complex equipment. In addition, the three stages can be performed in the same unit. However, it imposes research challenges associated to the ability to decrease solute occlusion and to achieve an industrial viable operation. The research on this technique has increased in recent years. Table 1.2 shows the main research on block freeze-concentration.

Table 1.2. Main researches on block freeze concentration

Author, year	Fluid	Main results
(Chen et al., 2001)	Protein and salt solutions	Solute concentration depended on freezing rate, operational protocol, and molecular size of the solutes. Movement of solutes during freezing was demonstrated.
(Yee et al., 2003)	Milk protein, sugar and salt solutions	The concentration was successful. The three first fractions showed the highest concentrations. Supercooling affected the concentration level.
(Ayel et al., 2006)	Antifreezing solution	Dendrite growth rate increases with supercooling degree and decreases with solute concentration.
(Aider et al., 2008)	Fruit juice	Cooling temperature did not affect the concentration level. The type of juice and the number of stages were highly significant for the separation.
(Aider and de Halleux , 2008a)	Maple syrup	The separation level was not affected by the microwave-assisted thawing. Thawing time was reduced by the microwave energy. The technique was viable and economic.
(Aider and de Halleux , 2008c)	Whey	The separation was not affected by the thawing method. A negative effect on protein denaturation was identified.

(Burdo et al., 2008)	Grape juice	Application of ultrasound in the freezing stage was tested. Ice porosity increased with oscillation frequency.
(Nakagawa et al., 2009)	Binary model solutions	The freeze concentration phenomenon was governed by the water drop thawing rate during the thawing stage.
(Aider et al., 2009)	Acidified milk whey	A highly concentrated liquid was obtained. However, the level of solute occlusion was high. Foam capacity decreased and foam stability of the whey increased with freeze concentration.
(Gao et al., 2009)	Waste water	The partial block technique was tested. A good level of impurity removal was achieved. Separation was increased by applying agitation. Freezing temperature did not have any effect on separation.
(Nakagawa et al., 2010a)	Apple juice	The level of concentration was affected by the thawing temperature. Separation efficiency is determined by solute elution in the thawing stage. Solute concentration increased with time and low thawing temperatures.
(Nakagawa et al., 2010b)	Ternary model solutions	The separation was controlled by the thawing stage.
(Aider and Ounis, 2012)	Milk whey	Successive stages were proposed for the block technique. The thawing method did not affect separation but decreased processing time.
(Petzold et al., 2013)	Sucrose solution	Separation efficiency was increased by vacuum separation of the liquid fraction. Processing time was also reduced through this technique.
(Petzold and Aguilera, 2013)	Sucrose solution	A centrifugal force is proposed to separate the concentrated fraction from the ice matrix. Solute recovery was increased through this technique.

The state of the art of freeze concentration was supplemented by five papers published as a result of the research herein. These publications will be presented in the following chapters.

1.2. Research question

Freeze concentration is a technology used to eliminate water from aqueous solutions, preserving quality through low processing temperatures. This technology is used in the food, pharmaceutical, and biotechnological industries. Freeze concentration is used in the process to obtain freeze-dried coffee. The most implemented technique is suspension freeze concentration, which is effective for separation; however, this technique requires systems of ice separation and many moving parts, which increases initial and operating costs. For this reason, other freeze concentration techniques have been studied. Different techniques, such as falling-film, and block freeze-concentration are being developed seeking to reduce operational costs. The operational conditions of these new techniques have not been defined, hindering their industrial implementation. The use of these techniques in coffee extraction through concentration has not been tested yet.

A key problem for researchers is to establish the relationship between the operational variables and the phenomena required to reduce solute occlusion and to increase separation efficiency of block and falling-film freeze concentration. In addition, the functional quality and sensory quality of the product are highly important in the coffee industry. For this reason, the effect of freeze concentration on the organoleptic quality and functional quality of coffee extract should be studied. From this context, the following research questions can be formulated:

¿What is the effect of the operational variables of block and falling-film freeze concentration on separation efficiency and quality of coffee extract?

1.2. Objectives

1.2.1. General Objective

The main objective of the present study was to establish the effect of the operational variables of block and falling-film freeze concentration on separation efficiency and quality of coffee extract.

1.2.1.1. Specific Objectives

1. Design and implement an equipment to study block and falling-film freeze concentration.

2. Determine the effect of operational variables of freeze concentration on separation efficiency.

3. Assess the effect of freeze concentration on volatile and bioactive compounds of coffee extract.

4. Propose operative strategies to integrate block and falling-film freeze concentration of coffee extract in order to increase solute recovery.

1.3. Structure of the document

The present thesis document is organized in ten chapters.

The first chapter offers a brief presentation of the state of the art, the research question, and the objectives of the study. The second chapter presents the design of a test unit for studying block and falling-film freeze concentration.

Chapter three presents the characterization of the main physical properties of coffee extract at temperatures close to freezing. The relations between coffee mass fraction and Brix degrees, freezing curve, rheological behaviour, and density of coffee solutions at temperatures close to the freezing point were measured and modelled mathematically.

Chapter four focuses on the study of the effect of the operational variables of block and falling-film freeze concentration on separation efficiency. This chapter presents the evaluation of the effect of the initial coffee mass fraction, the cooling temperature, the heating temperature, and the freezing direction on the solute yield and concentration index of block freeze-concentrated coffee extracts. In addition, it discusses the impact of the technique on the bioactive compound concentration and antioxidant activity of the coffee extract.

The effect of different separation and thawing methods in block freeze-concentration is provided in chapter five. The effect of gravitational and vacuum assisted separation, thawing temperature, and thawing method on solute yield is also studied.

The effect of the operational variables on solute occlusion in falling-film freeze concentration is studied in chapter six. The aim of this chapter is to evaluate the behaviour of coffee extract during falling-film freeze concentration at different coffee mass fractions, ice growth rates, and film velocities on the plate, and to obtain the parameters for average distribution coefficient modelling.

A comparison of solute retention, productivity, ice morphology, volatile compounds preservation and sensory quality between block and falling-film freeze concentration of coffee extract is presented in chapter seven.

Chapter eight proposes a process for integrating block and falling-film freeze concentration seeking to increase separation efficiency. The process presented in chapter eight includes recovery of coffee solids by fractionated thawing and block freeze-concentration techniques.

The main results of the study are summarized in chapter nine. Finally, conclusions and suggestions for future work are provided in chapter ten.

This document of doctoral thesis, the published papers derived from this work, and its relationship with the objectives of the thesis are presented according to the structure shown in Fig 1.3.

PUBLICATION	CHAPTER	OBJECTIVE
	2. Design of an equipment for the study of block and falling-film freeze concentration	1. Design and implement an equipment to study block and falling-film freeze concentration.
International journal of food properties. (2014). Doi: 10.108010942912.2013.833221	3. Rheological behaviour, freezing curve and density of coffee solutions at temperatures close to freezing	2. Determine the effect of operational variables of freeze concentration on separation efficiency.
Journal of food Engineering (2014) 120, 158-166	4. Block freeze-concentration: effect of freezing and thawing stages on solute recovery and bioactive compounds of coffee extract	
Food and Bioproducts Processing (2013), 91(4), 396-402	5. Effect of separation and thawing mode on block freeze-concentration of coffee brews	3. Assess the effect of freeze concentration on volatile and bioactive compounds of coffee extract.
Journal of Food Engineering (2014) 141, 20-26	6. Behaviour of falling-film freeze concentration of coffee extract	
	7. Volatile compounds preservation and solutes retention of block and falling-film freeze concentration of coffee extract	4. Propose operative strategies to integrate block and falling-film freeze concentration of coffee extract in order to increase solute recovery.
Journal of Food Engineering (2014), 128, 88-95.	8. A process to concentrate coffee extract by the integration of falling film and block freeze concentration	**General Objective**

Figure 1.3. Structure of the document.

11

1.4. Published papers

The following research papers were published as a result of the present work:

1. Moreno F.L., Raventós M., Hernández E., Santamaría N., Acosta J., Pirachican O., Torres L. and Ruiz Y. (2014) Rheological behaviour, freezing curve and density of coffee solutions at temperatures close to freezing. International Journal of Food Properties. DOI: 10.1080/10942912.2013.833221

2. Moreno, F.L., Raventós, M., Hernández, E., & Ruiz, Y. (2014). Block freeze-concentration of coffee extract: effect of freezing and thawing stages on solute recovery and bioactive compounds. Journal of Food Engineering, 120, 158-166

3. Moreno, F.L., Robles, C. M., Sarmiento, Z., Ruiz, Y., & Pardo, J. M. (2013). Effect of separation and thawing mode on block freeze-concentration of coffee brews. Food and Bioproducts Processing, 91(4), 396-402

4. Moreno, F.L., Raventós, M., Hernández, E., Ruiz, Y. (2014). Behaviour of falling-film freeze concentration of coffee extract. Journal of Food Engineering 141, 20-26.

5. Moreno, F.L., Hernández, E., Raventós, M., Robles, C., & Ruiz, Y. (2014). A process to concentrate coffee extract by the integration of falling film and block freeze-concentration. Journal of Food Engineering, 128, 88-95.

In addition, the following works were presented in scientific congresses:

1. Moreno, F.L., Hernández, E., Raventós, M., Robles, C., & Ruiz, Y. (2012). Mathematical modelling of rheological behaviour of coffee extract at temperatures close to freezing. In: Congreso Español de Ingeniería de Alimentos CESIA VII. Ciudad Real, España.

2. Ramírez, A. Moreno, F.L. Ruiz, Y. Block freeze concentration of coffee extract. (2012). Revista Vitae 19, (1). In: I Congreso Internacional de investigación e innovación en ciencia y tecnología de alimentos IICTA. Bogotá, Colombia.

3. Moreno, F. L., Raventós, M., Hernández E., Gulfo R., Ruiz, Y. (2014) Technical, energetic and economic comparative of three concentration systems in a fruit juice industry: Case of study. In: Congreso Iberoamericano de Ingeniería de Alimentos CIBIA 9. Valencia, España.

4. Moreno, F. L., Raventós, M., Hernández E., Gulfo R., Robles, C., Ruiz, Y. (2014) Integration of block and falling-film freeze concentration applied to concentrate sucrose solutions. In: Congreso Iberoamericano de Ingeniería de Alimentos CIBIA 9. Valencia, España.

5. Moreno, F. L., Hernández A.J., Moreno Y., Ruiz, Y. (2014). Soluble solids and sediments determination during block freeze concentration of coffee extract. In: II Congreso Internacional de investigación e innovación en ciencia y tecnología de alimentos IICTA. Medellín, Colombia.

2. DESIGN OF AN EQUIPMENT FOR THE STUDY OF BLOCK AND FALLING-FILM FREEZE CONCENTRATION

A unit for the study of block and falling-film freeze concentration was designed to develop the present research. The main results of the design process are presented in this chapter.

2.1. Systems of the Test Unit

The unit for the study of freeze concentration must control the main operational variables of freeze concentration required to develop the tests. Firstly, the unit should provide cooling and heating fluids with the possibility of temperature and freezing direction controlling. Secondly, the temperature and concentration of the solution should be measured during the tests. In addition, the equipment should be able to couple a block or a falling-film freeze concentration device. For these reasons, the freeze concentration unit is composed by the systems shown in Table 2.1.

Table 2.1 Systems of the concentration unit.

SYSTEM	DESCRIPTION
Cooling system	Thermostatic bath to provide a cooling fluid (ethylene glycol-water 50% m/m). The fluid is pumped to the freeze concentration device.
Heating system	In block freeze concentration a thawing stage is needed. For this reason a thermostatic bath to provide a heating fluid (ethylene glycol-water 50% m/m) was used. The fluid is pumped to the block freeze-concentration device during the thawing stage.
Block freeze-concentration device	The block freeze-concentration device is a cylindrical container. The container consists in a double jacket device for the circulation of cooling and heating fluids. The device has thermal insulation and exit valves to collect the thawing fraction.
Falling-film freeze concentration device	The falling-film freeze concentration device is a chamber with an internal cooling plate to freeze the solution. The cooling fluid circulates inside the plate. The fluid flows through a descending film over the cooling plate, and it is collected in a tank and re-circulated by peristaltic pump. Ice grows on the surface of the plate.
Valves and connexions	It consists in a system of flexible hosepipe that conducts cooling and heating fluids to the block device and the plate of the falling-film chamber. A set of valves is provided to control freezing and thawing direction according to experimental requirements.
Support structure	It consists in a structure that supports the freezing container, the falling-film chamber, the hosepipe, and the valves.

2.2. Structure of the Freeze Concentration Unit

The structure of the equipment is represented by the piping and instrumentation diagram (P&ID) shown in Fig 2.2 and 2.3. Freezing devices, connexions, valves, sensors, and control systems are also shown in these figures. The P&ID of the block freeze concentrator is shown in Fig 2.2.The P&ID of the falling-film freeze concentrator is shown in Fig 2.3.
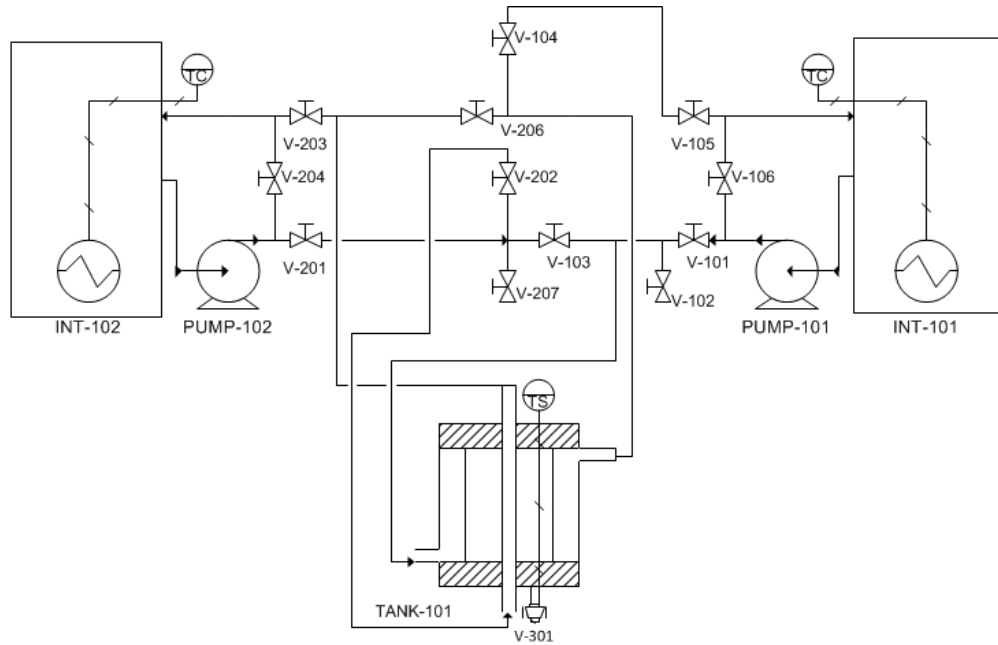
Figure 2.1. Piping and instrumentation diagram of block freeze concentrator.
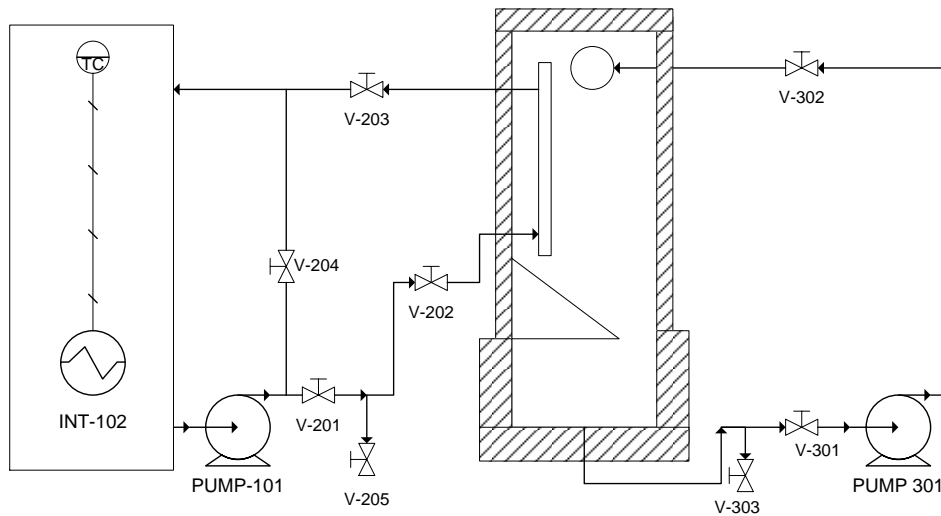
Figure 2.2. Piping and instrumentation diagram of falling-film freeze concentrator.

Fig. 2.3 shows the overall setup of the freeze concentration unit. It includes the cooling system, the heating system, the block freeze-concentration device, the falling-film freeze concentration device, valves, and connexions.

a)

b)
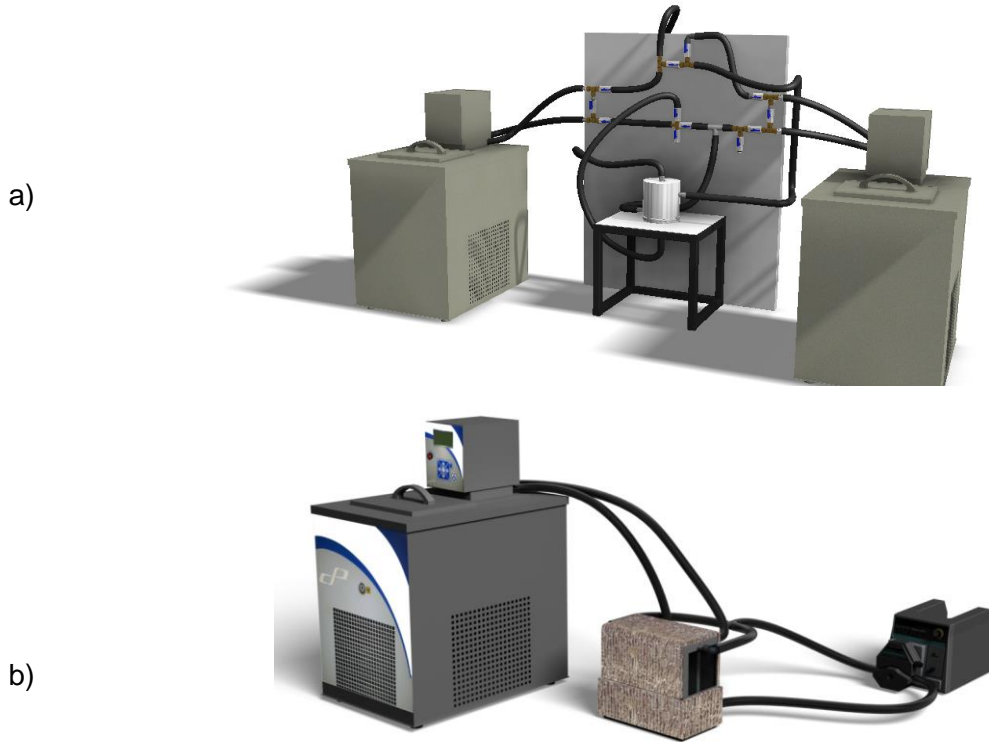
Figure 2.3. Overall setup of the freeze concentration unit.

a) Block freeze concentrator. b) Falling-film freeze concentrator.

The mechanical drawings of the equipment were generated using the Autodesk-Inventor software. A sample of the planes shows the isometric projection, the overall scheme and the exploded view are shown in Figures 2.4 and 2.5.
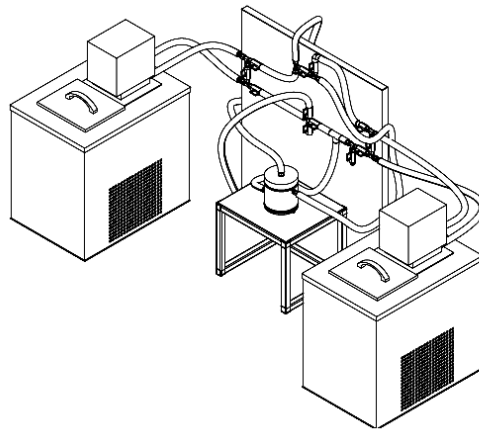
Figure 2.4. Mechanical planes of freeze concentrator. Isometric projection.
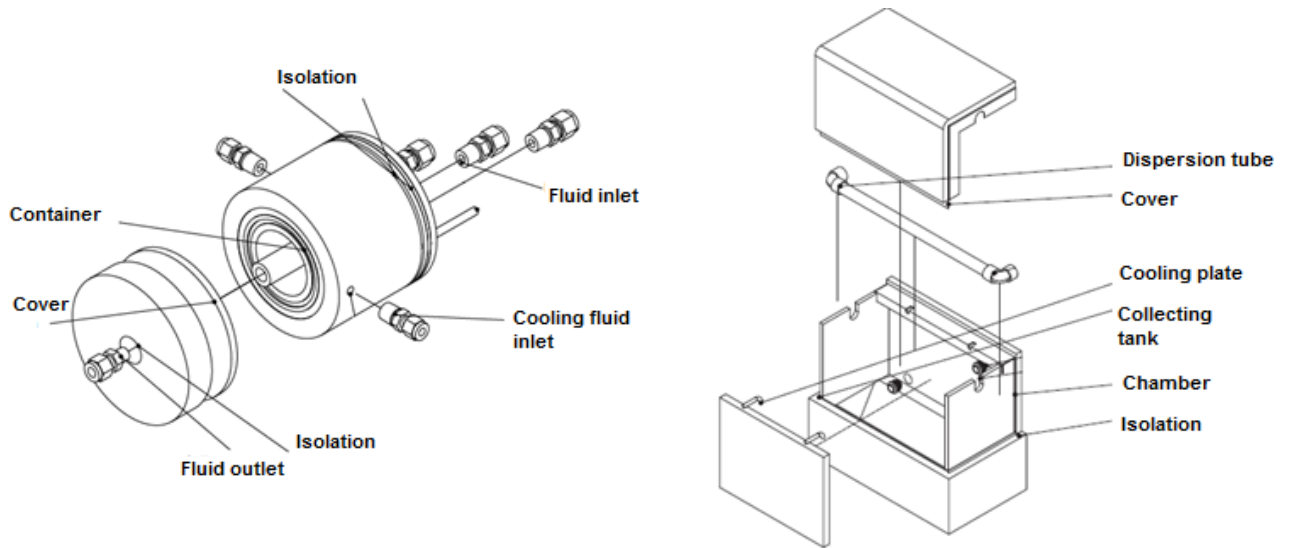
Figure 2.5. Mechanical planes of freeze concentrator.

a) Explosion drawing of block freeze concentrator; b) Explosion drawing of falling-film chamber

2.3. Design Parameters and Operational Intervals.

The following design parameters were established according to the identified functions:

- **Heating and cooling system**: Thermostatic baths CP12122-58 (Cole Parmer, USA); temperature interval: -35°C to 150°C +/- 0.01°C; dimensions: W 14.6" H 27.8" L 20.8"; temperature sensor stability: ±0.025°C; cooling power: 800W; pumping head at zero pressure 10.8 psi (750mbar); heating power: 2 kW; maximum flow rate: 21 L/min.

- **Block freeze concentrator:** Cylindrical container made of stainless steel 304, with double jacket for the circulation of refrigerant fluids. It has a capacity of 160 mL, 52.5 mm in diameter, and 85 mm in height. Insulation is provided at the bottom, the top, and the external side of the container to ensure unidirectional freezing. Two valves are located at the bottom, near the internal and external walls, to separate the concentrated liquid fraction. A digital scale PA3102 (Ohaus, USA) of 3100 g * 0.01 g is located behind the valves to collect and weight the samples.

- **Falling film freeze concentrator:** Chamber made of stainless steel 304. A rectangular cooling plate can be located inside the chamber. A dispersion tube is located in front of the plate to disperse the solution to be concentrated. A storage tank is located at the bottom of the chamber. The plate has dimensions of 25-cm width and 20-cm height. Cooling fluid from the cooling bath flows inside the plate.

- Structure, valves and connexions: The structure made of stainless steel supports the freezing container, the falling film chamber, the hosepipe, and the valves. A polyethylene flexible hosepipe is used to conduct cooling and heating fluids. A set of 12 ball valves, 8 mm in diameter, is provided to control freezing and thawing direction.
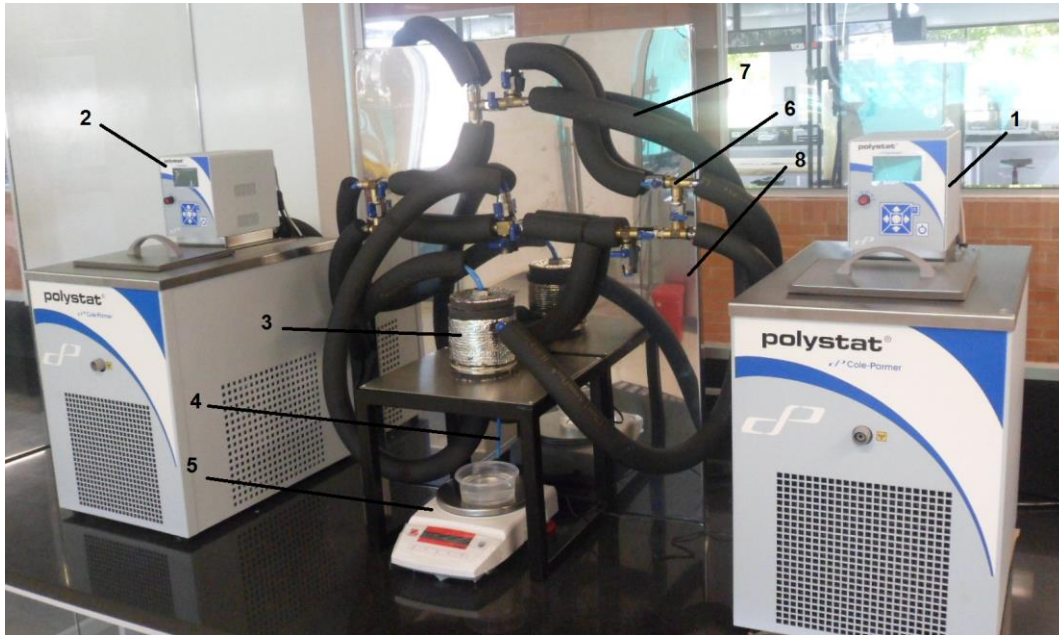
Figure 2.6. Block freeze concentrator.

1) Heating thermostatic bath; 2) Cooling thermostatic bath; 3) Block freeze concentrator container; 4) Thawed sample collecting system; 5) Scale; 6) Valves to control freezing and cooling direction; 7) Hosepipe for heat transfer fluid flow.; 8) Support structure.

Figure 2.7. Cooling container

Figure 2.8. Falling-film freeze concentrator.

1) Freezing chamber; 2) Cooling plate; 3) Peristaltic pump; 4) Thermostatic bath.
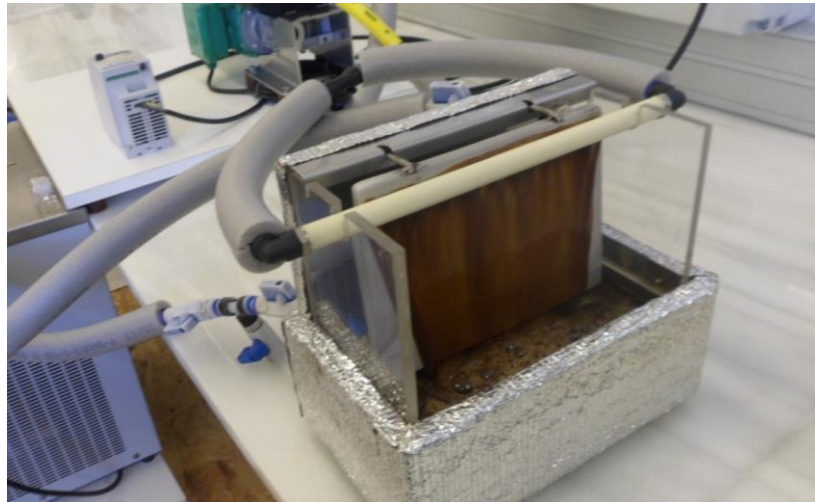
Figure 2.9. Freezing chamber.

3. RHEOLOGICAL BEHAVIOUR, FREEZING CURVE, AND DENSITY OF COFFEE SOLUTIONS AT TEMPERATURES CLOSE TO FREEZING

3.1. Abstract

The physical properties of coffee solutions were determined for temperatures close to the freezing point. Rheological behaviour, freezing curve, density and their relationship between coffee mass fraction and brix degrees were determined for coffee mass fractions between 5 and 50% (wet basis) in the -6°C to 20°C temperature interval. Values of viscosity varied from 1.99 to 1037 mPa·s and values of density from 1000 to 1236 kg·m-3. The freezing curve was generated using the undercooling method, giving values within freezing curves for food fluids. The results were used to generate mathematical models to predict viscosity, freezing point depression, and density as a function of coffee mass fraction and temperature.

Keywords: Coffee; Properties; Rheology; Freezing; Modelling; Freeze-Concentration

Nomenclature	
°Brix	Brix degrees
a, b, c, d	parameters of Eq. 3 and Eq. 4
a_1, a_2, b_1, b_2, c_1	parameters of Eq. 5
a_3, a_4, a_5, a_6 a_7	parameters of Eq. 7
Ea	Activation energy (kJ•mol-1)
FPD	Freezing point depression
γ	Shear rate (s-1)
K	Consistency coefficient (Pa•sn)
k0	Frequency factor (mPa•s)
n	Flow behaviour index
nD	Refractive index
R \	Universal gas constant (8.314 kJ•mol-1•K-1)
R^2	Coefficient of determination
T	Temperature (°C)
Xs	Coffee mass fraction (g coffee/ g solution)
ρ	Density
ρc	Density of coffee solids
ρw	Density of water
σ	Shear stress (Pa)
Φ	Temperature correction
ω	Rotational speed (rpm)
η	Viscosity (mPa•s)
η*	Standard reference Viscosity (1 mPa•s)

3.2. Introduction

Coffee is the second traded commodity in the world after petroleum and one of the most consumed food beverage worldwide (Cheong et al., 2013; Esquivel y Jiménez, 2012). In the coffee industry, preservation of quality is highly important; for this reason, low temperature technologies are commonly implemented. Technologies such as freeze-concentration and freeze-drying are used to produce soluble coffee thanks to the flavour preservation promoted for the low temperatures using (McLeod et al., 2016; Miyawaki et al., 2005; Sánchez et al., 2009).

The measurement of physical properties of food fluids at low temperatures is relevant in the designing of processes and equipment for freezing technologies. The freezing curve of food fluids represents the state of food as a function of solid concentration and temperature. The state diagram is useful for process conditions selection in freezing technologies (Rahman, 2006). Flux behaviour comprehension at temperatures just above the freezing point of fluids is required for sizing freeze-concentration equipment, such as falling film or tubular systems. In a similar way, determining of the viscosity and density is important to establish the power requirements for pumping during fluid processing (Chin et al., 2009). Determining of mathematical models for physical properties and rheological behaviour at low temperatures and at different mass fractions allows applying calculation methods for designing and sizing equipment for freeze concentration (Auleda et al., 2011).

The coffee mass fraction or solid content can be measured by gravimetric techniques; however, Brix degrees determination can be a faster technique. There is no coincidence between Brix degrees and solid content because the darker colour of coffee solutions and the minimum fraction of sediments of coffee extract can affect the diffraction of light. A relationship between Brix degree and coffee mass fraction has not been described.

There are several mathematical models for viscosity prediction of food fluids (Ibarz et al., 1992; Longinotty and Corti ,2008; Falguera and Ibarz, 2010). However, few studies report mathematical modelling of food fluids viscosity at low temperatures. In this sense, viscosities for sugar solutions, fruit juices, and dairy emulsions at low temperatures were reported by (Falguera et al.,2010; Ibarz et al., 2009; Ruiz et al., 2010;Tavares et al., 2007; Gabriele et al., 2011). In the case of coffee solutions, viscosity and some physical properties have been reported by (Sobolik et al., 2002; Telis-Romero et al., 2001) for temperatures ranging from 20 to 80°C. The freezing curve of coffee extract was obtained by Thijssen (1969) and Pardo et al. (2002); nevertheless, the authors report the dependence of data on the type of coffee and extraction methods. Additionally, telis-Romero et al. (2000) studied the physical properties of coffee extract. However, there are no reports of coffee solutions viscosity and physical properties for temperatures below 0°C. The modelling of viscosity and other physical properties at temperatures close to the freezing point could contribute to the design of processes and equipment for freezing technologies such as freeze concentration, freeze drying, and coffee extract handling in

the coffee industry. The aim of the present work was to measure and model the relation of coffee mass fraction and Brix degrees, freezing curve, rheological behaviour, and density of coffee solutions at temperatures close to the freezing point.

3.3. Materials and methods

Materials

Colombian freeze-dried coffee (Buencafé, Buencafé Liofilizado de Colombia) provided by the Colombian Coffee Growers Federation was used to prepare aqueous solutions at different coffee mass fraction. Soluble coffee granules were dissolved in distilled water at 30°C to obtain samples at different concentrations.

Relationship between Coffee Mass Fraction and Brix Degrees

Coffee solutions were prepared at different coffee mass fraction: X_s= 0.10, 0.20, 0.30, 0.40, and 0.50. The solutions were stored at 20°C. Brix degrees and index refraction were measured by refractometry (Atago Pal 100, Japan) at 20°C ±1°C. The total dry matter was measured by weight-loss after oven drying at 103 °C +/- 1°C for four hours according to technical standards (Icontec, 2009). Measurements were performed in quadruplicate.

Freezing Curve

The method of undercooling reported by (Auleda et al, 2011; Ayel et al., 2005; Jie et al., 2003) was used to determine the freezing point of coffee solutions. Coffee solutions at X_s= 0.10, 0.20, 0.30, 0.40 and 0.50 were tested. The method consisted of cooling the sample by immersion in a cooling bath. Four test tubes with 10 mL of the sample were immersed in a cooling bath (Polystat, Cole Parmer, USA). The cooling fluid was a mixture of ethylene glycol and water (53% w/w). The bath was temperature controlled at an interval from -35 °C to 150 °C +/- 0.01 °C. The temperature of the bath was settled at -13°C +/- 0.01 °C. The test tubes were immersed after the bath reached the temperature. The test tubes contained inside a PT100-IP65 temperature sensor (Testo, Germany) located in the centre of the sample. The sensor had a 2 mm diameter and a precision of ±0.01 °C, and it was connected to a 176 T2 datalogger (Testo, Germany). The temperature profile was stored in a PC. The freezing points were determined based on the cooling curves. The highest temperature reached after the undercooling due to nucleation corresponded to the freezing point. All the experiments were performed in quadruplicate.

The method was previously standardized by measuring the freezing curve of sucrose solutions and comparing it with reported data (Auleda et al., 2011; Longinotti y Corti, 2008). The solutions were prepared with sucrose analytic grade (Panreac Química, Colombia) at solid concentrations of 10-50% w/w and distilled water at 40°C. The solutions were stored and then freezing points were determined. The technique was accepted when

the difference between experimental and theoretical data was within 5%. This difference may be attributed to the solute inclusion in ice (Chen and Chen, 1996).

Rheological Measurements

Coffee solutions were prepared at Xs= 0.05, 0.20, 0.35 and 0.50. The solid content was verified by refractometry (Atago Pal 100, Japan) at 20°C+/-0.05°C using the equation obtained in the Brix degrees and coffee mass fraction measurements. The rheological behaviour of the samples was determined using a viscometer of coaxial cylinders (FungiLab Viscostar L, Barcelona) equipped with a device for low viscosity measurements, which is able to measure viscosities from 0 to 2000 mPa•s. The sample of 18 mL of coffee solution was placed on the device with a concentric inside spindle. The device was immersed in a cryostat (Polysience Model 9505, USA, temperature range: -30 to 150°C; temperature stability +/-0.5°C; readout accuracy: +/-0.5°C). The viscometer was connected to a PC for data storing. The sample temperature was verified using a thermocouple type K (Precision +/-0.5°C; measurement range: -50 to 1000°C) connected to a Datalogger (Testo 174 T4, Spain). Viscosity was measured after the sample reached the desired temperature.

The measurements were performed varying shear rate, sample temperature, and coffee mass fraction. Four shear rates were adjusted for each sample, from 5 to 120 s-1, depending on the solution's viscosity. The limit was established by the maximum torque of the viscometer. Shear rates were calculated using an equation given by the viscometer to convert rotational speed into shear rate, ɣ=1.2236*ω. Different temperatures above freezing point were tested (-6, -4, -2, 0, 2, and 4°C) depending on Xs, such that the solution remained in liquid state. Four different coffee mass fractions (0.05, 0.20, 0.35, and 0.50) were tested. Experiments were performed in triplicate. The rheological behaviour of coffee solutions was modelled using the power law shown in Eq. 1.

$$\sigma = K \cdot ɣ^n \quad (1)$$

An Arrhenius type equation (Eq. 2) was used to describe the effect of temperature on the viscosity of coffee solutions (Ibarz et al., 2009).

$$\eta = k_0 \exp\left(\frac{E_a}{RT}\right) \quad (2)$$

Activation energy and frequency factor were fitted to the Xs dependent model (Ibarz et al., 1992) shown in Eq. 3 and Eq. 4.

$$k_0 = a \exp(b * x_s) \text{ (3)}$$
$$E_a = c \exp(d * x_s) \text{ (4)}$$

Two general models to predict viscosity of coffee solutions as a function of temperature and coffee mass fraction simultaneously were fitted. Mathlouli and Genotelle, (1995 cited

by Longinotti and Corti, 2008) proposed a general model for sucrose solutions shown in Eq. 5.

$$\log_{10} \frac{\eta}{\eta^*} = a_1 + a_2 x + \varphi \left(b_1 + b_2 x_s^{c_1} \right) \text{ (5)}$$

Where:
$\varphi = (30-T)/(91+T)$ (6)

Moreover, Sobolik et al. (2002) proposed a model applied to coffee solutions at room temperatures and higher, shown in Eq. 7.

$$\eta = exp \left(a_3 + a_4 x + a_5 x_s^2 + \frac{a_6 + a_7 x_s^2}{T + 273.15} \right) \text{ (7)}$$

Density

The density of coffee solutions at Xs= 0.10, 0.20, 0.30, 0.40, and 0.50 was determined by using a pycnometer at temperatures of 0, 5, 10, 15, 20 and 25 °C ± 0.01°C. The pycnometers with the samples were immersed in a cooling bath at the settled temperature (Polystat Cole Parmer, USA). One blank sample had a PT100-IP65 temperature sensor (Testo, Germany) immersed to check temperature. After the sample reached the temperature, the pycnometers were closed and weighed in an analytical scale (Mettler Toledo, USA). The measures were performed in triplicate.

Statistical Analysis

The average and the standard deviation of all data were calculated by SPSS 20.0 software. The unknown parameters of the models showed in Eq. 1 to 10 were adjusted from experimental results using a linear regression fitting procedure with SPSS 20.0 for Eq. 2 to 4 and a non-linear regression procedure for the other intrinsically non-linear models. The goodness of model fit was based on coefficient of determination (R^2), defined by the ratio between the regression sum of square and the total sum of squares. For the best fit, the R^2 value should be high.

3.4. Results and discussion

Relationship between Coffee Mass Fraction and Brix Degrees
The Brix degrees are a measure of the soluble solid content of sugar solutions. The relationship between Brix degrees and coffee mass fraction is presented in Table 3.1. A linear relation was obtained as seen in Eq. 8. The equation allows measuring coffee mass fraction by refractometry. The equation can be modified to %Solids=0.87•°Brix, in order to obtain solid percentage. Similar relationships are used in the coffee industry (Moreno et al., 2013). The refractive index was also measured and its relation with Xs is presented in

Table 3.1. The relationship was fitted in the Eq. 9. The models allowed calculating coffee mass fraction using a quick technique such as refractometry.

$$Xs = 0.0087 \cdot °Brix \quad (8); \quad R^2 = 0.991$$

$$nD = 1.334 + 0.155Xs + 0.092Xs^2 \quad (9); \quad R^2 = 0.984$$

Table 3.1 Xs and refractive index as a function of brix degrees for coffee solutions

Brix degrees	Xs	Refractive index
11.3	0.094	1.3500
10.7	0.095	1.3488
11.4	0.103	1.3499
11.4	0.100	1.3499
22.8	0.183	1.3685
23.0	0.204	1.3661
21.3	0.191	1.3674
22.0	0.154	1.3680
33.2	0.305	1.3870
33.7	0.308	1.3890
34.3	0.297	1.3864
32.9	0.303	1.3870
41.3	0.381	1.4024
45.3	0.396	1.4087
44.5	0.393	1.4112
45.7	0.396	1.4080
55.4	0.494	1.4317
56.2	0.496	1.4428
60.3	0.493	1.4241
51.9	0.459	1.4290

Freezing Curve

The cooling curves of coffee solutions were determined in quadruplicate as shown in Fig. 3.1. The super-cooling can be observed by the temperature decrease until the nucleation process begins. Subsequently, a temperature increase was produced due to the latent heat of the phase change. The highest temperature reached corresponded to the freezing point of the sample (Auleda et al., 2011). From the cooling curves at different Xs, an average freezing point was calculated and the freezing curve for coffee solutions was obtained (Table 3.2.). Data correspond to average and standard deviation. The values are comparable to those reported by Thijsenn (1969) and Thaler (1978) for different types of coffee. The difference with the freezing point of water (0°C) corresponded to the freezing point depression. Data were fitted to Eq. 10 for freezing point depression prediction as a function of coffee mass fraction. The regression coefficient obtained was 0.998, showing a good fitness.

$$FPD = 35.01 \cdot Xs^2 + 2.05 \cdot Xs \quad (10) \quad R^2 = 0.998$$
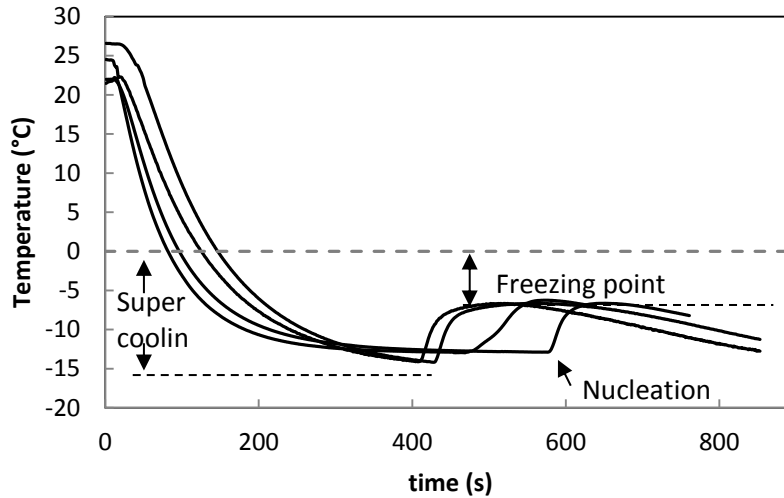
Figure 3.1 Cooling curves of coffee solutions. Xs=0.40

Table 3.2. Freezing point of coffee solutions as a function of coffee mass fraction

Xs	Freezing point (°C)
0.1	-0.76 ± 0.04
0.2	-1.92 ± 0.08
0.3	-3.45 ± 0.06
0.4	-6.54 ± 0.19
0.5	-9.79 ± 0.24

The freezing curve of coffee is between the freezing curves of glucose and sucrose, within the typical region of food fluids proposed by Auleda et al. (2011). This can be attributed to the polysaccharides content of coffee extract, which varies from 20 to 75% dry basis (Thaler, 1978; Franca et al., 2005; De Maria et al., 2006), depending on coffee variety, roasting and extracting processes.

Rheological Measurements

Rheological Behaviour

The rheograms of coffee solutions at Xs 5, 20, 35, and 50% and temperatures between -6 and 4°C are presented in Fig. 3.2, where shear stress (σ) as a function of shear rate (γ) is plotted. The dots correspond to experimental data and the lines were generated from parameters of Eq. 1, shown in Table 3.3. For this regression, coefficients of determination between 0.95 and 1.00 were obtained, suggesting good fitness of the models. A Newtonian behaviour was obtained with a flow index close to 1. Exponents of power law

were less than 1 for high Xs and low temperatures, showing a slightly pseudoplastic behaviour. However, this result is not significant according to standard deviation.
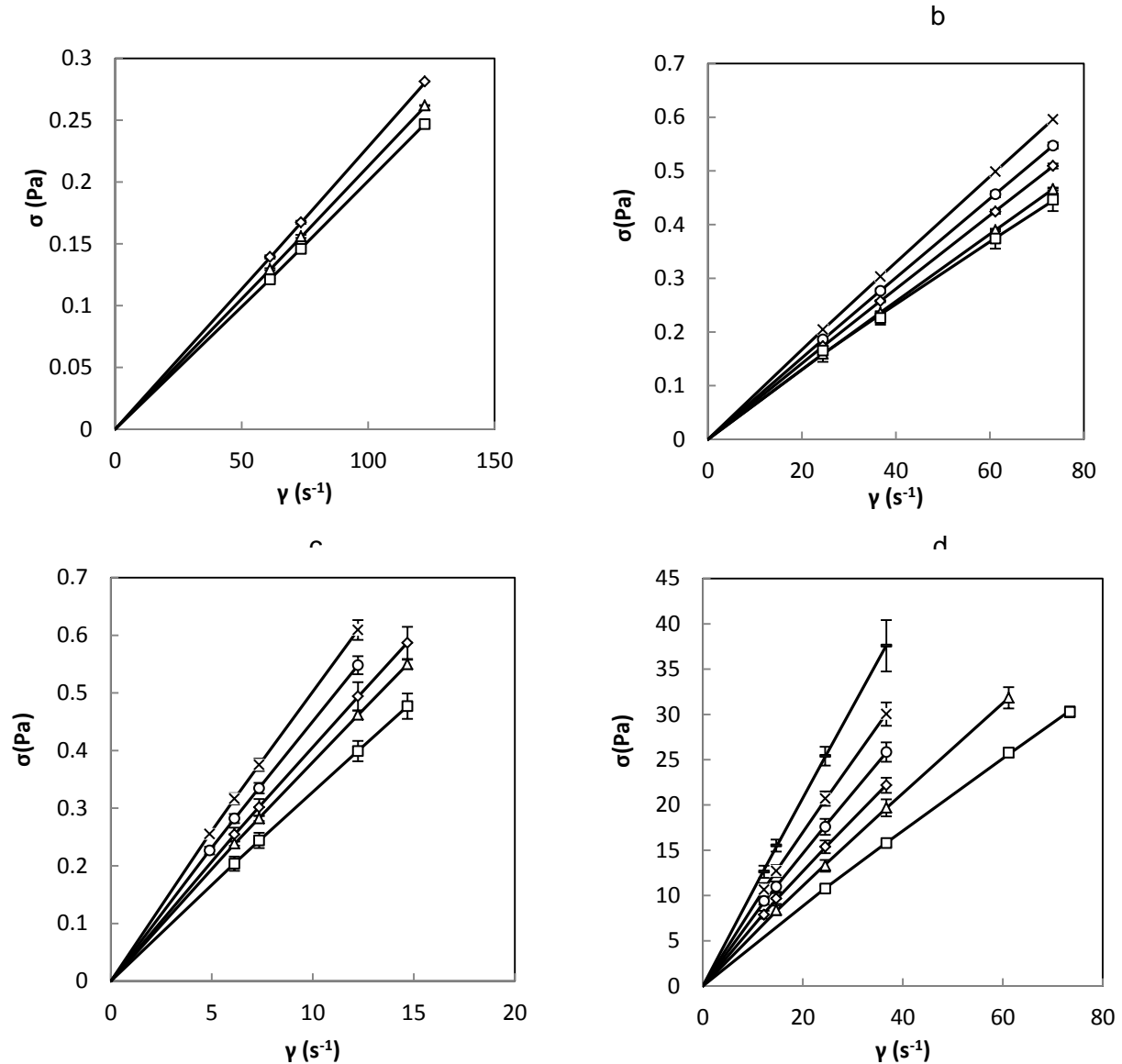
Figure 3.2. Rheogram of coffee solutions

4°C (□), 2°C (△), 0°C(◊), -2°C (○), -4°C(x) and -6°C(─). (a) Xs=0.05, (b) Xs= 0.20, (c) Xs=0.35 y (d) Xs=0.50. Lines are calculated values using parameters given in Table 3.3.

The Newtonian behaviour was reported by Sobolik et al. (2002) for concentrated coffee solutions at higher temperatures in the interval from 0 to 1574 s^{-1}. Moreover, the consistency coefficient of Eq. 1 was increased with Xs and decreased with temperature, as is indicated by several researchers (Chine et al.,2009; Magerramov et al.,2007). Assuming

a Newtonian behaviour, the values of viscosity of coffee solutions at the tested shear rates are presented in Table 3.4. As expected, the viscosity increased with increasing Xs and decreasing temperature. It was observed that influence of Xs on viscosity is greater than influence of temperature. These results are comparable with those obtained for other food solutions (Ruiz et al.,2010) and for coffee solutions at higher temperatures (Sobolik et al.,2002; Telis-Romero et al., 2001).

Table 3.3. Parameters of power law (Eq. 1) for different coffee mass fractions and temperatures

Xs	T (°C)	K	n	R^2
0.05	0	$2.10*10^{-3} \pm 0.90*10^{-3}$	1.01 ± 0.01	0.99
	2	$1.91*10^{-3} \pm 0.10*10^{-3}$	1.01 ± 0.01	1.00
	4	$1.80*10^{-3} \pm 0.10*10^{-3}$	1.03 ± 0.01	0.99
0.20	-4	$9.14*10^{-3} \pm 0.40*10^{-3}$	0.97 ± 0.01	0.99
	-2	$8.02*10^{-3} \pm 0.60*10^{-3}$	0.98 ± 0.02	0.99
	0	$7.52*10^{-3} \pm 0.40*10^{-3}$	0.98 ± 0.01	0.99
	2	$6.90*10^{-3} \pm 0.20*10^{-3}$	0.98 ± 0.01	0.99
	4	$0.81*10^{-3} \pm 2.70*10^{-3}$	0.93 ± 0.08	0.95
0.35	-4	$5.67*10^{-2} \pm 0.47*10^{-2}$	0.95 ± 0.04	0.98
	-2	$4.92*10^{-2} \pm 0.40*10^{-2}$	0.96 ± 0.03	0.98
	0	$4.48*10^{-2} \pm 0.47*10^{-2}$	0.96 ± 0.04	0.98
	2	$4.20*10^{-2} \pm 0.14*10^{-2}$	0.96 ± 0.01	0.99
	4	$3.52*10^{-2} \pm 0.37*10^{-2}$	0.97 ± 0.04	0.98
0.50	-6	1.10 ± 0.29	0.98 ± 0.08	0.95
	-4	1.01 ± 0.18	0.94 ± 0.05	0.97
	-2	0.91 ± 0.16	0.93 ± 0.05	0.97
	0	0.79 ± 0.14	0.92 ± 0.05	0.97
	2	0.65 ± 0.12	0.94 ± 0.04	0.98
	4	0.53 ± 0.06	0.94 ± 0.03	0.99

Viscosity Mathematical Modelling

The viscosity dependence on temperature is presented in Table 3.4. As expected, viscosity increased with Xs and decreased with temperature. Data was fitted to Eq. 2 and the parameters for coffee solutions are presented in Table 3.5. The activation energy was increased with Xs, similarly to the result obtained by (Telis-Romero et al., 2001) for coffee solutions at temperatures between 20 and 80°C. On the other hand, Ko values decreased with Xs. A good fit between experimental and modelled data was obtained. The results are comparable with those reported for other food solutions at temperatures close to freezing (Falguera et al., 2010; Ibarz et al., 2009; Ruiz et al., 2010).

Ea for sucrose solutions was reported by Galmarini et al. (2009), for sucrose concentration of 35% with a value of 22.0 kJ·mol^{-1} between 20 and 34 °C. For fruit juices, activation energy of 42 kJ·mol-1 is reported by Chin et al. (2009). Likewise, the reported activation energy of untreated sugar cane juice is 36.79 kJ· mol^{-1} (Galmarini et al., 2009). Ea value for mandarin juice at low temperatures is 33 kJ· mol^{-1} (Falguera et al., 2010). It is important to remember that Ea for water is 14.4 kJ· mol^{-1} and this value can be increased until 60 kJ· mol^{-1} with solid concentration (Astolfi-Filho et al.,2011). Ea for coffee solutions obtained in the present study varied from 22.0 to 51.3 kJ· mol^{-1}, giving values within the range for food fluids.

Table 3.4. Viscosity of coffee solutions at different temperatures (T) and coffee mass fractions (Xs). (mPa·s)

Xs	0.05	0.20	0.35	0.50
T (°C)				
4	1.99 ± 0.02	5.84 ± 0.08	32.9 ± 1.68	425.84 ± 16.94
2	2.13 ± 0.02	6.41 ± 0.07	36.8 ± 1.98	543.03 ± 44.73
0	2.29 ± 0.02	6.99 ± 0.09	40.7 ± 1.95	633.43 ± 54.68
-2		7.51 ± 0.18	45.6 ± 2.23	734.54 ± 58.74
-4		8.22 ± 0.12	51.1 ± 2.58	849.11 ± 74.89
-6				1037.24 ± 94.90

Table 3.5. Parameters of Arrhenius equation (Eq. 2.) for coffee solutions at different Xs

Xs	Ko (mPa·s)	Ea (kJ·mol^{-1})	R^2
0.05	1.39 *10^{-4} ± 0.82*10^{-4}	22.0 ± 1.35	0.974
0.20	7.60*10^{-5} ± 3.10*10^{-5}	25.9 ± 0.91	0.984
0.35	1.20*10^{-5} ± 1.40*10^{-5}	34.1 ± 2.56	0.933
0.50	9.27*10^{-8} ± 0.00*10^{-8}	51.3 ± 3.57	0.934

General Models

The Regression analyses were performed for four different models of viscosity prediction as a function of Xs and temperature. Parameters of models, standard deviation, and coefficients of determination are given in Table 3.6. Values are comparable with those reported by Ibarz et al, (1992), Longinotti and Corti, (2008) and Sobolik et al. (2002), although there are some differences in values due to specificity for coffee solutions at the present conditions. Eq. 5. had the highest R^2 value, thus, this model seems to be capable of adequately describing viscosity of coffee solutions at different temperatures (°C) and coffee mass fraction at the investigated conditions:

$$log_{10}\,\eta = 21.3 + 2.1Xs + \left(\frac{30-T}{91+T}\right)(31.5 - 12.7Xs^{2.53}) \quad (5)$$

The other two models tested presented a slightly lower regression coefficient, but the adjustment was also satisfactory. Consequently, it is assumed that all models properly describe the viscosity of coffee solutions in the temperature and coffee mass fraction intervals evaluated in this study.

The parameters of Eq.7 for coffee solutions at temperatures between 0 and 80 °C were reported by Sobolik et al. (2002). It is possible to compare a coincident point between the reported model and the model fitted in the present work. The viscosity of a coffee solution at Xs 0.20 and T=0 °C, generated by the model reported by Sobolik et al. (2002) is 0.0085 Pa·s and the corresponding value obtained in this work is 0.0069 Pa·s, showing a difference of 18%. Sobolik et al. (2002) compared their results with those obtained by Weisser in a previous work and found a maximum difference of 15%. This difference is attributed by the authors to the fact that viscosity depends on the type of coffee and its processing. The generation of parameters of this model at temperatures close to freezing expands the range of application of the model to sub-zero temperatures.

Table 3.6. Parameters of mathematical models for prediction of coffee solution's viscosity.

Eq.	Parameters	R^2
3, 4	$a = 8.1 *10^{-3} \pm 3.0 *10^{-5}$ $b = -15.8 \pm 1.43$ $c = 18.9 \pm 1.93$ $d = 1.87 \pm 0.27$	0.955
5, 6	$a_1 = 21.3 \pm 1.18$ $a_2 = 2.10 \pm 0.34$ $b_1 = 31.5 \pm 1.76$ $b_2 = -12.7 \pm 0.65$ $c_1 = 2.53 \pm 0.21$	0.999
7	$a_3 = -7.03 \pm 19.5$ $a_4 = 1.01 \pm 9.48$ $a_5 = -38.7 \pm 79.8$ $a_6 = 2.16 *10^3 \pm 5.31*10^3$ $a_7 = 1.60 *10^3 \pm 2.1*10^4$	0.992

A plot of viscosity values as a function of temperature and Xs was generated using the parameters of the Eq. 5 (Fig. 3.3). This figure showed that viscosity increased with Xs and decreased with temperature. The same result was reported by Diaz-Ocampo et al., (2013).

The curve on the surface represents the freezing point curve of coffee solutions, using values obtained in section 3.2. The viscosity values beyond the line do not have physical significance because they are below the freezing point. A higher dependence of viscosity on Xs than on T is evident in the studied interval.

Density

The density of coffee extract as a function of coffee mass fraction and temperature is shown in Table 3.7. As expected, density increases with Xs and decreases with temperature (Gundurao et al., 2011). Values between 1036 and 1277 kg·m^{-3} were obtained. The results are similar to those reported by Telis-Romero et al. (2000) between 1000 to 1200 kg m^{-3} for the same Xs intervals and higher temperatures. The density evidences a stronger dependence on solid content than on temperature. Density can be expressed as an average of coffee solids density and water density (Sobolik et al., 2002); in turn, density of these components is dependent on temperature. The model fitted is shown in Eq. 11 to 13. The regression coefficient was R^2=0.989, showing a good data fitting.
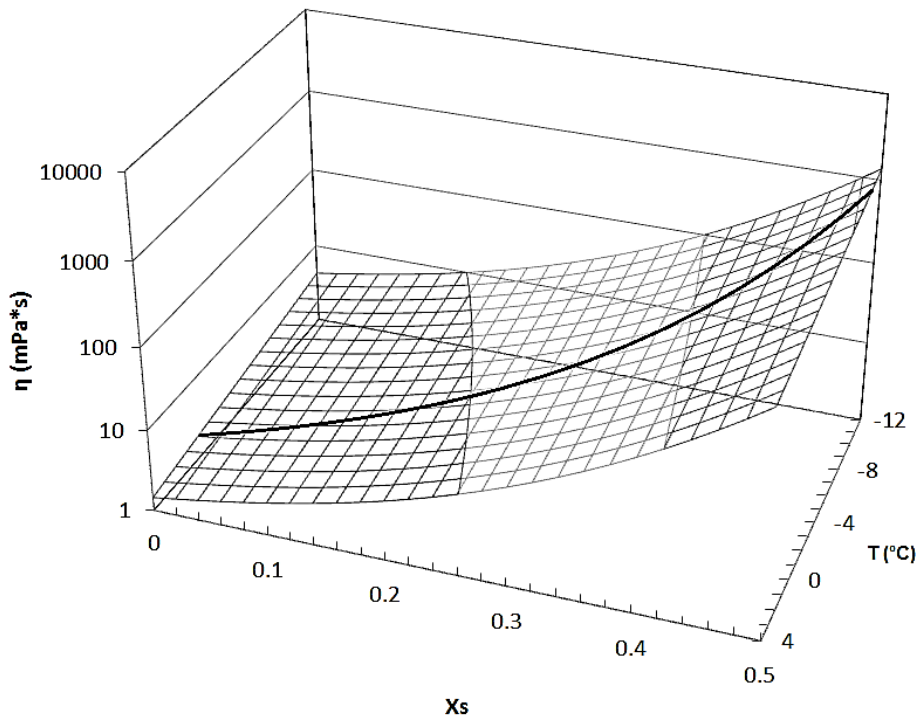
Figure 3.3. Coffee solutions viscosity as a function of temperature and coffee mass fraction.

Predicted values using Eq. 5. The curve on surface represents freezing point curve for coffee solutions modelled by Eq. 10.

$$\frac{1}{\rho} = \frac{Xs}{\rho_c} + \frac{(1-Xs)}{\rho_w} \quad (11) \quad R^2=0.989 \quad \text{Where,}$$

$$\rho_c = 1878.1 - 40.76T + 1.035T^2 \quad (12)$$

$$\rho_w = 1000 + 2.30T - 0.11T^2 \quad (13)$$

Table 3.7. Density of coffee extract (kg·m^{-3}) as a function of coffee mass fraction and temperature.

T(°C)	0	5	10	15	20	25
Xs						
0.1	1083.1 ± 11.7	1073.6 ± 12.2	1053.0 ± 14.3	1042.1 ± 11.4	1037.4 ± 8.2	1036.3 ± 8.9
0.2	1133.4 ± 11.3	1115.7 ± 13.0	1087.3 ± 14.9	1072.1 ± 15.0	1062.8 ± 8.4	1058.6 ± 16.4
0.3	1177.0 ± 9.6	1159.8 ± 19.9	1134.9 ± 22.6	1114.3 ± 17.2	1107.6 ± 20.7	1099.6 ± 7.5
0.4	1224.2 ± 8.4	1205.2 ± 5.8	1174.3 ± 16.3	1153.6 ± 13.2	1147.1 ± 13.7	1141.7 ± 26.6
0.5	1277.2 ± 3.5	1263.0 ± 11.9	1230.0 ± 4.4	1215.1 ± 6.9	1204.2 ± 10.9	1196.1 ± 16.5

3.5. Conclusions

The viscosity of coffee solutions at temperatures close to the freezing point can be predicted by three general models as a function of temperature and coffee mass fraction. The coffee solutions presented a Newtonian behaviour. A slight pseudoplasticity was found at high concentrations and low temperatures, but this result was not significant. In turn, a linear relationship between coffee mass fraction and brix degrees was found; this expression allows measuring coffee mass fraction by a simple technique, such as refractometry. Meanwhile, the freezing curve presented a quadratic behaviour within the zone for food fluids. Finally, the density of coffee solutions can be expressed as an average of coffee solids and water densities. The characterisation of physical properties, rheological behaviour, and freezing curve of coffee solutions is useful for designing operations such as freeze-concentration and freeze drying. Mathematical models for Brix degrees, viscosity, freezing point depression, and density of coffee solutions were fitted. These models can contribute in designing technologies such as freeze-concentration and freeze drying in the coffee industry.

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4. BLOCK FREEZE-CONCENTRATION OF COFFEE EXTRACT: EFFECT OF FREEZING AND THAWING STAGES ON SOLUTE RECOVERY AND BIOACTIVE COMPOUNDS

4.1. Abstract

Coffee extract was freeze-concentrated using the total block technique. The effects of four parameters were evaluated: the initial coffee mass fraction (5 and 15% w/w), the cooling temperature (-10 and -20 °C), the heating temperature (20 and 40 °C) and the freezing direction (parallel and counter-flow to the thawing direction). The solid concentration was measured during the thawing stage to quantify the solute recovery and the concentration index for one stage of freeze concentration. The coffee mass fraction, the freezing direction and the cooling temperature significantly influenced the solute recovery. A concentration index between 1 and 2.3 was obtained in one cycle. The effect of block freeze concentration on the bioactive compound concentration and the antioxidant activity was measured. The coffee bioactive compounds were distributed in proportion to the total solid content in the ice and liquid. Therefore, block freeze concentration is an effective technique to preserve functional properties of coffee extracts.

Keywords: Cryoconcentration; solute yield; coffee; chlorogenic acids; antioxidant activity

Nomenclature

CI	Concentration index
CI_{cum}	Cumulative concentration index
C_{FCL}	Concentration of bioactive compounds in the freeze-concentrated liquid
C_{RI}	Concentration of bioactive compounds in the residual ice
f	Thawing fraction
F_D	Freezing direction
IL	Ice loss percentage
$m_{s\,0}$	Initial solute mass
$m_{s\,liq}$	Solute mass in the liquid fraction
m_0	Initial mass
m_{liq}	Collected liquid mass
T_C	Cooling temperature
T_H	Heating temperature
$X_{s\,0}$	Coffee mass fraction in the initial solution
X_S	Coffee mass fraction
$X_{s\,liq}$	Coffee mass fraction in the freeze-concentrated liquid fraction
Y	Solute yield

4.2. Introduction

Coffee is the most traded food in the world, and its production has great economic and social importance worldwide (Esquivel & Jiménez, 2012; Vignoli et al., 2011). For the consumer, the value of coffee is provided by its sensory and functional properties; for this reason, technologies that promote quality preservation are highly valued in coffee processing. In the production of freeze-dried coffee, freeze concentration (FC) technology is used to remove water from coffee extracts to increase the solid content and reduce the time and cost of the freeze-drying process. At the same time, the sensory properties of the product are preserved using low temperatures (Boss et al., 2004; Joët et al., 2010; Sánchez et al., 2009).

Water removal in FC is achieved by cooling the solution until the ice crystals form and separate (Miyawaki et al., 2005). Three techniques are used according to the ice crystal growth: suspension FC, film FC (progressive or falling film FC) and block FC (total or partial) (Aider & de Halleux, 2009; Sánchez et al., 2009). Suspension FC is a unique technique implemented at the industrial level. Different techniques, such as falling film FC, (Chen et al., 1998; Sánchez et al., 2011), progressive FC (Miyawaki et al., 2005) and block FC (Aider & Ounis, 2012; Nakagawa et al., 2010a), are being developed to reduce operational costs.

In the block FC method, also known as freeze–thaw concentration, the solution to be concentrated is completely frozen and then partially thawed to recover a fraction of liquid with a higher concentration (Aider & de Halleux, 2009; Nakagawa et al., 2010b). Block FC consists of three stages: freezing, thawing and separation of the concentrated liquid fraction (Moreno et al., 2013). These stages define the separation efficiency (Nakagawa et al., 2009). Additionally, the process can be repeated in successive cycles to increase the concentration index (Aider & Ounis, 2012).

The technical viability of the block FC method has been proposed recently by several researchers (Gao et al., 2009; Nakagawa et al., 2010a; Aider & Ounis, 2012; Boaventura et al., 2012; Miyawaki et al., 2012; Petzold et al., 2013). During the freezing stage, heat and mass transfer phenomena can modify the solute occlusion, which should be as low as possible. Chen et al. (2001) reported that the solute elution in the freezing front in FC depends on the molecular size of the compounds. Certain authors have reported that the solute separation is controlled by the thawing stage (Nakagawa et al., 2010b). For coffee solutions, Moreno et al. (2013) studied the use of aids in the separation stage. These authors reported the influence of the FC protocol and solution type on solute recovery and the concentration index; for this reason, there is no agreement on the significance of the process variables. The effects of the process variables of block FC on the separation efficiency of coffee extracts have not been reported.

Coffee can be considered to be a functional beverage due to its radical scavenging capabilities (Cheong et al., 2013; Esquivel & Jiménez, 2012). Several studies have

reported the health benefits of coffee consumption related to the components with antioxidant activity, such as the group of chlorogenic acids and caffeine. Chlorogenic acid (3-caffeoylquinic acid), cryptochlorogenic acid (4-caffeoylquinic acid), neoclorogenic acid (5-caffeoylquinic acid) and caffeine are the major bioactive compounds present in coffee (Ferruzzi, 2010; Fujioka & Shibamoto, 2008; Sopelana et al., 2013; Vignoli et al., 2011). The block FC method has been shown to retain nutritional and functional properties of the product using low processing temperatures (Belén et al., 2013; Boaventura et al., 2012); however, this effect has not been tested for coffee extracts.

The aim of the present study was to evaluate the effect of the initial coffee mass fraction, the cooling temperature, the heating temperature and the freezing direction on the solute yield and concentration index of block freeze-concentrated coffee extracts. Additionally, the impact of the technique on bioactive compound concentration and the antioxidant activity of the coffee extract was tested.

4.3. Materials and Methods

4.3.1. Materials

Coffee solutions were prepared from freeze-dried soluble coffee supplied by the company Buencafé Liofilizado de Colombia (Colombian Coffee Growers Federation, Colombia) for the FC tests. The coffee was added to distilled water at 35 °C and mixed for 20 min. The samples were stored at 4 °C for 12 h. The solid concentration is expressed as the coffee mass fraction (X_S), which is defined as the mass of coffee solids per unit of coffee solution mass. The relationship between Brix degrees and X_S is represented by the equation $X_S=0.0087$ °Brix ($R^2=0.991$). This expression was obtained by preparing coffee solutions at 10, 20, 30, 40 and 50 °Brix and by measuring coffee mass fraction using the weight loss technique in the oven at 103 °C for four hours according to technical standard NTC4602 (Icontec, 2009). The measurements were performed in triplicate. The coffee mass fraction of the solutions was ascertained immediately before the FC tests by refractometry (Atago Pal 100, Japan). A liquid coffee extract was used for the measurement of bioactive compounds. This extract belonged to the same batch of soluble coffee and was also provided by Buencafé Liofilizado de Colombia.

4.3.2. Methods

Freeze concentration protocol

The effects of the initial coffee mass fraction (X_S), cooling temperature (T_C), heating temperature (T_H) and the freezing direction (F_D) were studied. A full factorial design with four factors and two levels was used for a total number of 16 tests (Table 4.1). The coffee solutions were subjected to one cycle of freezing, thawing and separation to study the effect of process variables on solute yield after one cycle of FC.

Table 4.1. Experimental design

Test	X_S	T_C	T_H	F_D
1	0.05	-10	20	1
2	0.05	-10	20	-1
3	0.05	-10	40	1
4	0.05	-10	40	-1
5	0.05	-20	20	1
6	0.05	-20	20	-1
7	0.05	-20	40	1
8	0.05	-20	40	-1
9	0.15	-10	20	1
10	0.15	-10	20	-1
11	0.15	-10	40	1
12	0.15	-10	40	-1
13	0.15	-20	20	1
14	0.15	-20	20	-1
15	0.15	-20	40	1
16	0.15	-20	40	-1

F_D +1: counter-flow to thawing; F_D -1: parallel to thawing

The block FC device is shown in Fig. 4.1. In total, 160 g of the coffee sample was placed into a cylindrical container (1) measuring 52.5 mm in diameter and 85 mm in height. The container is a double jacket device for the flux of cooling and heating fluids. The internal jacket is 19 mm in diameter (2). The cooling/heating fluid was a mixture of ethylene glycol and water (53% w/w) coming from two circulated baths (4 and 5) (Polystat, Cole Parmer, USA). The baths were temperature controlled (6 and 7) at an interval from -35 °C to 150 °C +/- 0.01 °C. The baths pumped the heat exchange fluid to the jackets through a system of ducts and valves (7).
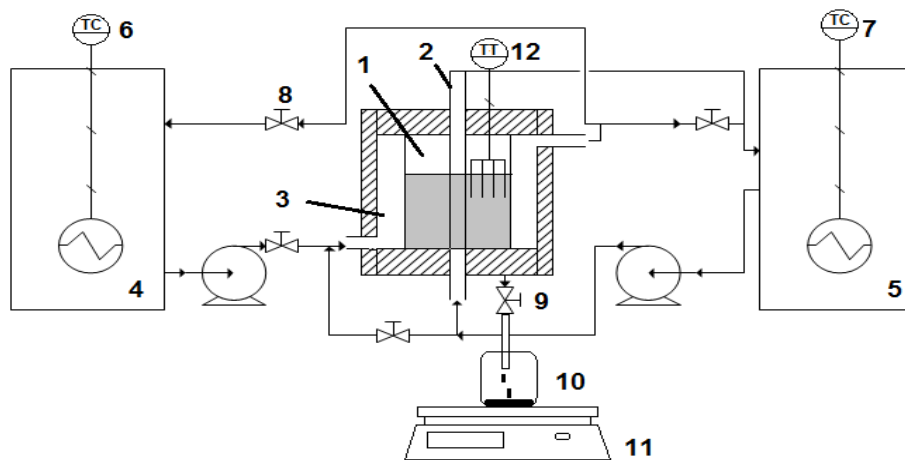
Figure 4.1. Experimental set up for block freeze concentration

During the tests, the heat exchange fluid temperature was settled in one bath. After the fluid reached the temperature, it was circulated to the jackets to freeze the solution inside. The heat transfer was in the radial direction from the internal wall (for freezing parallel to thawing) or from the external wall (for freezing in counter-flow to thawing). Meanwhile, the heating temperature of the second bath was settled. When the sample was frozen and the temperature was approximately constant, the thawing stage was begun by pumping the heating fluid through the external jacket. The exit valve (9) was opened and the liquid fraction was separated in a collector vessel (10) on a scale (11) (Ohaus PA3102, USA) with a capacity of 3100 g and a precision of 0.01 g for weight measurement. During the thawing stage, the temperature of the internal jacket was maintained one Celsius degree below the freezing point of the coffee solution to avoid thawing the internal side and to preserve unidirectional thawing. Ten liquid fractions of the same mass were collected. Lastly, the coffee mass fraction (X_S) was measured by refractometry (Atago Pal 100, Japan).

Temperature profile
The FC device seen in Fig. 4.1 has four temperature sensors (12) inside of the container to measure the temperature profile during one test. These sensors were used during the temperature measuring tests but not during the FC tests. The sensors PT100-IP65 (Testo, Germany) had a 2 mm diameter and a measuring interval of -50 to 300 °C +/- 0.01 °C and were placed equidistant from the centre of the container (sensor 1) and the external wall (sensor 4). The sensors were connected to a datalogger 176 T2 (Testo, Germany) connected to a PC for data collection.

Data analysis

Thawing fraction (f)

A thawing fraction (f) was used to follow the development of the process. The f was measured as the ratio between the thawed mass and the mass of the original solution, defined by Eq. 1. (Miyawaki et al., 2012; Nakagawa et al., 2010a):
$f = m_{liq}/m_0$ (1)
where
f: thawing fraction
m_{liq}: collected liquid mass
m_0: initial mass.

Solute Yield (Y)

Solute yield was calculated for analysing the solute recovery. Y was defined as the relationship between the mass of solute present in the separated liquid and the mass of solute present initially in the original solution, as seen in Eq. 2. (Moreno et al., 2013; Nakagawa et al., 2010a):

$Y = m_{s\,liq}/m_{s\,0}$ (2)
where
Y: solute yield
$m_{s\,liq}$: solute mass in the liquid fraction
$m_{s\,0}$: initial solute mass.

Concentration Index

The concentration index (CI) was used to express the concentration of solutes reached after the FC process. CI was defined as the relationship between the solid concentration in the liquid fraction and the solid concentration in the initial solution. CI is also known as relative concentration (Nakagawa et al., 2009):
$CI = X_{s\,liq} / X_{s\,0}$ (3)
where
CI: concentration index
$X_{s\,liq}$: coffee mass fraction in the freeze-concentrated liquid fraction
$X_{s\,0}$: coffee mass fraction in the initial solution.

When the CI is calculated using the mixture of the thawed fractions at a given time, Eq. 3. can be expressed as the cumulative index (CI_{cum}). Cumulative CI is the relationship between X_S in the accumulated liquid fraction and X_S in the initial solution.
Eq. 4. was obtained by combining Eq. 2. and Eq. 3.:
$Y = CI_{cum}*f$ (4).

Area under curve Y vs. f

During the thawing stage of FC, the graph Y against f represents the percentage of coffee solids that was recovered from the initial solution for each thawed liquid fraction. The behaviour of a freeze concentration test can be represented by Fig. 4.2, as proposed by Nakagawa, et al. (2010a).
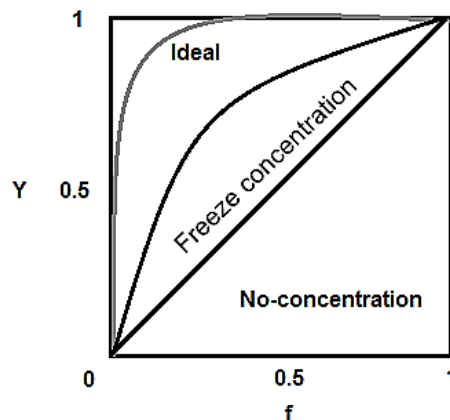
Figure 4.2. Solute yield during freeze concentration tests.

Adapted from (Nakagawa et al., 2009)

The diagonal line represents the case in which the thawed liquid fraction had the same concentration as the initial solution; therefore, there was no FC. A higher curve from the diagonal indicates the amount of recovered solute for a given f and the efficiency of the separation were greater. An ideal situation would be a curve very close to the y-axis in which all of the solute was recovered at the beginning of the thawing stage. The curve of ideal separation can be calculated from the freezing curve of coffe extract of Fig. 3.3. and Table 3.2. With this curve, the highest amount of recovered solutes can be calculated at the average temperature of the ice. Therefore, the area under the curve Y vs. f can be used as a single parameter to compare the efficiency of the separation process and to examine the effect of the studied factors.

The area under the curve represents the integral of the function Y vs. f. The area value is bounded between 0 when the solutes are not recovered and by 1 when all the solutes are recovered instantaneously and there is no solute occlusion. The diagonal line of no-concentration has an area of 0.5. An area value closer to one indicates a better result of the FC process. The area under the curve can be understood as the sum of the solute yield achieved in a thawing fraction during the FC. The area under curve Y vs. f was used as an identifying parameter of the effect of each studied variable.

Freezing front growth rate

The average freezing front growth rate was calculated by measuring the distance from the cooling surface to the front of the ice during the freezing stage with a calliper. The average of the ratios of distance to time was used as the rate. The rate was expressed in micrometres per second.

Bioactive compound measurement

The major bioactive compounds of coffee extract, chlorogenic acid (CGA), cryptochlorogenic acid (c-CGA) and caffeine, were measured for the initial solution, the freeze-concentrated liquid recovered at a f value of 50% and for the residual ice at the same f as a comparative parameter. The measurements were performed for tests 1 and 16 (Table 4.1), which correspond to the extreme values of X_S, T_C, T_H and total process time. The measurements were performed in triplicate.

The concentration of bioactive compounds was determined by reversed-phase high performance liquid chromatography (RP-HPLC) as described by Fujioka & Shibamoto (2008) and Owen et al. (2003) with modifications. The RP-HPLC apparatus, LaChrom (Merck-Hitachi, Germany-Japan), was equipped with a quaternary pump, degasification system and a diode array detector (UV/VIS). The separation was achieved in a Gemini column C-18 (Phenomenex, USA) measuring 250 mm * 4.6 mm and 5 μm at 25 °C. The mobile phase used was acetic acid 2% (A) and methanol (B). The gradient was adjusted as follows: 0-10 min, A/B 96/4; 65 min, 85/15; 75 min, 75/25; and 85 min, 25/75 at a flow

rate of 1 mL·min^{-1}. CGA and c-GCA were detected at 325 nm, and caffeine was detected at 276 nm. The injection volume was 5 µL. The concentrations of bioactive compounds were calculated using a regression equation of their concentrations and the peak area obtained from pattern grade HPLC (Sigma-Aldrich, USA).

The loss of bioactive compounds in the residual ice due to FC was calculated using Eq. 5. (Ramos et al., 2005):

$$IL = C_{RI} / (C_{RI} + C_{FCL})*100 \quad (5)$$

where

IL: ice loss

C_{RI}= concentration of bioactive compounds in the residual ice

C_{FCL}= concentration of bioactive compounds in the freeze-concentrated liquid.

Antioxidant activity

The antioxidant activity of coffee samples was determined by the ABTS (2,20-azinobis (3-ethylbenzothiazoline-6-sulphonic acid assay) and DPPH (2,2-diphenyl-1-picrylhydrazyl assay) methods.

ABTS methodology

Antioxidant activity was estimated in terms of radical scavenging activity using the procedure described by Vignoli et al. (2011) with modifications. Briefly, ABTS radical cations (ABTS$^+$) were produced by reacting 3.5 mM ABTS stock solution with 12.5 mM potassium persulphate prepared in a 10% phosphate buffer solution at a pH of 7.4 in distilled water. The solution was stored in the dark at room temperature for 12 h. Before the analysis, the solution was settled at 0.8 +/- 0.2 nm. Lastly, 50 µL of the coffee sample was added to 200 µL of ABTS+ solution and the absorbance was read after 30 min of incubation in complete darkness using an iMark Microplate Reader spectrophotometer (Bio-Rad, USA). The same procedure was conducted for calibration with ethanol solutions containing known concentrations of Trolox between 3 and 15 µL·mL^{-1}. The results were expressed in g of Trolox per 100 g of coffee (dry matter). The experiments were performed in triplicate.

DPPH methodology

The DPPH technique was performed according to Vignoli et al. (2011). A DPPH solution was prepared at 0.6 mM of methanol. The absorbance was settled to 1.1 nm before the tests. For the analysis, 50 µL of DPPH solution was added to 75 µL of each coffee sample. The absorbance was measured at 515 nm after 30 min of incubation at room temperature in complete darkness. The calibration was performed with Trolox at concentrations between 3 and 15 µL·mL^{-1}. The antioxidant activity was expressed as mg of Trolox/mL. The experiments were performed in triplicate using methanol as a blank.

Statistical analysis

All the tests were performed in triplicate. The area under the curve of Y vs. f was obtained by a spline regression procedure. A response surface regression procedure was used to determine the effect of each studied factor listed in Table 1 on the area under the curve with a confidence interval of 95%. One-way analysis of variance (ANOVA) was applied to the results of the area under the curve followed by a LSD test with a level of significance of 95%. For the bioactive compound measurement, the mean values were calculated and a correlation analysis was performed by comparing the Pearson coefficients. All statistical analysis were performed using the SAS 9.2 software package.

4.4. Results and discussion

4.4.1. Temperature profiles

The temperature profiles during FC tests for tests 1 and 8 described in Table 4.1 are shown in Fig. 4.3. These tests corresponded to the lowest and highest overall process time; therefore, the other tests were within this time interval. Temperature sensor 1 was located beside the internal wall of the container and sensor 4 was located in the external wall. In test 1, the freezing was achieved from the centre and the thawing from the external wall. For this reason, the temperature dropped first in sensor 1 and last in sensor 4, as can be seen in Fig. 3a; during the thawing stage, the order was reversed.

Point "a" shows the nucleation phenomenon that caused a temperature increase due to the latent heat of the phase change. The latent heat released from the portion of liquid closest to the centre (line 1) caused a temperature increasing of the external portion before it was frozen (line 4). For this reason, a temperature increasing in the interval 0°C to 5°C was observed. After that, the whole solution was frozen and the temperature tended to be constant. A similar behaviour was reported by Nakagawa et al. (2010b).

When the temperature was stable, the thawing phase began (point b). A change in the temperature was observed in the opposite order than it was in the freezing stage. For test 1, the thawing time was 180 min and the average freezing growth rate was 1.84 $\mu m \cdot s^{-1}$. Alternatively, in test 8 (Fig. 4.3b), the freezing and the thawing were both achieved from the external wall in parallel. The first portion that was frozen and thawed corresponded to sensor 4, which was located beside the external wall. A freezing time of 45 min and an average ice growth rate of 7.17 $\mu m \cdot s^{-1}$ were obtained.

4.4.2. Freeze-concentration tests

The results of the block FC tests are shown in Table 4.2 in descending order of the area under the curve of Y vs. f. The greatest area was obtained for test 1, which corresponded to the lowest coffee mass fraction, the greatest cooling temperature, the lowest heating temperature and freezing direction in counter-flow to the thawing. The treatments showed

significant differences at p<0.05. The LSD test indicated differences among treatments for X_S=0.05. Differences in F_D and T_C can be observed. On the contrary, the tests with the highest X_S did not show significant difference because the solid concentration is predominant over the effect of the other factors.
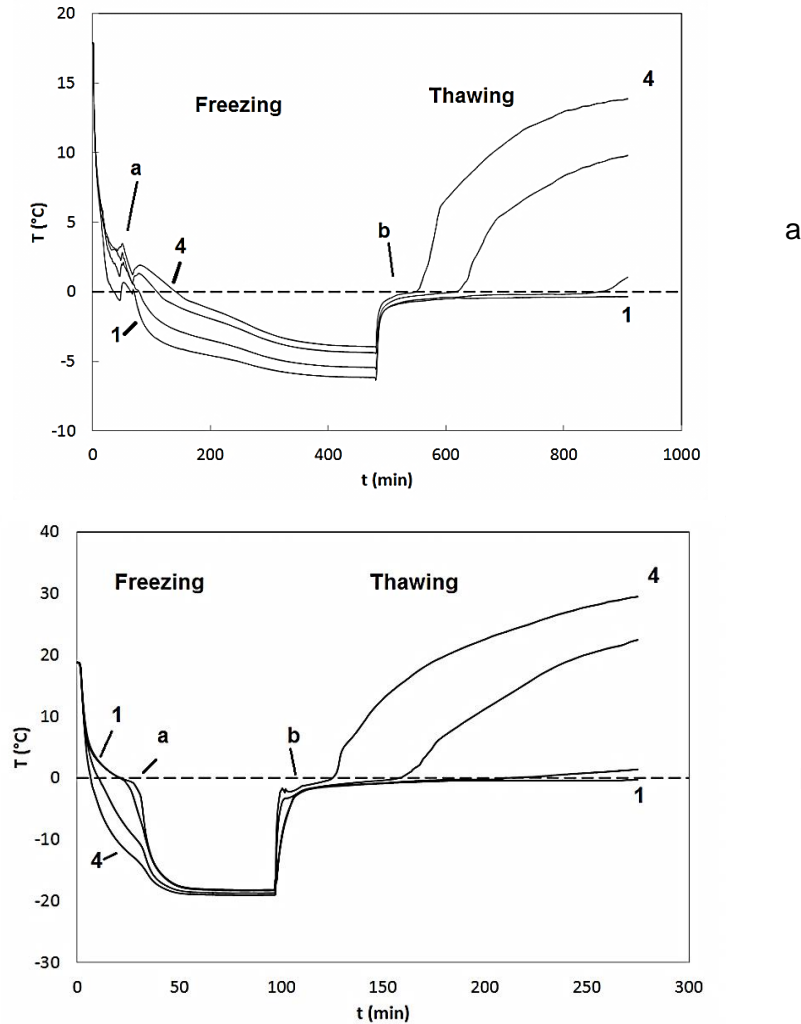
Figure 4.3. Temperature profile during freezing and thawing stages.

a) Test 1. T_C = -10 °C, T_H = 20 °C; b) Test 8 T_C = -20 °C, T_H = 40 °C. 1: Temperature sensor 1 (interior) and 4: temperature sensor 4 (exterior)

The values for Y and f when the CI was equal to one are shown in Table 4.2. At this value of f, solute yields between 67 and 83% were obtained. At this point, the cumulative CI values were between 1.10 and 1.67. A CI of 1.8 for one cycle of FC was reported by Aider & Ounis (2012). For falling film FC, a CI between 2 and 3 was reported by Sánchez et al. (2011) and Belén et al. (2012). Miyawaki et al. (2005) reported a CI between 2 and 3 for progressive FC. However, all of these authors reported that the results depended on the fluid being concentrated, the type and size of the equipment and the process time.

Table 4.2. Freeze concentration tests in descending order of area under the curve

TEST	X_S	T_C	T_H	F_D	Area under curve	f at CI=1	Y at CI=1	Cumulative CI at CI=1	CI max	Freezing front growth (μ s^{-1})
1	0.05	-10	20	1	0.802 [a]	0.5	0.83	1.67	2.22	1.84
3	0.05	-10	40	1	0.778 [a,b]	0.5	0.78	1.56	1.49	1.83
5	0.05	-20	20	1	0.777 [b,c]	0.5	0.81	1.62	1.89	2.87
2	0.05	-10	20	-1	0.762 [b,c,d]	0.5	0.82	1.64	2.26	3.71
4	0.05	-10	40	-1	0.746 [e,c,d]	0.6	0.91	1.51	2.23	3.71
7	0.05	-20	40	1	0.741 [e,d]	0.5	0.73	1.47	1.87	2.87
6	0.05	-20	20	-1	0.736 [e,d]	0.6	0.88	1.47	1.79	7.17
8	0.05	-20	40	-1	0.735 [e]	0.6	0.90	1.50	2.38	7.17
9	0.15	-10	20	1	0.657 [f]	0.7	0.81	1.16	1.25	1.19
10	0.15	-10	20	-1	0.653 [f]	0.7	0.81	1.16	1.29	5.10
11	0.15	-10	40	1	0.652 [f]	0.7	0.78	1.12	1.17	1.19
14	0.15	-20	20	-1	0.647 [f]	0.7	0.80	1.14	1.32	7.53
16	0.15	-20	40	-1	0.646 [f]	0.8	0.89	1.11	1.23	7.53
13	0.15	-20	20	1	0.644 [f]	0.6	0.67	1.12	1.22	2.58
15	0.15	-20	40	1	0.640 [f]	0.7	0.77	1.10	1.18	2.58
12	0.15	-10	40	-1	0.635 [f]	0.7	0.78	1.11	1.16	5.10

Different letters indicate statistically significant differences (p<0.05)

The maximum CI obtained was 2.38 for test 8. The maximum CI for each test was reached in the first thawing fractions and these values descended during the thawing stage. The concentrated fraction percolates through the frozen matrix (Petzold et al., 2013) and its concentration descended until values close to zero during the thawing stage. It therefore was possible to know the f value at which the CI reached a value of 1. This situation corresponded to the moment at which it becomes convenient to separate the thawing fraction to avoid a cumulative concentration decrease. The f values are shown in Table 2 (f at CI=1) and varied from 0.5 to 0.8. The f value at which the thawing stage has to be stopped depends on the process conditions.

Freezing front growth rates from 1.8 to 7.5 μm·s^{-1} were obtained. The values depended on the cooling temperature, the heat transfer area and the initial coffee mass fraction. The area under the curve tended to be higher for lower freezing rates. The result is more evident at low solid concentrations. For high solid concentrations the effect of freezing rate was not observed because of the effect of solid interactions. No concentration was obtained for a freezing rate of 7.5 μm·s^{-1}. At this rate, the ice occluded solutes during the freezing stage. A critical rate value was also obtained by Nakagawa et al. (2010a). The authors reported that for velocities higher than 8 μm·s^{-1}, the freezing was too fast to expect a considerable separation of the concentrated solution phase.

4.4.3. Effect of each operational factor on solute recovery

A regression analysis was performed to determine the statistical significance of the factors of the study on the area under the curve of Y vs. f. The result is shown in Table 4.3. The analysis showed a good fitting of the experimental data (R^2=0.9874 and RMSE=0.0123). The parameters with a Pr<0.05 significantly affected the area under the curve. The main effects X_S, T_C and F_D and the interaction terms $T_C \cdot X_S$ and $F_D.X_S$ significantly affected the freeze concentration.

Table 4.3. Significance analysis for freeze concentration factors

Parameter	Estimator	Pr > |t|	
Intercept	0.917	<0.001	
X_S	- 1.617	0.0002	*
T_C	0.004	0.039	*
T_H	- 0.001	0.077	
F_D	0.037	0.010	*
$T_C \cdot X_S$	- 0.020	0.049	*
$T_H \cdot X_S$	- 0.006	0.184	
$T_H \cdot T_C$	- 0.001	0.545	
$F_D \cdot X_S$	- 0.133	0.019	*
$F_D \cdot T_C$	0.001	0.141	
$F_D \cdot T_H$	0.001	0.358	

* statistically significant at α<0.05

The coffee mass fraction had the greatest influence with a negative correlation; in other words, the grade of concentration achieved with the block FC decreased with the increase in X_S. The second main effect was the freezing direction followed by the cooling temperature. The interactions between X_S and the other two mean factors were also significant, indicating the influence of these variables. Alternatively, the T_H did not significantly affect the studied intervals. Nakagawa et al. (2010b) and Moreno et al. (2013) reported that the T_H influenced the solute yield when lower thawing temperatures were compared. This result depended on the FC protocol and the level of T_H.

Effect of initial coffee mass fraction (X_S)

The curves Y against f and CI against f for tests 5 and 13 are shown in Fig. 4.4. These test had different values of X_S, but the other factors were constant. A higher solute recovery was obtained for X_S = 0.05. This result was the same for all of the tests. Comparing the curve with the diagonal line of no-concentration, the area under the curve was higher for the lowest X_S.

This result can be explained by different factors. First, during the freezing stage, the ice grows by the diffusion of water molecules to the ice surface and the counter-diffusion of solutes to the liquid phase (Petzold & Aguilera, 2009). The diffusion rate of solutes decreases when the solid concentration increases due to the interactions between

molecules; consequently, the achieved concentration decreases. The same result was reported by Chen et al. (2001) and Hindmarsh, Russell, & Chen (2005). Second, the coffee solution viscosity increases with X_S; this factor can cause the separation of the liquid phase during the thawing stage to be difficult (Raventós et al., 2007). Additionally, the ice tends to grow in dendritic form for high solid concentrations, occluding higher amounts of solutes (Yee et al., 2003). Lastly, the volume of water that can be frozen and separated is lower for higher concentrations (Aider & de Halleux 2008a). The combination of these four effects explains why X_S was the factor with the greatest effect on Y and CI.

(a)

(b)
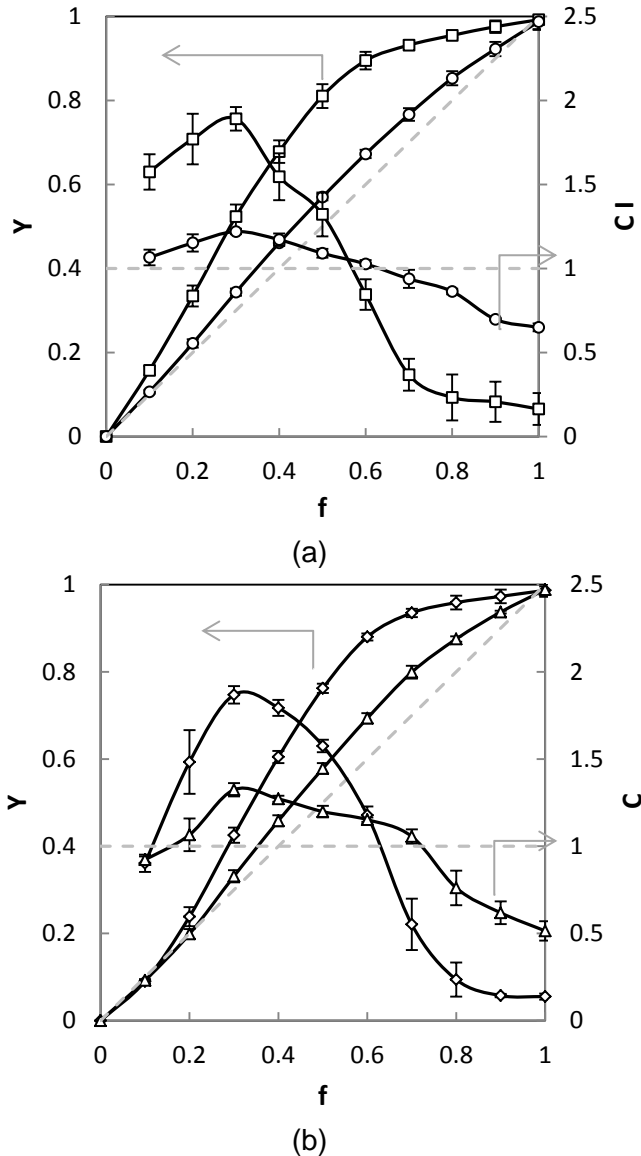
Figure 4.4. Effect of coffee mass fraction on solute yield and the concentration index.

a) Test 5, X_S = 5% (□); Test 13, X_S = 15% (○); b) Test 6, X_S = 5% (◊); Test 14, X_S = 15% (Δ)

In the CI vs. f curve, the value at which the CI crossed the horizontal line of CI=1 is shown in Fig. 4 to 7. This intersection corresponded to the moment at which the thawing stage has to be completed to avoid a sample dilution and to recover as much solute as possible. For test 1, at f=0.5, 83% of the coffee solids had been recovered and the cumulative CI was 1.67. These results indicate a good separation efficiency.

Effect of freezing direction (F_D)

Tests 1 and 2 are shown in Fig. 4.5a. Tests 9 and 10 are shown in Fig. 4.5b. Table 4.2 shows the differences in freezing direction. A better FC was obtained for the tests in which the freezing and thawing directions were opposite.
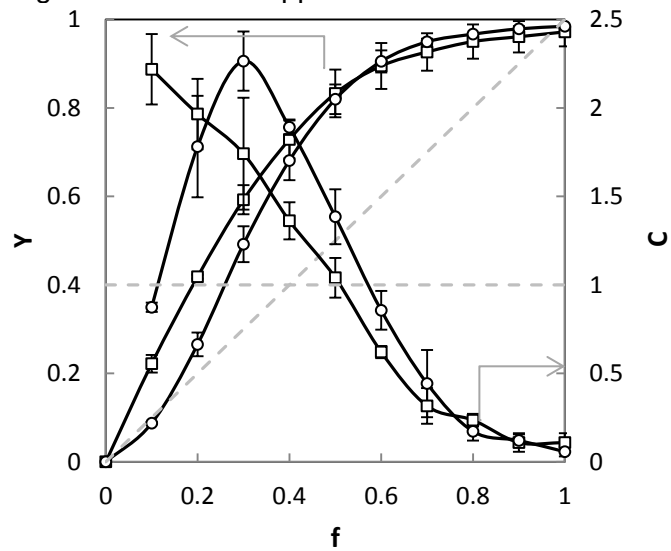
(a)
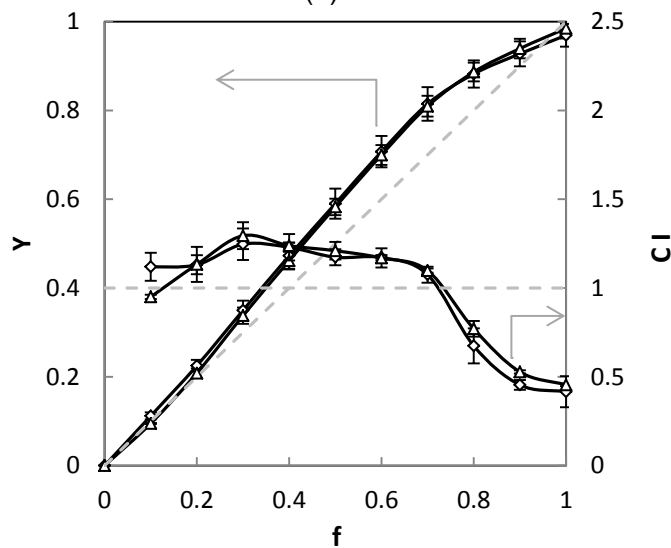
(b)

Figure 4.5. Effect of freezing direction on solute yield and the concentration index.

a) Test 1, F_D = +1 (□); Test 2, F_D = -1 (○); b) Test 9, F_D = +1 (◊); Test 10, F_D = -1 (Δ)

For the F_D during counter-flow, the CI began in maximum values and descended during the thawing. This result indicates that the solutes moved during the freezing stage to the farthest zone from the container centre, which was the last area frozen and the first area thawed. Additionally, the lower heat transfer area in the internal wall compared to the external wall facilitated the solute elution due to the slower ice front growth.
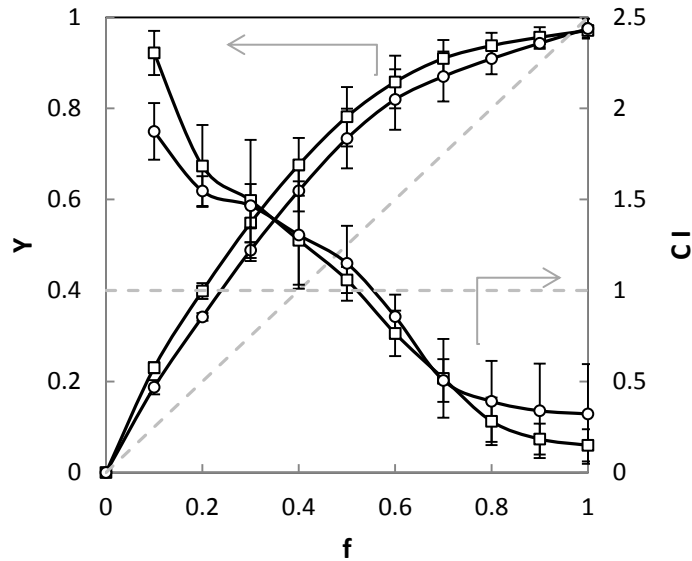
(a)
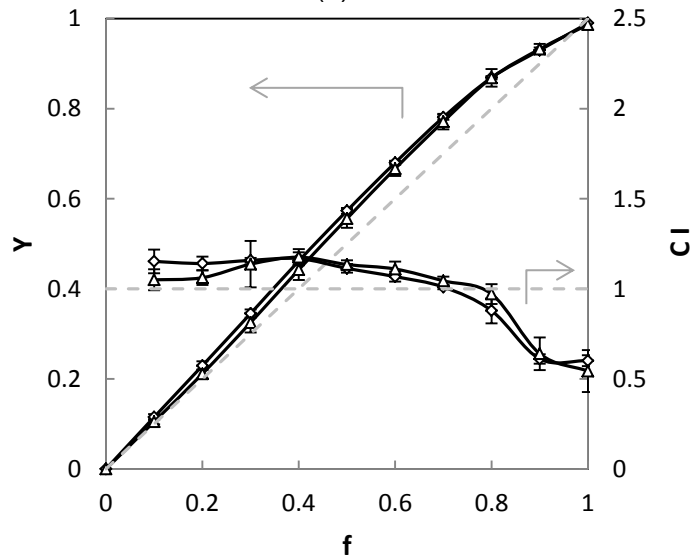
(b)

Figure 4.6. Effect of cooling temperature on solute yield and the concentration index.

a) Test 3, T_C = -10 °C (□); Test 7, T_C = -20 °C (○); b) Test 11, T_C = -10 °C (◊); Test 15, T_C = -20 °C (Δ)

Alternatively, the initial CI was lower than the CI for the tests when the F_D was in parallel. The solutes moved from the external region of the container, as evidenced by the smaller X_S compared to the initial X_S. This finding can be explained by the elution phenomenon, in which a movement of the solutes was produced by counter-diffusion during ice crystals formation that expelled the solutes to the liquid fraction. This result was also observed by Nakagawa et al. (2009). Moreover, Chen et al. (2001) reported that elution depends on the molecular size of the solutes. The effect is smaller with increasing initial solute contents.

(a)

(b)
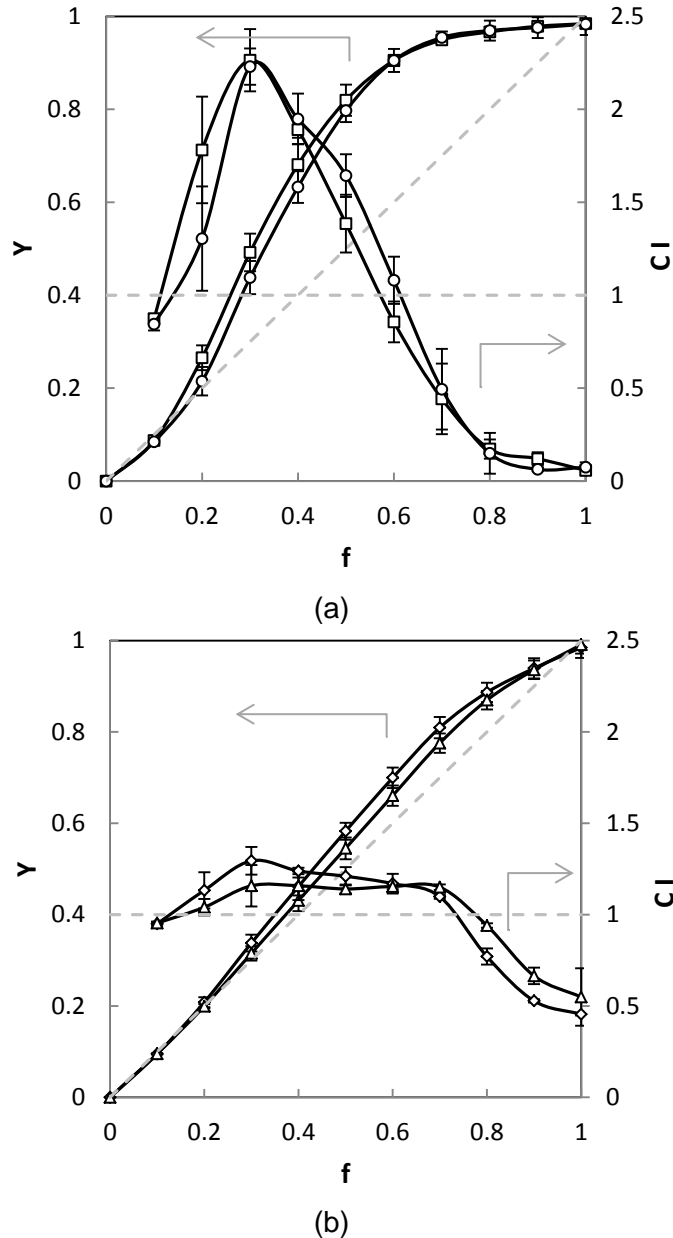
Figure 4.7. Effect of heating temperature on solute yield and the concentration index.

a) Test 2, T_H = 20 °C (□); Test 4, T_H = 40 °C (○); b) Test 10, T_H = 20 °C (◊); Test 12, T_H = 40 °C (Δ)

For the tests when the F_D was in parallel, the CI was lower than counter-flow direction at the beginning, and then it increased at f values from 0.2 to 0.4. This result could have occurred because the solutes diffused from the concentrated liquid fractions to the droplet of water that had melted during thawing. This phenomenon is known as sweating. This result was also reported by Nakagawa et al. (2009). Likewise, the concentrated portions were the first fractions to be thawed and separated due to the difference in densities, as reported by Yee et al. (2003). The results show the freezing direction as a variable of interest in the study of block FC to promote the intensification of solute recovery.

Effect of cooling temperature (T_C)

Fig. 4.6 shows the tests comparing the effect of T_C. Better outcomes were obtained at -10 °C. The heat transfer rate was slower at higher cooling temperatures. The ice crystals were able to grow in a more ordered pattern that occluded a smaller amount of solutes. For the elution to occur, the solutes mass transfer rate must be greater than the ice growth rate (Caretta et al., 2006; Petzold & Aguilera, 2009). In addition, the ice crystal size depends on the cooling rate, which can affect the level of occlusion (Pardo et al., 2002). Certain authors have reported that the cooling temperature is not a significant factor impacting block FC (Aider & de Halleux, 2008b; Gao et al., 2009). These reports suggest that the effect of T_C depends on the FC protocol during both the freezing and thawing stages and depends on the separation mode of the liquid phase.

Effect of heating temperature (T_H)

A slightly higher solute recovery was obtained at a T_H of 20 °C (Fig. 4.7). The average temperature in the empty region of the container after each liquid fraction separation during the thawing was 10 °C (Fig. 4.3). The treatments with the lowest T_H allowed for a slower thawing and avoided the dilution of the concentrated phase. However, the effect was not significant at the studied levels. The T_H may be significant at different levels, as reported by Moreno et al. (2013) where the tested heating temperatures were closer to the freezing point.

4.4.4. Bioactive compounds and the antioxidant activity of coffee

The concentrations of the major bioactive compounds in coffee solutions were determined for the initial solution (C_0), the liquid freeze-concentrated liquid (C_{FCL}) and the residual ice (C_{RI}) obtained for a thawing fraction of 50%. A typical chromatogram is shown in Fig. 4.8. Chlorogenic acids were the major component in the solutions. The bioactive compounds concentration and the ice loss percentage are shown in Table 4.4.
The ice loss percentage was approximately 16% for the lowest X_S and 41% for the highest X_S. This factor was related to the concentration index. When the ice loss (IL) was calculated on a coffee dry matter basis, the result was approximately 50%. This result indicates that the functional compounds were equally distributed in the ice and liquid

fractions. There was a greater amount of bioactive compounds in the liquid phase because the concentrated liquid had a higher X_S. The results correspond to tests 1 and 16 (Table 1), which had extreme values of X_S, T_C, T_H and total process time. All of the other tests were inside the intervals of tests 1 and 16.

Figure 4.8. Typical chromatogram of a coffee solution sample: Test 1.

The CI of total coffee solids for tests 1 and 16 at f=0.5 were 1.60 and 1.15, respectively as seen in table 4. These values were statistically equal to the CI for the bioactive compounds, according to the LSD test. A higher significant correlation (1.00) was found (p<0.01) between X_S and the concentrations of CGA, 4-CQA and caffeine. The same correlation between CI and %LI was found. Consequently, the amount of bioactive compounds was maintained in proportion to the amount of total coffee solids. Therefore, the concentration of bioactive compounds was enhanced through freeze concentration and the bioactive compounds of the beverage were preserved by block FC.

Highly significant correlations (p<0.01) between antioxidant activity measured by DPPH and the concentrations of CGA, c-CGA and caffeine were demonstrated, as seen in table 4.5. The correlations of the ABTS measurements were significant (p<0.05). These results confirm that the antioxidant activity of coffee depends on the CGA and caffeine content, as reported by Fujioka & Shibamoto (2008).

A ratio between the antioxidant activity of the liquid fraction and the initial solution was calculated to represent the antioxidant activity relative index (C_{FCL}/C_0) (Table 4.4). There was no significant difference between the antioxidant activity relative index and the CI of the total coffee solids. The antioxidant activity was increased until 2.4 in one FC cycle. The increase of the antioxidant activity of mate extract was also reported by Boaventura et al. (2012) using block freeze concentration. This finding suggests block FC is an effective technique to preserve the functional properties of coffee extracts.

Table 4.4. Changes in bioactive compounds and the antioxidant activity of coffee during freeze concentration

Test	Compound	C_0 (mg/mL)	C_{FCL} (mg/mL)	C_{RI} (mg/mL)	% Ice loss	% Ice loss (dry basis)	C_{FCL}/C_0
1	CGA	0.29 ± 0.01	0.48 ± 0.04	0.09 ± 0.02	16.03 ± 4.05	48.68 ± 0.37	1.66 ± 0.14 [a]
	c-CGA	0.20 ± 0.00	0.33 ± 0.03	0.06 ± 0.01	16.28 ± 3.89	49.21 ± 0.79	1.66 ± 0.12 [a]
	Caffeine	1.21 ± 0.01	2.02 ± 0.17	0.39 ± 0.08	16.07 ± 3.83	48.79 ± 0.77	1.67 ± 0.13 [a]
	Total solids	0.05 ± 0.00	0.08 ± 0.01	0.01 ± 0.00	16.87 ± 4.30	50.0 ± 0.00	1.60 ± 0.14 [a]
	DPPH*	2.61 ±0.39	4.01 ± 2.42	1.17 ±0.25	27.10 ± 13.5	61.50 ± 19.82	1.58 ± 1.00
	ABTS*	24.02 ±2.64	58.22 ± 22.70	12.63 ±1.97	18.84 ±5.97	53.10 ± 10.40	2.47 ± 1.08
16	CGA	0.93 ± 0.01	1.07 ± 0.02	0.76 ± 0.01	41.50 ± 0.74	49.62 ± 0.77	1.16 ± 0.03 [b]
	c-CGA	0.63 ± 0.01	0.73 ± 0.01	0.52 ± 0.01	41.65 ± 0.70	49.79 ± 0.70	1.17 ± 0.12 [b]
	Caffeine	3.93 ± 0.03	4.56 ± 0.08	3.28 ± 0.03	41.81 ± 0.68	49.96 ± 0.58	1.16 ± 0.03 [b]
	Total solids	0.15 ± 0.00	0.17 ± 0.01	0.12 ± 0.00	41.86 ± 0.43	50.0 ± 0.00	1.15 ± 0.01 [b]
	DPPH*	53.15 ±3.99	72.90 ±9.01	33.5 ±2.97	30.77 ±0.51	37.92 ± 0.32	1.41 ± 0.31
	ABTS*	136.90 ±9.01	171.31 ±1.50	114.8 ±8.20	39.52 ±2.25	47.32 ± 2.08	1.27 ± 0.13

Different letters indicate statistically significant differences (p<0.05)

* Expressed as mg Trolox/mL

Table 4.5. Correlations between antioxidant activity and bioactive compounds concentration

	CGA	cCGA	CAFFEINE	ABTS	DPPH
CGA	1	1.00[**]	1.00[**]	0.557[*]	0.913[**]
cCGA	1.00[**]	1	1.00[**]	0.561[*]	0.915[**]
CAFFEINE	1.00[**]	1,000[**]	1	0.561[*]	0.914[**]
ABTS	0.557[*]	0.561[*]	0.561[*]	1	0.744[**]
DPPH	0.913[**]	0.915[**]	0.914[**]	0.744[**]	1

** The correlation is significant p<0.01 (bilateral).
* The correlation is significant p<0.05 (bilateral).

4.5. Conclusions

Coffee extract was freeze-concentrated by the total block technique. A significant effect of the initial coffee mass fraction, freezing direction and cooling temperature on solute recovery was found. The highest solute recovery was achieved at the lowest coffee mass fraction, when the freezing direction was in counter-flow to the thawing direction and at the highest cooling temperatures. The thawing fractions at which completion of the thawing stage was convenient were found between the values of 0.5 and 0.8. The initial coffee mass fraction was the factor with the highest influence on the solute yield and the concentration index. Using a freezing direction in counter-flow to the thawing direction represents an interesting alternative to increase solute recovery due to solute elution.

Furthermore, the coffee bioactive compounds were distributed in the ice and liquid phase in proportion to the total solid content. Very significant correlations between the antioxidant activity and chlorogenic acid and caffeine contents in the freeze-concentrated extract were found. Consequently, the freeze concentration method increased the bioactive compound concentration and the antioxidant activity of the coffee extract. The block freeze concentration method is a potential technique to remove water and preserve the functional properties of coffee extracts.

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5. EFFECT OF SEPARATION AND THAWING MODE ON BLOCK FREEZE-CONCENTRATION OF COFFEE BREWS

5.1. Abstract

Coffee brews were freeze-concentrated using block technique to evaluate the effect of thawing temperature, thawing mode and separation mode on solute yield. Samples were frozen and solute recovered using different thawing and separation conditions. Three thawing temperatures (20, 4 and 1°C), two thawing modes (microwave assisted and free thawing) and two liquid fraction separation modes (gravitational and vacuum assisted) were tested. Solute yield was evaluated as a function of thawing ratio. Data were fitted to a monomolecular model to compare separation quality by means of the solute recovery ratio for each treatment. A combination of microwave assisted thawing and vacuum separation showed the best results in terms of solute recovery ratio. On the other hand, applying microwave assisted thawing or vacuum separation individually did not significantly enhance the solute recovery ratio. Additionally a thawing temperature effect on the solute recover ratio was also found. These results show that it is possible to improve the separation quality of Block FC by combining this technology with vacuum-assisted separation microwave heating. These results suggest that block freeze-concentration has potential industrial application.

Keywords: Cryoconcentration; thawing; coffee; vacuum; microwave; solute yield; monomolecular model

5.2. Introduction

Freeze-concentration (FC) is a technology used to remove water at low temperatures preserving the quality of the original material (Miyawaki et al., 2005). Water remotion is achieved once water ice crystals are formed, leaving behind a more concentrated fluid (Sánchez et al., 2009). Moreover, FC allows to reduce processing time during the industrial freeze drying (Boss et al., 2004).

FC techniques can be classified in three groups: suspension crystallization (Huige and Thijssen, 1972), film freeze concentration (Sánchez et al., 2009) and freeze-thaw method, known also as block freeze concentration (Aider and de Halleux, 2009; Sánchez et al., 2011a). For suspension crystallization a scraped surface heat exchanger is used to form a suspension of ice crystals that can be subsequently separated (Miyawaki et al., 2005), (Habib and Farid, 2006). In Film FC a single crystal layer is formed by contact with a refrigerated surface (Raventós et al., 2007; Sánchez et al., 2011b). Freeze-thaw FC can be achieved using two different techniques: total or partial block (Nakagawa et al., 2010a). In the partial block technique, the solution is partially frozen and the remaining

concentrated liquid is separated after a pre-determined time (Burdo et al., 2008). On the other hand, the total block technique consists of completely freezing the sample with a subsequent thawing until the desired amount of solute has been recovered (Aider and de Halleux, 2009). Consequently, block FC comprises three important steps: freezing, thawing and separation.

Increasing ice purity is a big challenge for block FC (Aider and de Halleux, 2008). Although, it is clear that the mass of the collected liquid increases with the collection time, increasing it until collection of the entire original solution will lead to no overall concentration effect. Therefore, it is important to determine the mass of the collected sample in which solute recovery and concentration are high enough in order to stop the process at this point. In the same way, it is important to establish the thawing conditions or aids in separation stage to recover as much solute as possible.

The block FC method has been recently studied as a way to improve solute yield (Gao et al., 2009; Okawa et al., 2009; Nakagawa et al., 2010a; Nakagawa et al., 2010b; Miyawaki, et al., 2012). Furthermore, microwave assisted and gravitational thawing have been studied for milk whey (Aider et al., 2008) and for maple sap (Aider and de Halleux, 2008). It is worth noting that there are no reported studies about vacuum application and its relationship with process variables during the thawing and separation stages of block FC.

Meanwhile, coffee is the most traded food commodity worldwide (Esquivel and Jiménez, 2011). The functional and organoleptic properties of coffee are highly important for its processing and trading. Coffee processing technologies play a large role in defining the quality of the beverage (Joët et al., 2010), therefore, in the soluble coffee industry, technologies that preserve the initial characteristics of the brew are useful. Currently, suspension FC is the unique technique that is being used by coffee industry. This technique shows a high efficiency and purity of separated ice crystals, however, it is recognized as an expensive method for food concentration (Aider and de Halleux, 2009). Therefore, the use of this separation process is restricted to large-scale processing plants. For this reason, the block FC technique has been proposed in order to reduce cost and maintain high crystal purity (Aider and the Halleux, 2009), including different modes to increase solute recovery in thawing and separation stages, looking forward to implement this technique at different industrial scales.

In this paper, the total block FC of coffee brews is studied, analyzing the effect of separation mode (gravitational and vacuum assisted), thawing temperature (1°C, 4 °C and 20 °C) and thawing mode (natural convection and microwave assisted) on solute yield.

5.3. Materials and methods

5.3.1. Materials

Coffee solutions were prepared from commercial soluble coffee, (Aroma brand, Colombia) and distilled water at 20 °C. An initial concentration of 4.3 grams of dissolved solids / 100 grams of solution (5 °Bx) was used. Concentration was measured using a refractometer (Abbe refractometer model RL3 Polskie Zaklady Optyczne Warszawa, Poland), together with a calibration equation in order to account for the deviation caused by the mixture of solids present in coffee. The calibration equation was obtained by preparing solutions at 10, 20, 30, 40 and 50 °Bx and measuring their solid contents using an oven drying procedure at 103 °C for four hours according to (NTC 4602, 1999). Measurements were performed in triplicate. The following equation was obtained: $X_s= 0.0087°Bx$ (R^2=0.99). Due to the precision of refractometer (+/- 0.5 °Bx), uncertainty in solid fraction measurement corresponded to +/- 0.00438. It is clear from other reports that the initial concentration affects the results of freeze concentration (Aider et al., 2008). However, in these experiments initial solid content was used as a constant parameter for the experiment to observe the effect of the other factors.

5.3.2. Methods

Freeze concentration protocol

Samples were frozen in cylindrical containers (200 mL) at -12 °C and then stored during 72 hours at the same temperature. Afterwards, samples were thawed and the concentrated fraction was separated under different conditions. As shown in Fig 5.1, frozen samples (1) were placed in a chamber with controlled temperature (5) and drops of liquid fraction were collected by gravity in an external collection vessel (2). The chamber consisted of an upright freezer with thermostat (Haceb 87L, Colombia) for the two lowest temperatures and an incubator chamber (Selecta Celmag-L, España) for the highest temperature level. Below the vessel was a scale (3) (Mettler Toledo AB 204 S, Switzerland. Precision +/- 0.1 g), used to record weight changes during thawing. The collection vessel was removed approximately every time that 7% of liquid was collected in order to measure the liquid concentration. Thawing procedure was done at three different thawing temperatures (TT) fixed in the chamber (1°C, 4°C and 20°C +/- 1°C), two thawing modes (TM) and two separation modes (SM) as it is showed in table 1 following a complete factorial design. Thawing and separation modes are explained in paragraphs 2.2.2 and 2.2.3. All experiments were performed in triplicate.

Thawing mode:

For some samples, as it is shown in Table 5.1, thawing stage was initiated by applying a microwave pulse (+1) and for others thawing was freely developed under settled external temperature (-1). Therefore, half of samples were exposed to 5.1 kJ of microwave energy that was delivered in one 1 minute by a microwave oven (Haceb Arezzo-0.7, China). This

energy pulse was made of three short pulses of 2 seconds at 1.7 kJ, leading to an average power delivery of 85 Watt during one minute. Afterwards, thawing and separation procedure was carried out at the settled thawing temperature following the procedure described in paragraph 2.2.1.
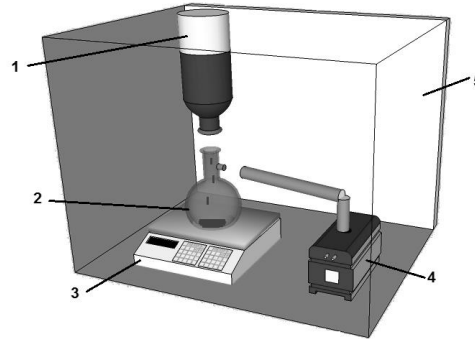
Figure 5.1. Experimental set up.

1. Frozen solution container; 2. Collecting sample vessel; 3. Scale; 4. Vacuum pump; 5. Temperature controlled chamber

Table 5.1. Experimental design

Treatment	Thawing temperature (°C) (TT)	Thawing mode (TM)	Separation mode (SM)
1	20	-1	Gravitatonal
2	4	-1	Gravitational
3	1	-1	Gravitational
4	20	+1	Gravitational
5	4	+1	Gravitational
6	1	+1	Gravitational
7	20	-1	Vacuum
8	4	-1	Vacuum
9	1	-1	Vacuum
10	20	+1	Vacuum
11	4	+1	Vacuum
12	1	+1	Vacuum

+1: Microwave assisted thawing
-1: Free thawing (without microwaves)

Separation mode

Two different separation modes were carried out: gravitational and vacuum assisted. The first consisted in drop collecting by gravitational effect without any interference. In the second, vacuum pressure of 1 kPa (74.7kPa abs) was applied using an aspirator (Büchi model B-169, Switzerland) to route and increase the movement of the liquid fraction that was trapped inside the frozen portion. Thawing and separation procedures were carried

out as described in paragraph 2.2.1.Vacuum pump was disconnected in order to measure mass and solid concentration and reconnected after collecting the sample.

5.3.3. Data analysis and modeling

Thawing fraction

Thawing fraction (f) was used to follow the development of the process. f is measured as the ratio between thawed mass and that of the original solution, defined by Eq. (1) (Nakagawa et al., 2010b) and (Miyawaki et al., 2012):

$f = m_{liq}/m_0$ (1)
Where,
f: thawing fraction
m_{liq} : collected liquid mass
m_0: initial mass

Solute Yield

Solute yield is defined as the fraction of recovered solute, calculated by the relation between mass of solids present in the separated liquid and the mass of solute present initially in the original solution (Nakagawa et al., 2010a):

$Y = m_{s\ liq}/m_{s\ 0}$ (2)
Where,
Y: Solute yield
$m_{s\ liq}$: Solute mass in liquid fraction
$m_{s\ 0}$: Initial solute mass

Concentration factor

Concentration factor is defined as the relation between the solid concentration in the liquid fraction and the solid concentration in the initial solution:

$CF = X_{s\ liq} / X_{s\ 0}$ (3)
Where,
CF: Concentration factor
$X_{s\ liq}$: solid fraction in freeze concentrated liquid fraction
$X_{s\ 0}$: solid fraction in initial solution

Additionally, Y can be obtained as shown in the Eq. 4 by combining Eq. 1, 2 and 3:
$Y = CF * f$ (4)

5.3.4. Mathematical model

Both Solute yield (*Y*) and thawing fraction (*f*) vary between 0 and 1. It is important to note that a diagonal line with slope equal to one in the plot *Y* against *f* represents a process without concentration and is considered a process with a perfect solute inclusion (Nakagawa et al., 2010a). Therefore, at any point on the diagonal line, concentration of solids in the portion sample is that of the initial sample as seen from Eq. (5).

If $Y=f \Rightarrow m_{s0}/m_0 = m_{s\,liq}/m_{liq}$ (5)

It can be inferred from Y-f plot that the further a point is from the diagonal line, the higher the concentration of the sample. It is worth pointing out that the behavior of the FC process in this plot is a curve bounded between the points (0,0) and (1,1). This relationship can be represented by a "monomolecular" model Eq. (6), which is frequently used in the statistical analysis of nonlinear relationships (Nothnagl et al., 2004).

$dY/df = r(1-Y)$ (6)
Where,
Y: Solute Yield
f: thawing fraction
r: solute recovery ratio (constant for each condition)

Eq. (7) is obtained solving the differential equation and transforming it into a linear equation using natural logarithm:

$ln(1/(1-Y)) = r \cdot f$ (7)

Therefore, constant *r* is the slope of straight line calculated from Eq. (7) and is not directly related with time. Furthermore, it represents the solute yield per thawed liquid fraction and can be named "solute recovery ratio". The higher slope *r*, the fewer amount of ice that should be melted to recover a defined amount of solute, thus *r* can be used as an indicator of separation quality. Monomolecular model is an intrinsically linear model with one parameter (*r*). As *CF* is the ratio between *Y* and *f* according to Eq. 4, the *r* parameter can be understood as the change of concentration factor in the graph *Y* vs *f*.

5.3.5. Statistic analysis

Parameters of monomolecular model for each treatment were obtained by a simple linear regression procedure using SAS 9.2. The result was the *r* value for each of twelve evaluated treatments. A ratio comparison with confidence interval procedure at $p<0.05$ was used to determine differences of *r* value between treatments.

Additionally, it is possible to identify the influence of factors TT, TM and SM on solute recovery ratio (*r*). The *r* value can be considered as a functional value, it represents the relationship between *Y* and *f*. A multiple linear regression procedure (p<0.05) was applied using SAS 9.2 to this purpose. Significance of mean and combined effects on *r* value was established.

5.4. Results and discussion

Solute recovery ratio (r), defined in Eq. (7), was obtained for each treatment and these values are presented in decreasing order in table 5.2. In this table, the best conditions for solute recovery in freeze concentration correspond to those with the highest *r* values. There, it can be seen that regression coefficients vary between 0.93 and 0.99, showing a good adjustment of the model. The majority of treatments were statistically different from each other, except for the treatments 10, 11 and 12 that showed statistically the same values (95% confidence) as well as treatments 1, 4 and 7.

Table 5.2. Solute recovery ratio.

Treatment number	TT (°C)	TM	SM	Solute recovery ratio(r)	R^2	RMSE	*
11	4	MW	vacuum	6.74	0.978	0.078	a
10	20	MW	vacuum	6.42	0.976	0.117	a
12	1	MW	vacuum	6.26	0.931	0.216	a
6	1	MW	gravitational	5.61	0.979	0.052	b
9	1	-	vacuum	5.60	0.980	0.047	c
3	1	-	gravitational	5.12	0.943	0.419	d
1	20	-	gravitational	5.01	0.989	0.031	e
4	20	MW	gravitational	5.00	0.977	0.117	e
7	20	-	vacuum	4.74	0.990	0.018	e
2	4	-	gravitational	4.32	0.984	0.041	f
5	4	MW	gravitational	3.37	0.968	0.106	g
8	4	-	vacuum	3.04	0.963	0.030	h

*Treatments with the same letter do not differ significantly

Fig. 5.2 shows the comparison between the Ŷ values that were estimated using Eq. 7 and *Y* values obtained from experimental data. It is clear that data points were distributed close and around the continuous line that represents (Ŷ=Y). Analyzing the slope of predicted and experimental data line (m=0.999) and regression coefficient (R^2=0.94), it can be inferred that predicted values tend to be similar to experimental values. This result confirms the good adjustment of experimental data to the monomolecular model.

At this point, it is important to highlight the usefulness of parameter *r* in FC quality analysis. As it has been discussed earlier, *r* value represents the amount of sample that needs to be melted in order to recover a defined amount of solids. It can be seen from experimental data (Table 2), that solute recovery ratios vary from 3.04 to 6.74. Thus, these *r* values are showing that under some experimental conditions (treatment 8), it is necessary to thaw near half of the sample in order to recover 75% (Y = 0.75) of the solids. On the other hand, in the best case scenario (treatment 11), it will be necessary to thaw only 20% of the sample in order to recover the same amount of solute. Furthermore, the concentration of recovered liquid X_{liq} can be calculated using *r* values and, Eqs. (1), (2) and (7).

$X_{liq} = (Y.m_{s0})/(f.m_0) = (Y.X_0)/f$ (8)
Where:
X_0: initial solids concentration in the sample.

If Eq. (7) is included the resulting expression is a function of *r*:

$X_{liq}=(Y.X_0 \ r)/(ln(1/(1-Y)))$ (9)
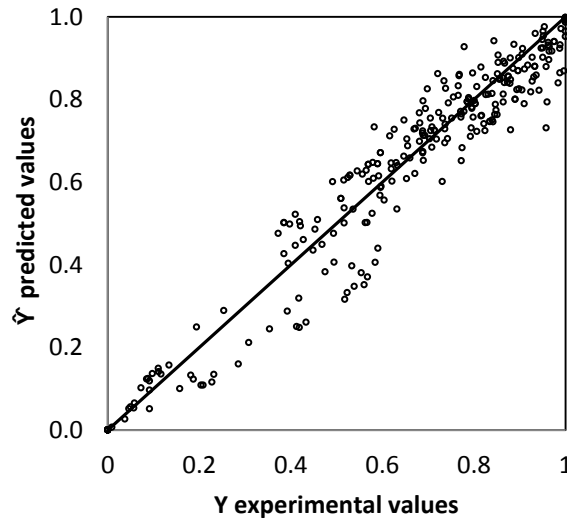
Figure 5.2. Parity plot: e*xperimental Y* values against predicted Ŷ values.

Regression line obtained: y=0.999·x; R^2= 0.94.

Therefore, using experimental data which have *r* values between 3.04 and 6.74, it can be estimated that to recover 75% of solids, the concentration of solids in the liquid samples will vary between 0.08 and 0.18 depending on the procedure selected. This information, combined with information on mass transfer speed, is a useful tool to define block FC processing strategies. Therefore, modeling heat and mass transfer kinetics should be part of the future work.

A regression analysis was used to quantify the effect of each parameter on solute recovery ratio (Table 5.2). The experimental design selected for this work, made it possible to obtain linear main effect and linear combined effect of the evaluated parameters. These results are presented in Table 5.3. Two parameters showed a significant effect on solute recovery ratio: thawing temperature (both TT and TT*TT) and the combination of separation mode with thawing mode (SM*TM).

Table 5.3. Effect of TT, TM and SM on solute recovery ratio.

Parameter	Standard Estimator	Pr > |t|
Intercept	6.028	<.0001
TT	-0.608	0.0028
TM	-0.310	0.6110
SM	-0.186	0.7595
TT*TT	0.027	0.0023
TT*TM	0.018	0.6586
TM*TM	-	-
SM*TT	-0.003	0.9348
SM*TM	2.184	0.004
SM*SM	-	-

Thawing temperature had a significant effect on solute yield as illustrated in Fig. 5.3. The trend was not linear because the significant influence of TT*TT (Table 5.3). Therefore, TT = 1 °C is better than TT=20 °C and better than TT=4 °C for all separation and thawing conditions where the combination of MW-Vacuum is not present.
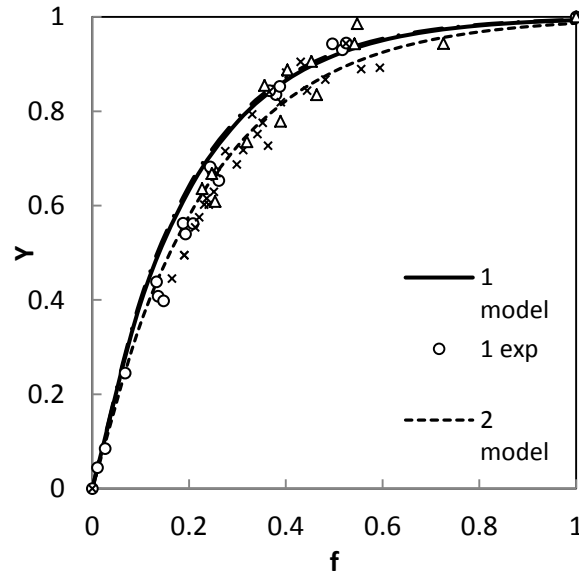
Figure 5.3. Effect of temperature on Solute Yield.

Treatments numbered according to table 1. (1=20°C, 2=4°C, 3=1°C). Lines are modeled by Eq. 7 and parameters in table 3. Dots correspond to experimental data.

Significance of thawing temperature can be explained by changes in ice structure. Solute recovery depends on capacity of the separation system to collect concentrated liquid fractions and this is related to porous structure and density of frozen matrix. Water solutions experiment density changes during freezing and thawing (Akyurt et al., 2002). Freezing and thawing temperatures influence freezing and thawing speeds, affecting the ice porous structure (Pardo et al., 2002) and the movement of liquid through it. Moreover, if diffusion of liquid is slower than heat transfer, some ice would be expected to melt and to dilute the solution before it can be recovered. Therefore, mass transfer speed affects solute recovery ratio because at low diffusion rates, greater portions of the sample should be melted in order to obtain a certain amount of solute. Thus, for this kind of freeze concentration process it is important to find a good balance between thawing speed (heat transfer) and separation speed (mass transfer) not only to optimize processing speed, but also to find the best recovery condition. Meanwhile, TT did not show a linear effect, which was not expected, therefore, further work in order to relate changes of frozen sample´s microstructure with processing parameters can lead to a deeper understanding of block FC.
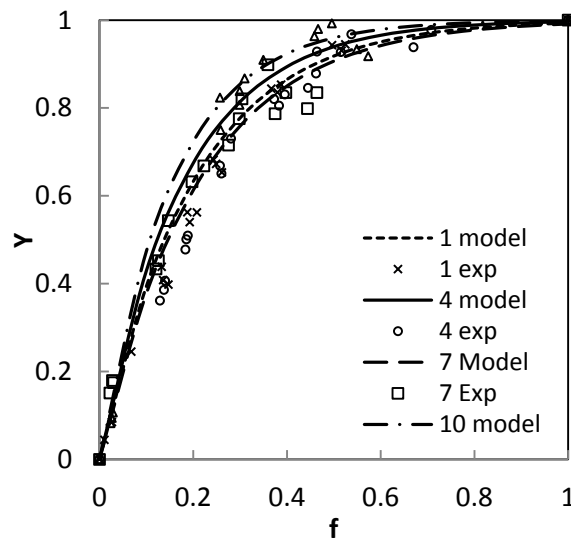
Figure 5.4. Effect of separation mode on Solute Yield

Treatments numbered according to table 5.1. (1, 4 = gravitational, 7, 10 = vacuum) Lines are modeled by Eq. 7 and parameters in table 3. Dots correspond to experimental data.
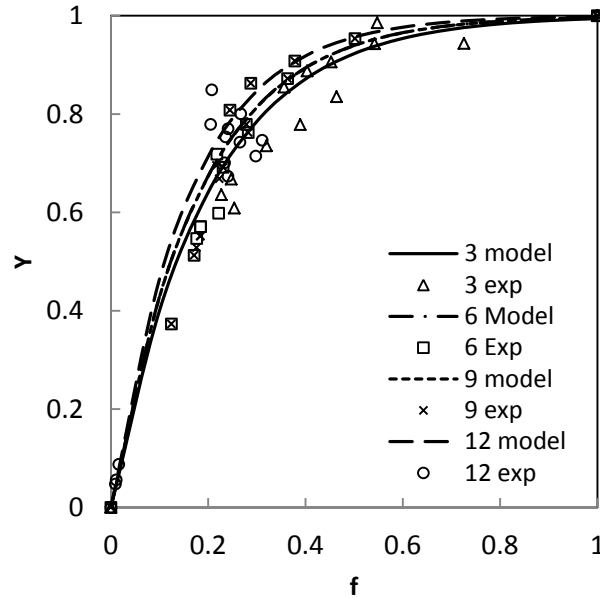
Figure 5.5. Effect of Thawing mode on Solute Yield

Treatments numbered according to table 1. (3, 9 = free, 6, 12 = Microwave). Lines are modeled by Eq. 7 and parameters in table 3. Dots correspond to experimental data.

It was seen from experimental data (Table 5.2) that, the highest solute recovery ratio was obtained for treatments 10, 11 and 12, in which a combination of microwave thawing and vacuum separation was used. Moreover, under former conditions, temperature did not show a significant effect. This observation is in accordance with results of regression analysis (Table 5.3) in which the combined parameter had a bigger standard estimator than TT and TT*TT parameters. Other parameters such as TM and SM had no significant influence when analyzed alone. A similar result, where MW thawing has not a significant effect on separation efficiency was reported by (Aider and Ounis, 2012). Fig. 5.4, 5.5 and 5.6 depict this situation, in which the effect of microwave thawing and vacuum separation is significant only when both of them are present in the treatment.

Experimental results showed that *r* value was increased up to two times when MW was combined with vacuum separation. This means that a similar *Y* can be reached with a lower *f*, increasing concentration of separated liquid portion. On the other hand, effect of vacuum was very small without microwave assisted thawing as it is showed in Fig. 5.5. Actually, *r* values decreased when vacuum was present, but table 5.3 shows that this effect is not significant when compared with other parameters. This suggests that vacuum separation promotes the separation of concentrated liquid fraction from the ice matrix and increases process efficiency only when microwave thawing is present. Therefore, this synergy present when MW and vacuum are combined shows that this operating condition is an appropriate tool to improve separation quality in block FC.
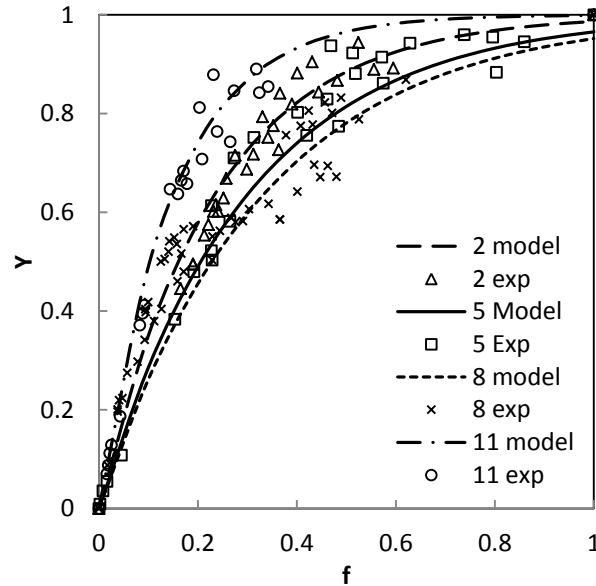
Figure 5.6. Effect of Thawing mode on Solute Yield

Treatments numbered according to table 1. (2, 8 = free, 5, 11 = Microwave). Lines are modeled by Eq 7 and parameters in table 5.3. Dots correspond to experimental data.

This synergistic behavior can be explained using two different mechanisms: accelerated internal thawing and hydrodynamic movement of molten portions of the sample. As it is known, the absorbed microwave energy is related to the loss factor of the material. Thus, substances with a high loss factor will readily absorb microwave energy, while those with a low loss factor are either reflecting or transparent to microwave energy (Wu et al., 2004), (Wang et al., 2011). It is important to highlight that loss factor of liquid water is greater than that of ice (Ryyniinen, 1995). Microwave can penetrate frozen layer and reach up the unfrozen liquid (Rattanadecho, 2004). Therefore, it would be expected that during a microwave pulse, liquid pockets will be formed in regions with higher concentration of solids and lower melting points. However, these liquid pockets cannot be easily separated from the sample because of the tortuosity of diffusion path inside the frozen matrix. Here, vacuum plays a synergistic role because pressure difference helps evacuating the concentrated liquid phase easily promoting liquid movement and separation. Experimental data showed that this hydrodynamic movement enabled by vacuum is a good way to accelerate liquid removal. Therefore, in a future paper, the effect of these parameters on the Block FC process kinetics will be analyzed.

As solute yield indicates the amount of solute recovery but not the process velocity, it is useful to combine this parameter with the analysis of thawing time. Thawing time (t) required to collect 50% of liquid (t at f=0.5) is showed in table 4 in increasing order. Also, the Solute yield at the moment (Y at f=0.5) and the concentration factor (CF at f=0.5) are presented.

Thawing time was lower for treatments 10, 4, 7, and 1, which correspond to TT= 20°C. Treatments with TT=4°C and TT=1°C presented until 25 times more thawing time. The result is similar for solute recovery rate, in which TT showed a significant effect. Comparing treatments with the same TT, microwave thawing slightly allows spending less time.

Vacuum separation helped to reduce *t* slightly. At the same time, vacuum separation allowed to recover more solute. This suggests that vacuum separation promotes separation of concentrated liquid fraction from the ice matrix and increases process efficiency, showing this separation mode as an interesting topic in block FC.

The concentration factor (CF) at 50% of thawing is presented for each condition. Values between 1.4 and 1.9 were obtained. These values are comparable with those obtained using other concentration techniques`. For example, in falling film FC, CF is around 2 for one stage of FC (Raventós et. al., 2007), in progressive FC, where CF is around 2.8 (Miyawaki et. all, 2005), in Block FC, CF=1.4 without separation assistance (Nakagawa et. al., 2010) and in microwave assisted thawing Block FC, CF is close to 1.7 (Aider and Ounis, 2012) for one stage. The highest CF was obtained for treatments with vacuum separation, due to the positive effect of pressure difference on the movement of the concentrated liquid fraction.

On the other hand the lowest thawing time was obtained for treatment 10 (TT=20°C, MW thawing and vacuum separation). The same treatment showed the highest solute recovery rate. Consequently, this condition is appropriate for the performance of FC, recovering 98% of solute when 50% of mass is thawed and just spending 2.7 h of thawing.

5.5. Conclusions

The relationship between solute yield and thawing fraction can be represented using the monomolecular model. Linearization of this model, using slope *r* which is not related to time, allows to ease analysis in terms of the separation efficiency, and quality of the recovered liquid. Combination of microwave assisted thawing and vacuum separation exerts a synergistic positive effect on solute recovery ratio. Experimental results showed that this operating condition is an appropriate tool to improve separation quality in block FC.   Thawing temperature has a significant effect on solute recovery ratio; both TT and TT*TT, are highly influential parameters. Therefore, under the experimental conditions used in this work temperature did not show a linear effect on separation quality. Block freeze-concentration is a potential technology for food concentration. Process alternatives such as, thawing temperature control, microwave thawing and vacuum separation are helpful to increase solute recovery and should be taken into account when scaling up this technology.

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6. BEHAVIOUR OF FALLING-FILM FREEZE CONCENTRATION OF COFFEE EXTRACT

6.1. Abstract

The behaviour of falling-film freeze concentration of coffee extract was studied through determining the solute inclusion in the ice produced in a single-plate freeze concentrator. The effect of the initial coffee mass fraction of the extract, the average ice growth rate and the film velocity were studied. The coffee extract at four coffee mass fractions (0.05, 0.15, 0.25 and 0.35 w/w) was freeze concentrated at three different cooling temperatures (-10, -15 and -20°C) and three flow rates ($5 \cdot 10^{-5}$, $7.5 \cdot 10^{-5}$ and $10 \cdot 10^{-5}$ $m^3 \cdot s^{-1}$). The solute inclusion in the ice and the effect of each parameter were determined. The coffee mass fraction, ice growth rate and film velocity affected the average distribution coefficient. The coffee mass fraction had the greatest effect on average distribution coefficient. The Chen model parameters to predict the average distribution coefficient and the concentration index were found. A logistical model was proposed to predict the concentration reached in successive stages, which tended to 35% at the studied intervals. The model showed an adjusted regression coefficient of 0.98 and the experimental values were within the 95% confidence intervals. The model can be used to predict the behaviour of falling film freeze concentration of coffee extract; this technique is an economic and simple alternative to conventional freeze concentration.

Keywords: cryoconcentration; coffee; average distribution coefficient; falling-film; modelling

Nomenclature

a:	width of the ice sheet (m)
CI:	concentration index (unitless)
f:	liquid fraction (unitless)
g:	acceleration due to gravity (9.8 m s^{-1})
h:	height of the ice sheet (m)
K:	average distribution coefficient (unitless)
m_{ice}:	mass of the ice sheet (kg)
m_{s0}:	initial solute mass (unitless)
$m_{s\,liq}$:	solute mass in the liquid fraction (kg)
m_0:	initial mass (kg)
m_{liq}:	collected liquid mass (kg)
n:	number of stages (unitless)
Q:	fluid flow rate ($m^3 \cdot s^{-1}$)
T:	temperature (°C)

t:	time of freezing (s)
$U_{s,\infty}$:	fluid film velocity (m·s^{-1})
V_{ice}:	average ice growth rate (mm·s^{-1})
$X_{s\,ice}$:	coffee mass fraction in the ice (w/w)
$X_{s\,0}$:	coffee mass fraction in the initial solution (w/w)
$X_{s\,liq}$:	coffee mass fraction in the freeze-concentrated liquid fraction (w/w)
Y:	solute yield (unitless)
η:	coffee extract viscosity (Pa·s)
ρ:	coffee extract density (Kg·m^{-3})
ρ_c:	coffee solids density (Kg·m^{-3})
ρ_{ice}:	ice density (Kg·m^{-3})
ρ_w:	water density (Kg·m^{-3})

6.2. Introduction

Freeze concentration (FC) is a technique used to remove water from solutions by cooling the solution until ice crystals are produced and separated (Sánchez et al., 2009). The final liquid fraction has a higher concentration than the initial solution because of the water removed in the form of ice. This technique is used in the food industry due to its ability to preserve sensitive properties in products such as coffee extract.

Depending on the growth of ice crystals, there are three techniques of FC, suspension FC, film FC (progressive or falling-film FC) and block FC (also known as freeze-thaw FC) (Aider and de Halleux, 2009; Boaventura et al., 2013; Sánchez et al., 2011a). Suspension FC is the most implemented technique in the coffee industry. This is an efficient technique to obtain high ice purity despite the high operational costs (Miyawaki et al., 2005; Qin et al., 2006; Sánchez et al, 2011a; Van der Ham et al., 2004).

The falling-film freeze concentration (FFFC) is a simple technique in which the solution to be concentrated is re-circulated on a cooled vertical plate. The fluid descends in a film, and an ice sheet is produced by freezing. The ice forms a single layer on the cold surface. The solution is collected and re-circulated continuously (Sánchez et al., 2011b). FFFC has been studied with several food fluids (Belén et al., 2013; Chen et al., 1998; Flesland, 1995; Hernández et al., 2009, 2010; Raventós et al., 2007; Sánchez et al., 2010). Coffee extract freeze concentration has been studied using the block technique (Moreno et al., 2014b; Moreno et al., 2013) and progressive FC (Miyawaki et al., 2005). Moreno et al. (2014a) studied falling-film freeze concentration to propose an alternative process to concentrate coffee extract.

The solutes retained in the ice sheets determine the concentration efficiency (Raventós et al., 2007). Although the solute can be recovered by partial thawing of the ice (Gulfo et al., 2013), a low amount of solute occluded in the ice is desired. One way to express the level of solid occlusion is the average distribution coefficient. The average distribution coefficient

is defined as the ratio between the concentration of solute in the liquid fraction and the concentration of solute in the ice. Chen and Chen (2000) studied the solute occlusion of the ice in falling-film freeze concentration for model solutions. The authors proposed a correlation to evaluate the average distribution coefficient for model solutions and food fluids. The solute inclusion of the ice produced in FFFC has not been studied for coffee extract, and the effect of the ice growth rate and the fluid flow rate has not been determined. This information is useful in the design of falling-film freeze concentration systems as a simpler alternative than the suspension technique.

The aim of the present study was to evaluate the behaviour of coffee extract during falling-film freeze concentration at different coffee mass fractions, ice growth rates and film velocities on the plate and to obtain the parameters for average distribution coefficient modelling.

6.3. Materials and Methods

6.3.1. Materials

Coffee extract was prepared from soluble coffee supplied by Buencafé Liofilizado de Colombia (Colombian Coffee Growers Federation, Colombia). The coffee was added to distilled water at 35 °C and mixed for 20 min. The samples were stored at 4 °C for 12 h.

6.3.2. Methods

Experimental design

The coffee extract was freeze concentrated using a complete factorial design with three variables as shown in Table 6.1. Four different coffee mass fractions were tested within the typical interval for freeze-concentration processes (Moreno et al., 2014a). Three plate temperatures were tested to achieve different ice growth rates. Finally, three fluid fluxes were adjusted to obtain different film velocities of fluid falling on the ice sheet.

Table 6.1. Experimental design.

Variable	Level
Xs*	0.05, 0.15, 0.25, 0.35
T_P (°C)	-10, -15, -20
Q ($m^3 \cdot s^{-1}$)	$5 \cdot 10^{-5}$; $7.5 \cdot 10^{-5}$; $10 \cdot 10^{-5}$

*The coffee mass fraction (Xs) was expressed as a fraction (w/w). It can be converted to a percentage by multiplying 100.

Freeze concentration tests

In each test, 800 mL of coffee extract was freeze concentrated by the falling-film technique. The experimental setup is shown in Fig. 6.1. The coffee extract flows in a descending film over the cooling plates, and it was collected in a collector tank and re-circulated by a VGC-400 peristaltic pump (Seditesa, Spain) and a VFD007L2 frequency variator (Seditesa, Spain). The ice growth on the surface of the freezing plates was then removed in a batch operation. The plate had dimensions of 25-cm width and 20-cm height.
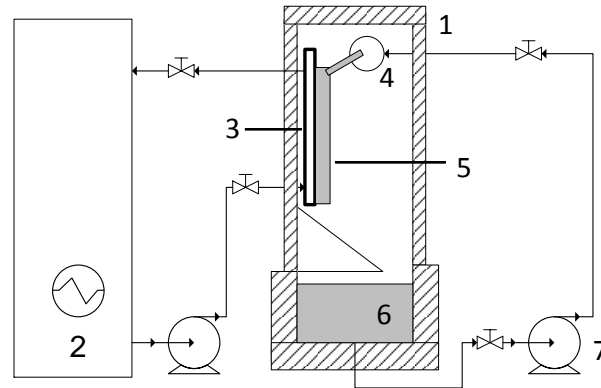
Figure 6.1. Experimental setup.

(1) Chamber; (2) Cooling bath; (3) Cooling plate; (4) Distribution duct; (5) Ice sheet; (6) collector vessel; (7) pump.

The coffee mass fraction of the liquid fraction and the ice were measured after one hour of processing by a Pal 100 refractometer (Atago, Japan). The coffee mass fraction is defined as the mass of coffee solids per unit of coffee solution mass. The relationship between Brix degrees and X_S is represented by the equation $X_S=0.0087$ °Brix reported by Moreno et al. (2014c) for the same product used in the present work.

Mathematical model

The solid inclusion in the ice is determined by the average distribution coefficient. The concentration of the solute in the solid and liquid fractions can be calculated from this value. The average distribution coefficient is defined as the ratio of the coffee mass fraction of the ice to the coffee mass fraction of the freeze concentrated liquid as shown in Eq. (1).

$$K = \frac{x_{S\,ice}}{x_{S\,liq}} \quad (1)$$

The mathematical model used in the present work was proposed by Chen et al. (1998). The model expressed the average distribution coefficient as a function of the ice growth rate on the plate of a falling-film freeze concentrator and the film velocity of the fluid on the ice sheet produced.

The average ice growth rate depends on the heat transfer rate, the degree of supercoiling and the thickness of the ice film, among other variables (Qin et al, 2009). The average ice

growth rate is related to the plate temperature. The average ice growth rate was calculated from the mass of the ice sheet at the end of the process, the solid concentration in the ice, the process time, the ice density and the dimensions of the plate, according to the Eq. (2) (Chen et al., 1998).

$$\bar{v}_{ice} = \frac{m_{ice}(1-x_{s\,ice})}{t\,h\,a\,\rho_{ice}} \cdot 10^6 \quad (\mu m\,s^{-1}) \quad (2)$$

Meanwhile, the fluid film velocity depends on the fluid flux regulated through the pump, the viscosity and density of the coffee extract and the dimensions of the plate. The film velocity is related to the mass transfer coefficient which is proportional to the fluid velocity to a power of 0.5 (Chen et al., 1998). Consequently, the Chen model includes the average ice growth rate and the falling film velocity to represent heat transfer and mass transfer rates. The fluid film velocity was calculated by Eq. (3). The Eq. (3) is valid for films descending on a plate, in laminar flow and without superficial traction forces (Rane and Jabade, 2005; Perry et al. 1992).

$$u_{s,\infty} = \frac{Q}{a\left(\frac{3\,Q\,\eta}{\rho\,a\,g}\right)^{1/3}} \quad (m\,s^{-1}) \quad (3)$$

The viscosity and density of the coffee extract were calculated from the average coffee mass fraction and the average temperature of the extract using Eq. (4) and Eq. (5-7), respectively. Eq. (4-7) were reported by Moreno et al. (2014c) for the same coffee used in the present work and the same temperature and concentrations intervals used in these tests.

$$log_{10}\,\eta = 21.3 + 2.1x_{s\,liq} + \left(\frac{30-T}{91+T}\right)\left(31.5 - 12.7x_{s\,liq}^{2.53}\right) (4)$$

$$\frac{1}{\rho} = \frac{X_{s\,liq}}{\rho_c} + \frac{(1-X_{s\,liq})}{\rho_w} \quad (5)$$

$$\rho_c = 1878.1 - 40.76T + 1.035T^2 \quad (6)$$

$$\rho_w = 1000 + 2.30T - 0.11T^2 \quad (7)$$

Once the model variables were calculated, the correlation can be applied for prediction of the average distribution coefficient. This correlation is presented in Eq. (8). The equation proposed by Chen and Chen (2000) is composed of a term related to the coffee mass fraction, a term related to the heat transfer and mass transfer and an independent term.

$$K = A + Bx_{s0} + C\frac{\bar{v}_{ice}}{u_{s,\infty}^{0.5}} \quad (8)$$

The assumptions of the model presented in Eq. (8) were the following: The solid distribution in the ice is uniform, the falling-film flows in laminar flow, the ice growth rate is the average of the ice growth rates during the process, the time of one stage is 60 min and the freezing process is developed in vertical plate.

The concentration index, the solute yield and the liquid fraction are variables used to evaluate the behaviour of the freeze concentration process. They can be calculated from the average distribution coefficient. The liquid fraction is the ratio of the mass of the concentrated liquid fraction to the mass of the original solution defined by Eq. (9) (Miyawaki et al., 2012; Nakagawa et al., 2010).

$f = m_{liq}/m_0$ (9)

The solute yield was defined as the ratio of the mass of solute present in the separated liquid to the mass of solute present in the original solution and was calculated by Eq. (10) (Moreno et al., 2013; Nakagawa et al., 2010).

$Y = m_{s\ liq}/m_{s\ 0}$ (10)

The concentration index was used to express the concentration of solutes reached after the FC process. The concentration index, CI, was defined as the ratio of the solid concentration in the liquid fraction to the solid concentration in the initial solution. CI is also known as relative concentration (Nakagawa et al., 2009).

$CI = X_{s\ liq} / X_{s\ 0}$ (11)

Eq. (12) can be obtained by combination of Eq. (9-11).

$Y = f * CI$ (12)

Eq. (13) and Eq. (14) were obtained by combining Eq. (1) and Eq. (12) and by the application of mass balance.

$$K = \frac{1-Y}{CI-Y} \quad (13)$$
$$K = \frac{1-f*CI}{CI-f*CI} \quad (14)$$

The average distribution coefficient can be predicted from Eq. (8) at different operational conditions of the freeze-concentration process. The amount of solute recovery and the concentration index can be calculated from Eq. (13 -14) for different liquid or ice fractions.

Statistical analysis

The parameters of Eq. (8) and Eq. (16) were fit by the least squares regression method. A multiple regression analysis was performed using the statistical software SAS 9.0. The fit was evaluated by the adjusted regression coefficient. The 95% confidence intervals were calculated.

6.4. Results

6.4.1. Effect of the average ice growth rate and the fluid velocity

The effect of the ratio of average ice growth rate to fluid velocity to the power of 0.5 on the average distribution coefficient at different coffee mass fractions is shown in Fig. 6.2. The average distribution coefficient increased slightly with the velocities ratio. A high value of K indicates greater occlusion of solids in the ice sheet and lower concentration efficiency. The ratio of velocities is proportional to the ice growth rate and inverse to the squared root of the fluid velocity. The ratio, and consequently the average distribution coefficient, increased with the ice growth rate and decreased with the fluid film velocity.
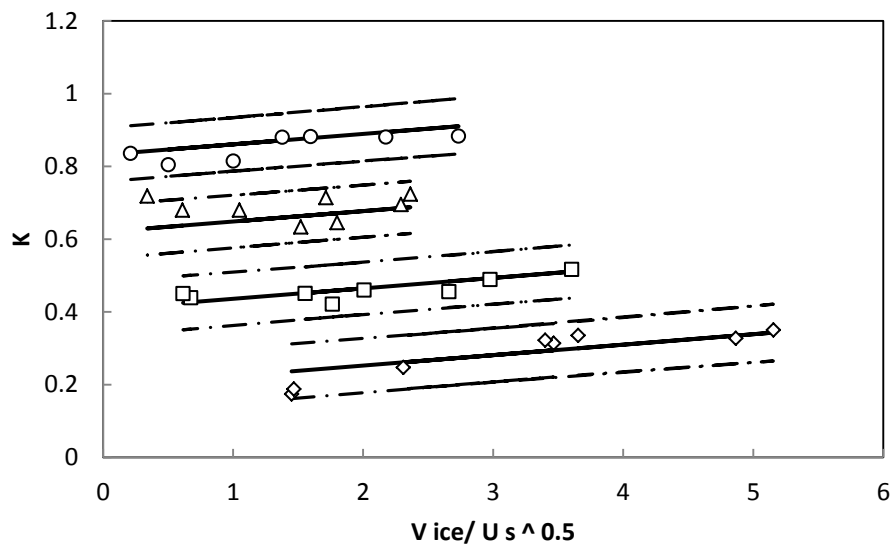
Figure 6.2. Effect of the ratio between average ice growth rate and fluid velocity on the average distribution coefficient.

Dots represent experimental data (Δ)Xs=0.05; (○)Xs=0.15; (□)Xs=0.25; (◊)Xs=0.35. Continuous lines represent the predicted data. Segmented lines represent the 95% confidence intervals.

This result can be explained by the effect of the growth of the ice front. When the ice growth rate exceeds the velocity at which solids can be expelled from the ice crystals to the ice-liquid interface, the solids stay trapped in the ice sheet (Caretta et al., 2006; Moreno et al., 2014b; Petzold and Aguilera, 2009). On the other hand, a high fluid velocity can remove solids from the ice front to the falling liquid, decreasing the solid occlusion.

The effect of the average ice growth rate was most obvious at low solid concentrations, as reported by (Moreno et al., 2014b). For low solid concentration, heat transfer is the controlling phenomenon during freeze concentration. Omran et al. (1974) reported that mass transfer controls the FC for solid concentrations higher than 15% for sugar solutions and fruit juices. In the same way, Sánchez et al. (2010) reported values lower than 17%

solids when the FC is controlled by heat transfer. In the present work, the effect of the average ice growth rate on the average distribution coefficient was highest for the lowest coffee mass fractions evaluated, which were 5% and 15%. This confirms the observations described by Omran et al. (1974) and Sánchez et al. (2010).

The average ice growth rate varied from 0.2 to 4 $\mu m \cdot s^{-1}$. The highest rates were obtained at the lowest temperatures and concentrations of solids. Moreno et al. (2014b) and Nakagawa et al. (2010) reported that freeze concentration occurs for an ice growth rate lower than 6 $\mu m \cdot s^{-1}$ for the block technique for model solutions. Chen and Chen (2000) studied rates under 2 $\mu m \cdot s^{-1}$ for falling-film freeze concentration of food fluids. Meanwhile, Flesland (1995) reported rates between 0.2 and 2 $\mu m \cdot s^{-1}$ for sucrose solutions FFFC. The use of low supercooling temperatures decrease energy consumption and decrease the ice growth rate (Rane and Padiya, 2011). Low ice growth rates decrease solid occlusion, but, at the same time, the productivity of the process can be affected; as a consequence, both aspects have to be analysed.

On the other hand, the average distribution coefficient decreased slightly with film velocity. Chen et al. (1998) reported a reduction of the average distribution coefficient with the film velocity for sugar solutions. Nevertheless, the effect was low for the studied intervals. In contrast, in the progressive tubular freeze concentration, where the pump provided velocities of 4.8 $m \cdot s^{-1}$ (Miyawaki et al., 2005), this variable had a greater influence than FFFC. These results suggest that the film velocity had less influence in FFFC than other techniques because of the low velocity values of the free falling-film. However, the combined effect of the ice growth rate and the film velocity was significant as shown in p-values of the table 6.2.

Table 6.2. Multiple regression analysis of Eq. (15)

Variable	Estimator of the parameter	Standard error	Pr > ltl	Standardized parameter
Intercept	0.089	0.023	0.0006	0
Xs	2.123	0.067	<.0001	1.069
$V_{ice} / U_{s\infty}^{0.5}$	0.028	0.006	<.0001	0.161

6.4.2. Effect of solid concentration

Fig. 6.3 shows the effect of the coffee mass fraction on the average distribution coefficient. *K* increased linearly with the solid content of the extract. The solid content had the greatest influence on the average distribution coefficient according to the slope of the line shown in Fig. 6.3 and the standardized parameters showed in Table 6.2. The same result was obtained for block freeze concentration. Moreno et al. (2014b) reported that the solid content of coffee extract primarily affects the separation efficiency.
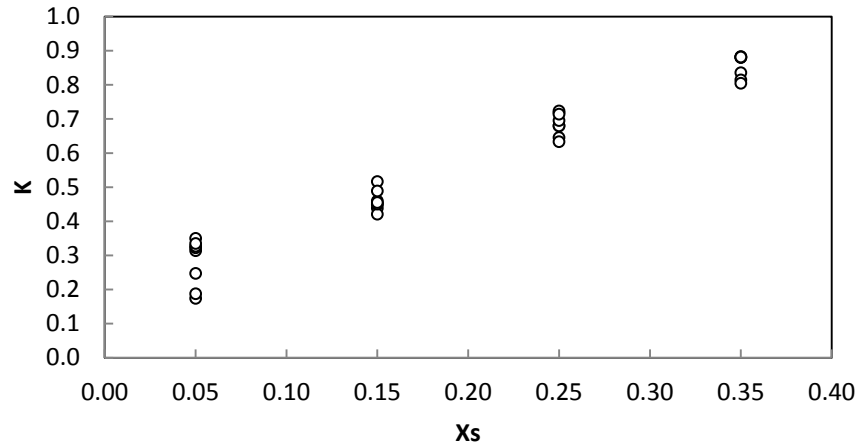
Figure 6.3. Effect of coffee mass fraction on average distribution coefficient

The solid occlusion was increased with the coffee mass fraction mainly for two reasons. First, the diffusion velocity of solutes from the ice front to the falling-film of fluid decreased with the solid content because of the interaction between solute molecules (Hindmarsh et al., 2005; Petzold and Aguilera, 2009). Secondly, the viscosity of the fluid increased with the solid concentration; consequently, solute movement is slower and is therefore more easily trapped in the ice front (Moreno et al, 2014c; Raventós et al., 2007).

The average distribution coefficient increased from 0.2 to 0.9 when the coffee mass fraction increased from 0.05 to 0.35. This result shows that when the solid extract concentration rises above 35%, the value of k tends to one. At this value of k, the liquid fraction has the same concentration as the ice, and the concentration efficiency tends to zero. A high value of the average distribution coefficient is a problem in terms of the purity of the ice and the concentration efficiency. However, this problem can be solved by fractionated thawing of the ice sheet. Gulfo et al. (2013) proposed a partial thawing of ice sheets to recover the retained solutes. Moreno et al. (2014a) proposed a process to concentrate coffee extract by the integration of the ice thawing with FFFC and block FC. With this strategy, the operational limit of progressive FC can be overtaken, and the concentration efficiency can be increased.

6.4.3. Mathematical modelling

The parameters of the Eq. (3) were obtained from experimental data. A multiple regression analysis was achieved to fit the parameters of the Chen model. The results are shown in Table 6.2. The parameters of the three variables were statistically significant for a confidence interval of 95%. These results confirm that the coffee mass fraction and the ratio of the average ice growth rate to the fluid velocity affected significantly the average distribution coefficient. An adjusted regression coefficient of 0.98 was obtained. According to these results, the average distribution coefficient in FFFC of coffee extract can be

calculated as a function of the coffee mass fraction of the extract, the average ice growth rate and the fluid film velocity by the Eq. (15).

The smallest average distribution coefficient was obtained for the smallest solid concentration and the smallest ratio of average ice growth rate to film velocity, as shown in Fig 6.4. Experimental data were compared with the predicted data generated from Eq. (15) in Fig. 6.5. A good fit was obtained as evaluated by the adjusted regression coefficient.

$$K = 0.089 + 2.123Xs + 0.028\frac{\bar{v}_{ice}}{u_{s,\infty}^{0.5}} \qquad R^2 = 0.98 \text{ (15)}$$

The experimental data, the predicted data generated from Eq. (15) and the 95% confidence intervals are shown in fig 6.2. The three parameters had significant effect on the average distribution coefficient as shown in Table 6.2. The parameter with the greatest effect on the average distribution coefficient was the term associated with the coffee mass fraction, according to the standardized parameters presented in Table 6.2. This confirms the higher influence of solid concentration on the solute occlusion in the ice.
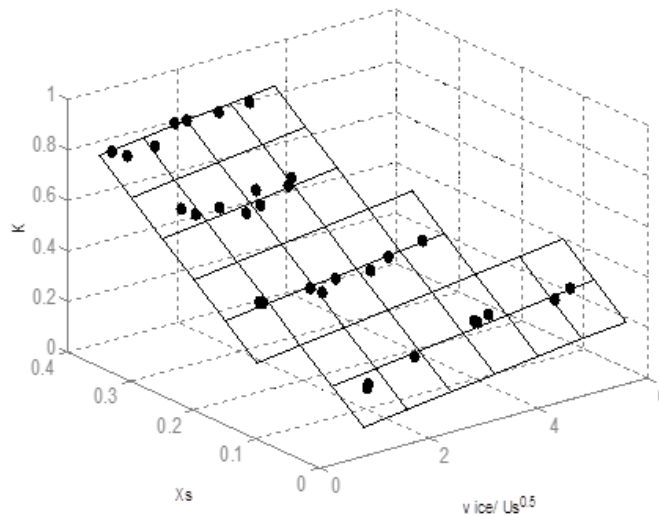
Figure 6.4. Modelling of the partition coefficient as a function of Xs, V $_{ice}$ and U$_s$.

Dots: experimental data; plane: predicted data from Eq. (15).
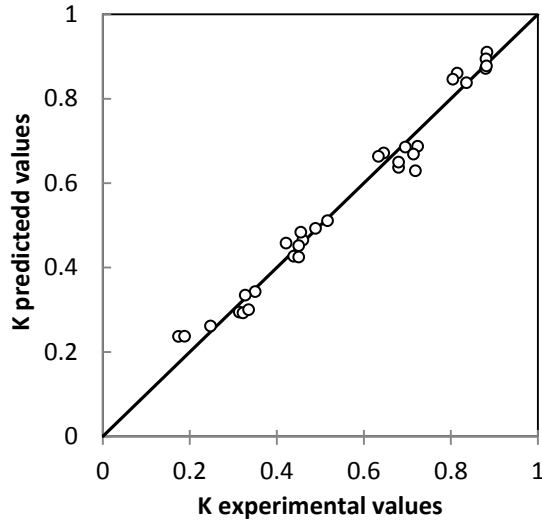
Figure 6.5. Parity plot of the average distribution coefficient.

Experimental vs predicted data from Eq. (15).

The parameters of Eq. (8) were compared with the parameters for other food fluids obtained by Chen and Chen (2000) in Table 6.3. The parameters of Eq. (8) for coffee extract were similar to those of orange juice, possibly due to the similar viscosity at low temperatures and similar freezing points (Moreno et al., 2014c; Ibarz et al., 2009). The behaviour of falling-film freeze concentration of orange juice reported by Sánchez et al. (2010) was similar to the FFFC of coffee extract (Moreno et al., 2014c).

Table 6.3. Parameters of Eq. (8) for several food fluids.

Fluid	A	B	C	R^2
Coffee extract (present work)	**0.09**	**2.12**	**0.03**	**0.98**
Sucrose solution (Chen and Chen, 2000)	-0.14	2.06	0.14	0.96
Orange juice (Chen and Chen, 2000)	-0.12	2.18	0.12	0.98
Milk (Chen and Chen, 2000)	-0.02	0.36	0.08	0.96

6.4.4. Model for solid concentration prediction in successive stages

The behaviour of falling-film freeze-concentration at can be predicted from the Chen model presented in Eq. (15). A simulation of the process is presented based on the conditions of FFFC of coffee extract reported by Moreno et al. (2014a). The following parameters were used for the simulation: A coffee extract with 5% solids entered the first stage of FFFC. The average ice growth rate was 2 $\mu m \cdot s^{-1}$, and the film velocity was 0.5 $m \cdot s^{-1}$. The simulation parameters were established to compare them with experimental data reported by Moreno et al. (2014) and Auleda et al. (2011) for falling-film freeze concentration of coffee extract and sugar solutions, respectively in a geometrical similar device. In addition, these parameters were all within the intervals tested in the present work.

The average distribution coefficient was predicted from Eq. (15). With this value, the solid concentration in the ice was calculated. After that, a mass balance was achieved assuming an ice fraction between 0.26 and 0.44 according to the data reported by Moreno et al. (2014a). These values were within the results obtained to generate the model in Eq. (15). With the ice fraction, the liquid fraction (*f*) was calculated. Subsequently, the solid concentrations of the extract were calculated from Eq. (13). This extract can be freeze concentrated again in a new stage, so the calculation process was repeated successively in six stages. The coffee mass fraction of the freeze-concentrated extract at each stage is shown in Fig. 6.6.

Figure 6.6. Predicted values of successive stages of falling film freeze concentration of coffee extract.

Bars: predicted data from Eq. 16. Lines: 95% confidence intervals. Dots (○): experimental data reported by Moreno et al. (2014a).

Starting with an extract of 5% coffee solids, the concentration of the freeze-concentrated extract tended to 37% solids at the end of the process. The concentration showed sigmoidal behaviour. The same behaviour was reported by Bayindirli and Ungan (1993) in the freeze concentration of apple juice and by Nonthanum and Tansakul (2008) for lime juice. At the beginning, the concentration increased linearly. However, at the end, the concentration tends to an asymptotic value due to the thermodynamic limit when the extract was close to the eutectic point concentration.

The Chen model can be applied for one stage of FFFC. A mass balance is needed to calculate the solid concentration in successive stages. However, a model to predict the coffee mass fraction from the number of stages used in FFFC can be adjusted from data generated with Eq. 13-15. The sigmoidal behaviour can be modelled with the logistic model presented in Eq. 16. The model predicts the coffee mass fraction of the concentrated liquid as a function of the initial coffee mass fraction and the number of

stages. The parameters of the Eq. 16 were obtained by least squares regression with data generated from the Chen model.

$$x_{S\,liq} = \frac{0.55x_0}{(1.30x_0 + (0.55 - 1.30x_0)\exp(-0.55n))} \quad R^2 = 0.998 \quad (16)$$

The concentration reached after successive stages of FFFC can be predicted by Eq. 16. Fig. 6 shows the predicted data from Eq. (16) (bars), the 95% confidence intervals (lines), and the experimental data of FFFC of coffee extract reported by Moreno et al., 2014a,. The experimental data presented a good fit with the models with an adjusted regression coefficient of 0.998. The generated parameters were significant for alpha 0.05. According to the simulation, after six stages of FFFC, a coffee extract of 31.8% solids was obtained. The concentration tended to 35%. Moreno et al. (2014a) reported an extract with 30.4% solids after six stages of FFFC starting with a 5% coffee extract. The results show that the Chen model accurately predicts the behaviour of falling-film freeze concentration of coffee extract. Likewise, the logistic model fit the data accurately for the first stages. A slight deviation of experimental data was observed for the three last stages. The differences can be attributed to the difference in the scale of the device reported by Moreno et al. (2014) and those used in the present work. However, the model showed a trend for the solid concentration increasing. The logistic model is useful to predict the solid concentration in terms of the number of stages used in FFFC.

6.5. Conclusions

This study showed that the mass fraction of solids and the ratio of the average growth rate of the freezing front to the velocity of the fluid film affected significantly the average distribution coefficient of the ice produced during the falling-film freeze concentration of coffee extract. The greatest effect was obtained for the coffee mass fraction of the extratc. The parameters of the Chen model were obtained for the prediction of average distribution coefficient of coffee extract. A logistic model was adjusted to predict the behaviour of successive stages of falling-film freeze concentration. In successive stages of falling-film freeze concentration, the coffee mass fraction tends to 35% at the studied conditions. From this information, it is possible to predict the coffee mass fraction of concentrated liquid and ice during falling-film freeze concentration at different operational conditions. The models properly fit the experimental data.

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7. VOLATILE COMPOUNDS PRESERVATION AND SOLUTES RETENTION OF BLOCK AND FALLING-FILM FREEZE CONCENTRATION OF COFFEE EXTRACT

7.1. Abstract

Coffee extract was freeze-concentrated through block and falling-film techniques. Solute retention and concentration efficiency were determined after one stage of the process. 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. Ice crystal size was lower for the falling-film technique; this explains the higher solute occlusion. Dewatering capacity was higher for the falling-film technique as this process is faster than block freeze-concentration. Major volatile compounds of the coffee extract 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. Results confirm the benefits of the block and falling-film freeze concentration techniques in preserving the quality of coffee extract.

7.2. Introduction

Coffee is the most traded food in the world. Coffee flavour is highly important during its processing (Caporaso et al., 2014). Freeze-dried coffee is a higher quality product than soluble coffee due to low processing temperatures (Fissore et al., 2014). The process to obtain freeze-dried coffee begins with an initial stage of aqueous extraction by percolation, followed by concentration and drying of the extract. The objective of the concentration stage is to eliminate part 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). This technology is used to reduce processing times in the freeze drying stage (Moreno et al., 2014c).

One of the advantages of using FC in soluble coffee production is the preservation of volatile compounds (Budryn et al., 2011; Cheong et al., 2013; MacLeod et al., 2006; Sopelana et al., 2013). 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; Farah et al., 2006; Korhonová et al., 2009). However, there are few reported works on the efficacy of volatile compounds preservation when using FC (Ramos et al., 2005).

Separation efficiency in freeze concentration (FC) is related to solid occlusion in the ice layer. This occlusion can be influenced by the morphology of ice crystals achieved by the freezing conditions and the solution type (Ayel et al., 2006; Butler, 2002; Okawa et al., 2009; Pardo et al., 2002). Food materials science attempts to develop structure-property relationships in foods. In particular, it has been demonstrated that many desirable traits of food depend on the way foods are structured (Aguilera, 2007).

Understanding the quantitative relationships between freeze concentration and ice crystal morphology is of practical importance. This knowledge can be applied, for example, to engineer processes with higher efficiencies thanks to material properties. Physical properties of ice layer can be deemed as the result of the characteristics (size) and spatial arrangement of 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. That is why it is important to evaluate the morphology generated by the processes mentioned above. Mean diameters and size distributions of ice crystals have been reported as the result of the freezing process; it has been observed that distributions of ice crystal sizes depend not only on the freezing rates, a well-known result, but also on sample size and freezing direction, among other variables (Hottot et al. 2007).

The most implemented FC technique is called 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, also known as freeze-thaw FC, the solution is completely frozen in a vessel. After that, the solution is partially thawed to recover a liquid concentrated 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).

Block and falling-film FC have been studied in coffee extract concentration (Moreno et al., 2014a). The preservation of bioactive compounds has been demonstrated (Moreno et al., 2014c); however, the effect of FC on volatile compounds and sensory quality of the

beverage has not been studied. In addition, the ice morphology achieved through these FC techniques and its relationship with solute occlusion has not been determined.

The aim of the present study was to compare solute retention, productivity of the operation, ice morphology, volatile compounds preservation, and sensory quality between falling-film freeze concentration and block freeze-concentration of coffee extract.

7.3. Materials and Methods

7.3.1. Materials

Coffee extract supplied by the company Buencafé Liofilizado de Colombia (National Federation of Coffee Growers of Colombia) 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 previously to the tests.

7.3.2. Methods

7.3.2.1. Freeze Concentration Tests

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 in 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 Fig. (7.1a). The coffee sample (160 g) was placed into a cylindrical double-jacketed container of 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 (C_s) of the liquid and the ice fractions was measured through refractometry (Atago Pal 100, Japan). C_s 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 $C_s=0.87$ °Brix, reported by Moreno et al., (2014d). The two fractions were stored at 4°C during 12 hours for the analysis of volatile compounds. Tests were performed in triplicate.

(a)   (b)
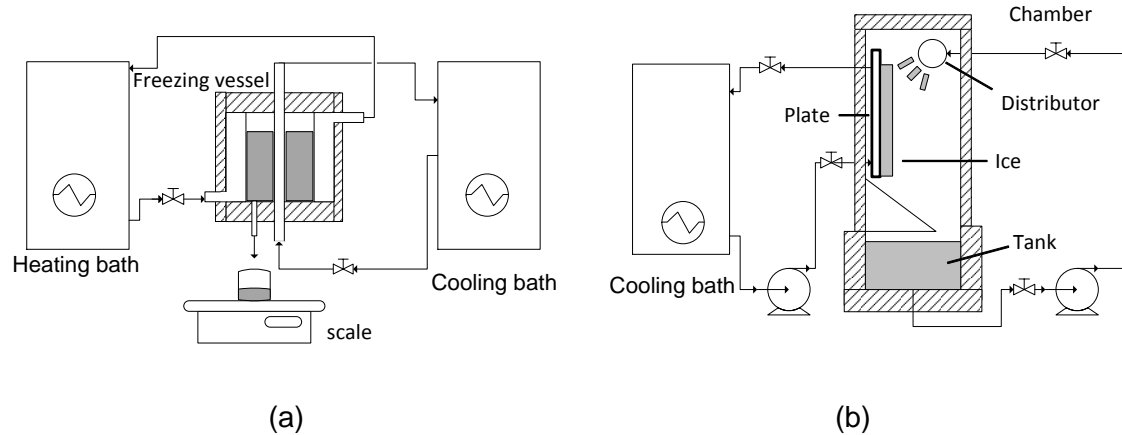
Figure 7.1 Experimental set up. (a) block freeze concentrator; (b) falling-film freeze concentrator

Falling Film Freeze Concentration Tests

One stage of FFFC was tested according to the parameters reported by Moreno et al., 2014b). The FFFC consisted in the 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 showed in Fig (7.1b). The coffee extract flowed through a descending film over a cooling plate of 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. Experiments were performed in triplicate.

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., 2013; Nakagawa et al., 2010), 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.

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

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), 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.

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

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 is 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 Vice is the ice growth rate, mice is the ice mass, Cs ice is the coffee concentration in the ice, t is the total freezing time, A is the heat transfer area, and ρice is he density of ice.

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

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)

7.3.2.2. Image Analysis of Morphological Structure of the Ice Crystals

Samples of the ice produced through 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. 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 the materials

employed in sample manipulation (spatula, coverslip glasses, tweezers and so on) were previously tempered at the freezing point of the freeze-concentrated sample (-21°C).

The images of the ice crystals formed in the samples of 20148 x 1536 pixels were captured using a Nikon microscope camera (Nikon, United States) fitted to the microscope and 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 an image analysis software. A threshold was applied to each image by using default settings. Spatial measurements, originally expressed as number of pixels, were calibrated using a micrograph taken from a 1-mm stage micrometer placed on the microscope stage.

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 in order to obtain a good reproducibility of the parameters of the ice crystals.

7.3.2.3. Identification and Quantification of Volatile Compounds

The major volatile compounds of the initial extract, the liquid, and the ice fractions of block FC and FFFC were identified and quantified through gas chromatography and mass spectrophotometry (GC/MS), according to the method reported by Ribeiro et al., (2010) with some modifications.

Extraction of volatile compounds was carried out through the Head Space Solid Phase Micro Extraction (HS-SPME) technique, using Divinylbenzene/Polydimethylsiloxane (DVB/PDMS) fibre with 65 µm thickness (Supelco, USA). Sealed glass vials (40 mL) were used to collect 2-g samples of the coffee extract, the liquid, and ice fractions obtained from Block FC and FFFC tests. Fibres were conditioned and then used in the injection port of the chromatographer for 30 min at 250°C in splitless mode. The fibres were inserted in the vials and exposed for 30 min at room temperature.

CG analyses were performed in an OP5050 GC-MS system (Shimadzu, Japan) equipped with a RTX-5 capillary column (30m×0.25mm× 0.25 µm). Helium (1.20 mL•min−1) was used as carrier gas. Oven temperature was programmed as follows: 40 °C→5°C/min→150 °C, followed by 30 °C/ min→260 °C. MS were performed using electron ionization (energy 70 eV). The scans were recorded within the 40-350 m/z range and compared to the Wiley 139 library using the Class 5K software.

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

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

7.3.2.4. Sensory Descriptive Analysis

A descriptive quantitative sensory evaluation was performed of the liquid and ice fractions obtained from block and falling-film FC and of the initial extract. Samples were evaluated by six panellists of the Trained Sensory Analysis Laboratory of the University of Antioquia. Coffee extracts were evaluated based on descriptive sensory attributes according to the National Standard NTC 4883. Coffee descriptors included aroma, acidity, bitterness, sweetness, tobacco, fruity, floral, aftertaste, body, global impact. A 10-point scale was used, with '0' indicating uncharacterised attribute intensity and '10' indicating very strong attribute intensity. Coffee extract samples were diluted to 1.5% solid content at 90°C and presented to the panellists. The results were averaged for each of the descriptive attributes and plotted in a web diagram.

7.3.2.5. Statistical Analysis

All the tests were performed in triplicate. Data reported included the mean and standard deviation. One-way analysis of variance (ANOVA) was applied to the results with a level of significance of 95% in order to evaluate 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.

7.4. Results

7.4.1. Freeze Concentration Tests

Table 7.1 shows the results on concentration of coffee solids in the liquid (C liq) and ice (C ice) fractions achieved through block and falling-film FC. 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, reaching a value of 17.8%. 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 solutes 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 by (Moreno, et al., 2014c; Nakagawa et al., 2010) and in falling-film FC by (Chen and Chen, 2000; Gulfo et al., 2013). 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.

Table 7.1. Results of freeze concentration tests

Technique	Block	Falling Film
C_0	13.4 ± 0.1	13.4 ± 0.1
C_{liq}	20.8 ± 0.9 [a]	17.8 ± 0.3 [b]
C_{ice}	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]

The lowest solute occlusion obtained through the block technique was contrasted with the result of the dewatering capacity per unit of time of both techniques. 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 process time, the ice growth would be more occluded and the concentration index would be lower in the concentration of coffee extract, as reported by (Moreno et al., 2014b). FFFC allowed high freezing rates with relatively low solute occlusion due to the solute dragging produced for the falling-film of 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.

7.4.2. Image Analysis of Morphological Structure of the Ice Crystals

Fig. 7.2 shows the images of ice crystals obtained during block and falling-film FC. Ice crystals were present as cells with a similar shape of solid prism or plate ice morphology, 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 identified 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 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.
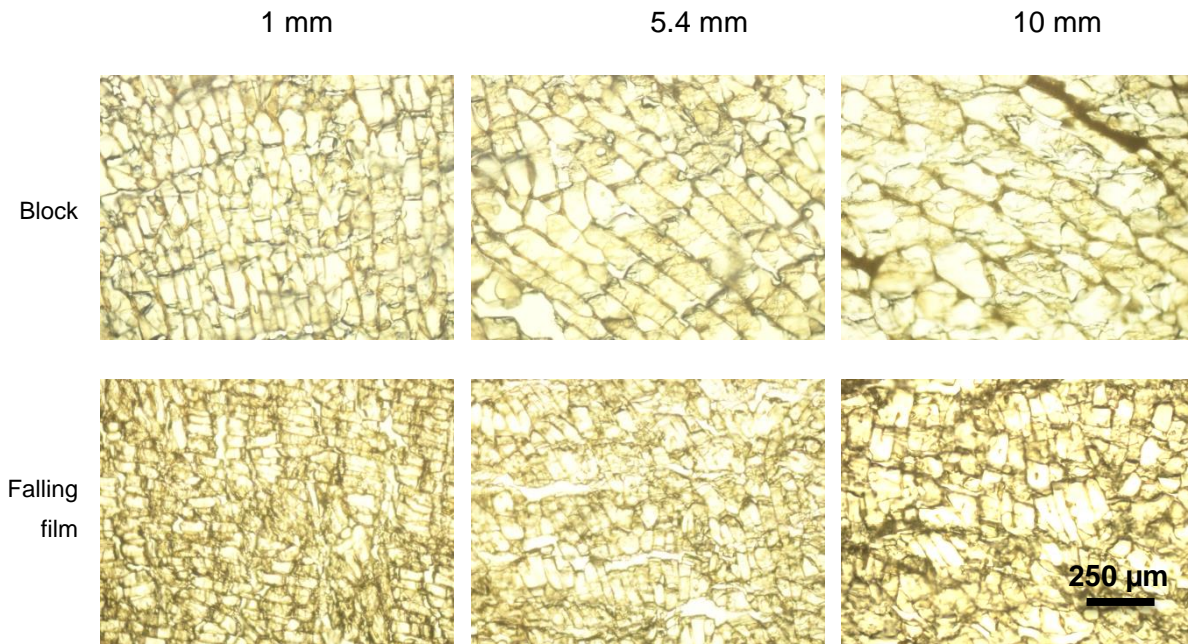
Figure 7.2. Microphotographs of ice crystals of block and falling film-freeze concentration at three positions from the cooling surface. 10X.

Table 7.2 shows the morphological characteristics of ice crystals determined through image analysis in Block and falling-film FC. 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 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 bigger the amount of liquid trapped in the channels. This result confirms that solute occlusion is higher when ice growth is faster.

Circularity of the ice crystals decreased with 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

partial thawing of the ice layer produced in FFFC, as described by (Moreno et al., 2014), and the shape of ice crystals can play an important role in this step. Morphometric parameters of ice crystals affect solute retention in the ice layer. These parameters can be an interesting topic of research to increase separation efficiency of block and falling-film freeze concentration.

Table 7.2. 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]		
	5.4	0.030 ± 0.001[b]	0.124 ± 0.001[g]	0.421 ± 0.007[l,]	0.29 ± 0.05 [m]	0.85 ± 0.02 [p]
	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]		
	5.4	0.013 ± 0.001[d]	0.080 ± 0.001[i]	0.431 ± 0.007[k,l]	0.45 ± 0.03 [n]	1.37 ± 0.12 [q]
	10	0.020 ± 0.001[e]	0.100 ± 0.001[j]	0.422 ± 0.007[l]		

7.4.3. Identification and Quantification of the Volatile Compounds

The major volatile compounds of the initial extract, the liquid, and the ice fractions of block FC and FFFC were identified and quantified through MS-GC. Chromatograms are shown in Fig. 7.3. The y-axis shows relative percentage area of the compound concentration and the x-axis shows retention time. Profiles were similar for all the samples, showing that major volatile compounds are contained in the samples after freeze concentration.

Eight major volatile compounds were identified in the coffee extract and the freeze-concentrated samples. The identification was made through mass spectrum and Kovats index (Sanz et al., 2002). Table 3 shows the identified compounds, including aldehydes, furans, pyrrols, pirazines, alcohols, and esters. These 8 major compounds represented 70% of the amount of total volatile compounds extracted from the coffee samples with the SPME technique.

Pentanal or valeraldehyde is a compound identified in coffee beverage (Toci & Farah, 2008) that has been associated with, vanilla, fruity, and nutty notes (Flament, 2002). Furans, such as furfural and furfuryl alcohol, are responsible for basic aromatic notes such as burnt, caramel, and fruity (Cheong et al., 2013; Roldán et al., 2003; Toci and Farah, 2008). On the other hand, 2-furanmethanol and 2-furanmethanol acetate provide herbal notes, and caramel and smoke notes, respectively (Caporaso et al., 2014; Piccino et al. 2014). Finally, pirazines found in the extract are a dominant group of volatile compounds in coffee aroma (Cheong et al., 2013), associated with roast and earth notes (Budryn et al.,

2011; Cheong et al., 2013; Korhonová et al., 2009; Sopelana et al., 2013; Sunarharum et al., 2014).
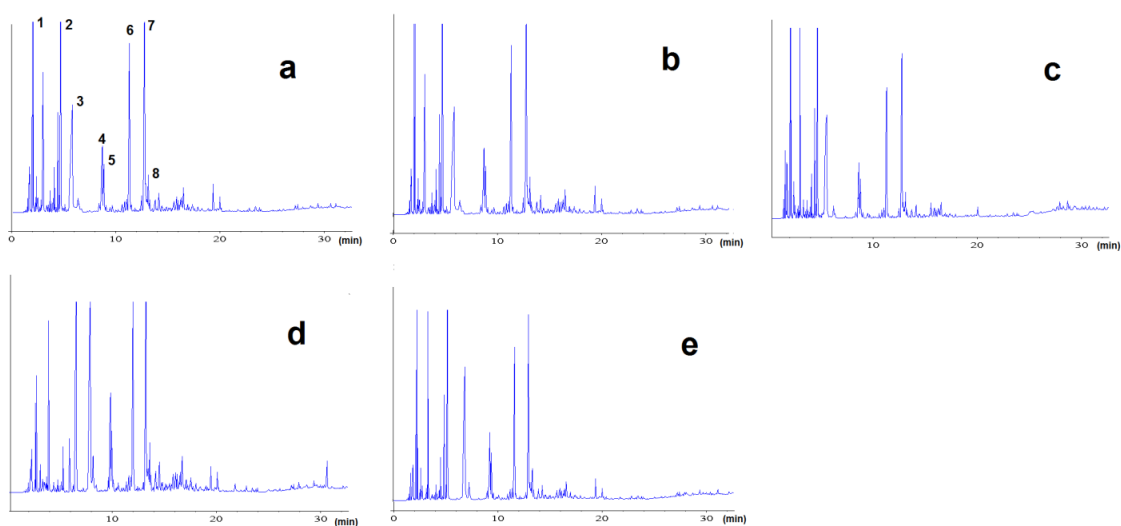
Figure 7.3. Chromatograms of coffee extract.

a) Initial extract; b) Block FC liquid fraction; c) Block FC ice faction; d) FFFC liquid fraction; e) FFFC ice fraction. 1. Pentanal; 2. Furfural; 3. Furfuryl alcohol; 4. Dimethyl pyrazine; 5. 5-methyl-2-furancarboxaldehyde; 6. 2-furanmethanol acetate; 7. 2-ethyl-3,5-dimethylpyrazine; 8. Nonenal

Major volatile compounds were identified in the liquid and ice fractions of both techniques and were the same as those identified in the initial extract. These results indicated that the profile of volatile compounds is preserved when using freeze concentration technology.

The relative percentage area, which represents the relative concentration of volatile compounds of the liquid and ice fractions obtained through Block FC and FFFC are shown in Table 7.3. Concentration was classified in four intervals with same size in order to compare the variation of the relative concentration between samples. The intervals were: Low (+) from 1.4043 to 5.9826, medium (++) from 5.9826 to 10.5610, high (+++) from 10.5610 to 15.1393, and very high (++++) from 15.1393 to 19.7176. In general, the relative concentration of volatile compounds was preserved in the freeze-concentrated liquid of both techniques. Differences were found in only three compounds. The relative concentration of Furfural decreased slightly for liquid fractions in both techniques. Furfuryl alcohol was preserved better in FFFC than in Block FC. On the contrary, 2-ethyl-3,5-dimethylpyrazine preservation was higher in block FC than in FFFC.

Table 7.4 shows ice loss percentage of relative concentration. An 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. On the contrary, a value lower than 50% indicates a higher presence of the volatile compound in the liquid freeze concentrated fraction.

Table 7.3. Relative percent area of major volatile compounds in coffee extract before and after freeze concentration.

Peak	Compound	IK	INITIAL	BLOCK LIQ	BLOCK ICE	FILM LIQ	FILM ICE
1	Pentanal	<800	+	+	+	+	+
2	Furfural	808.6	++++	+++	++++	+++	++++
3	furfuryl alcohol	850.2	++++	+++	++++	++++	++++
4	dimethyl pyrazine	949	+	+	+	+	+
5	5-methyl-2-furancarboxaldehyde	954	+	+	+	+	+
6	2-furanmethanol acetate	1032	++	++	++	+++	++
7	2-ethyl-3,5-dimethylpyrazine	1074	++++	++++	++	+++	+++
8	Nonenal	1085	+	+	+	+	+

Table 7.4. Ice loss percentage of volatile compounds after freeze concentration

#	Compound	BLOCK	FALLING FILM
1	Pentanal	63.2%	68.1%
2	Furfural	60.1%	58.1%
3	furfuryl alcohol	53.5%	49.9%
4	dimethyl pyrazine	53.0%	51.4%
5	5-methyl-2-furancarboxaldehyde	50.6%	52.2%
6	2-furanmethanol acetate	47.1%	46.8%
7	2-ethyl-3,5-dimethylpyrazine	40.5%	46.6%
8	nonenal	47.5%	49.6%

The ice loss percentage of volatile compounds was around 50% in most of the compounds. A value close to 50% indicated that there is not a selective loss of volatile compound in the ice or the liquid fraction, as the ice fraction was 50% in mass for block FC and 54% for FFFC. Volatile compounds were preserved in the freeze concentrated liquid and its loss was proportional to the total solid content in this fraction. The total concentration of volatile compounds was higher in the liquid fraction, which has a higher total concentration of coffee solids than the ice fraction, around 3.4 times in block FC and 2.2 times in FFFC according to the results shown in Table 1.

A slight loss in the ice of pentanal and furfural −compounds associated to woody, fruit and burnt notes− was obtained. A better concentration of 2-furanmethanol acetate, 2-ethyl-3,5-

dimethylpyrazine, and nonenal was obtained; these compounds are associated to aromatic, herbal, and earth notes. The preservation of volatile compounds in block FC and FFFC was similar, without remarkable differences. As a general result, both techniques preserved effectively the major volatile compounds of the coffee extract. The impact of this preservation on aroma and flavour profiles was analysed in the sensory evaluation presented in section 3.4.

7.4.4. Sensory Evaluation

Coffee cup testing was performed to evaluate aroma, acidity, bitterness, sweetness, tobacco, fruity, floral, aftertaste, body, and global impact of the samples before and after freeze concentration. Volatile and non-volatile compounds are responsible for these characteristics. Fig. 7.4 shows the results of the sensory parameters in a web chart. Samples were characterised by the highest scores in aroma, acidity, bitterness, body, and global impact. The lowest scores were obtained for sweetness, tobacco, fruity, floral, and aftertaste.
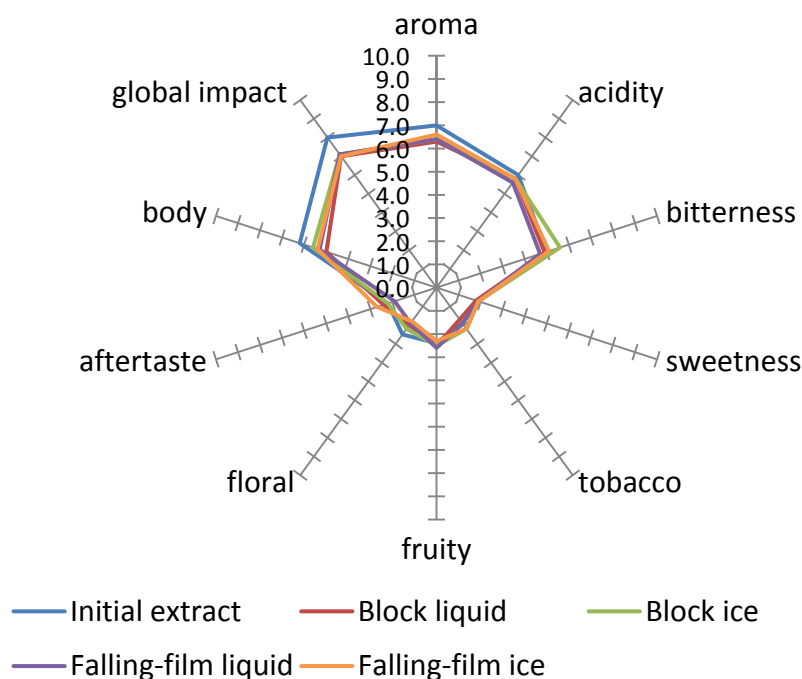
Figure 7.4. Quantitative descriptive analysis of initial extract and freeze-concentrated samples

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 than those evaluated in the initial extract. The aroma profiles of the freeze-concentrated samples and the initial extract were similar, which may be due to their close expression of volatile compounds. This results shows that freeze concentration is an effective technique to preserve the sensory quality of coffee extract.

The significance of the differences is shown in Table 7.5, including the mean and standard deviation of the scores. 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 ten attributes were equal to the initial extract. A slight difference in body and global impact was found, similarly to the block technique. 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 compound responsible for this note.

Table 7.5. 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]

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 similar 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 to 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 floral note can be attributed to minor volatile compounds loss associated to 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 can retain solute (Delgado et al., 2008; Thaler, 1978). Cryogels can 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 in the quality of freeze-concentrated coffee.

A comparable result for preservation of quality with freeze concentration was reported for 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 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.

7.5. Conclusions

Block and falling-film freeze concentration techniques were tested to compare 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 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, low size of ice crystals and high solute retention in the ice were obtained. The diameter and area of ice crystals produced through block FC were higher than those of ice crystals obtained from FFFC due to the freezing rate. The size of ice crystals defines the space where the concentrated liquid is retained, its control is important to increase concentration efficiency.

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

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8. A PROCESS TO CONCENTRATE COFFEE EXTRACT BY THE INTEGRATION OF FALLING FILM AND BLOCK FREEZE-CONCENTRATION

8.1. Abstract

A process to concentrate aqueous coffee extract by freeze concentration is proposed to achieve an industrially viable system. The techniques of falling film freeze concentration, fractionated thawing and block freeze concentration were studied. Batches of 40 kg of coffee extract with 5% initial solid concentration were freeze-concentrated in seven stages in a falling film multi-plate freeze concentrator. The ice from each stage was fractionally thawed to recover the coffee solids retained in the ice. The diluted fractions of the thawing stage were freeze-concentrated using the block technique. A concentrated extract with 32.6% solids and an effluent with 0.27% solids were obtained through the integration of these techniques. A concentration index of 6.5, a concentration efficiency of 99.2% and a solute yield of 95% were obtained. The integration of these simple techniques results in a concentration index and solute yield comparable to industrial standards in freeze-concentrated coffee extract production.

Keywords: cryoconcentration; freeze-dried coffee; coffee extract; thawing

8.2. Introduction

Coffee is one of the most consumed beverage worldwide (Esquivel & Jiménez, 2012; Sopelana et al., 2011). Freeze-dried coffee is a high-quality product of the coffee industry because of the flavour preservation due to the low-temperature processing conditions (MacLeod et al., 2006). The process of obtaining freeze-dried coffee begins with the extraction of roasted coffee beans by percolation. Subsequently, the extract is freeze-concentrated to remove part of the water and to obtain a concentrated extract. The concentrated extract may be the final product or may be freeze-dried to remove the remaining water to obtain soluble coffee (Boss et al., 2004). The use of freeze-concentration technology is justified by the reduction of the freeze-drying process costs by 25% (Van Pelt and Bassoli, 1990). In addition, the quality of the product is preserved by low processing temperatures (Rahman et al., 2007).

Freeze concentration (FC) is a technique used to remove water from food fluids by freezing (Sánchez et al., 2009). The solution is cooled below the freezing point to produce and separate ice crystals. Three techniques are used for growth of ice crystals, suspension FC, film FC (progressive or falling film FC) and block FC (also known as freeze-thaw FC) (Aider and de Halleux, 2009; Sánchez et al., 2011a).

The most implemented technique in coffee processing at the industrial level is suspension FC. This is an efficient technique in terms of ice purity and increased concentration (Qin et al., 2007; Qin et al., 2006; van der Ham et al., 2004). With this technique, it is possible to concentrate the coffee extract to 32 to 35% solids and to obtain a high-purity effluent with 0.1% solids (Van Mil & Bouman, 1990; Van Pelt & Bassoli, 1990). However, this technique requires complicated systems of ice separation and many moving parts, which increases the initial and operating costs (Aider and de Halleux, 2009; Miyawaki et al., 2005; Sánchez et al., 2009). For this reason, several other FC techniques have been studied. Recently, the industrial future of freeze concentration has shifted toward the configuration of one-step systems or a combination of systems rather than suspension freeze concentration because of the simpler separation step (Petzold & Aguilera, 2009; Petzold et al., 2013).

In falling film freeze concentration (FFFC), the solution to be concentrated is in contact with a cooled vertical plate on which the fluid descends. The ice forms a single layer on the cold surface, and the solution is re-circulated continuously (Sánchez et al., 2011b). FFFC has been studied with several food fluids (Belén et al., 2013; Chen et al., 1998; Hernández et al., 2009, 2010; Raventós et al., 2007; Sánchez et al., 2010). Flesland (1995) proposed multi-stage FFFC coupled to reverse osmosis for water desalination. In that study, water elimination was efficient. Recently, the recovery of solutes of sucrose solutions retained in ice was attempted using fractionated thawing of the ice (Gulfo et al., 2013; Miyawaki et al., 2012).

In contrast, in block freeze concentration (block FC), the whole solution is frozen and partially thawed to recover the concentrated liquid fraction (Aider and de Halleux, 2009). Block FC has been used for sucrose solutions, dairy products, syrup, mate extract and fruit juices (Aider and Ounis, 2012; Aider et al., 2009; Boaventura et al., 2012; Nakagawa et al., 2010). For coffee extracts, Moreno et al. (2014) and Moreno et al. (2013) studied the effect of process conditions on the freezing and thawing stages of block FC. The viability of the technique was primarily demonstrated for low solid concentrations.

In some food applications, FC can be used to maximise the final solid content of the solution. However, in the coffee industry, the minimisation of the solid content of the final effluent is also important due to the high value of the product. Currently, there is no plan to use FFFC or block FC to obtain an extract with a high solid concentration and an effluent with a low solid content that comply with industrial requirements.

The aim of the present study was to propose a process to freeze-concentrate coffee extracts through the integration of falling film freeze concentration, which includes coffee solids recovery by fractionated thawing and block freeze concentration techniques.

8.3. Materials and Methods

8.3.1. Materials

A coffee extract with 5% (w/w) wet basis of total solid content was prepared from freeze-dried soluble coffee supplied by Buencafé Liofilizado de Colombia (Colombian Coffee Growers Federation, Colombia) and water at 35 °C. The solution was stored at 4 °C for 24 hours prior to the tests.

8.3.2. Methods

Three techniques were studied for coffee extract freeze-concentration following the flowchart shown in Fig. 8.1. First, the initial extract was freeze-concentrated by the falling film technique. Second, the ice formed in the first technique was thawed fractionally to study the recovery of the retained solutes. Finally, the diluted fractions obtained in the thawing stage were concentrated by the block technique to recover the retained solids. Each technique was individually studied. Based on the results, an integration of the techniques in a global process was proposed.
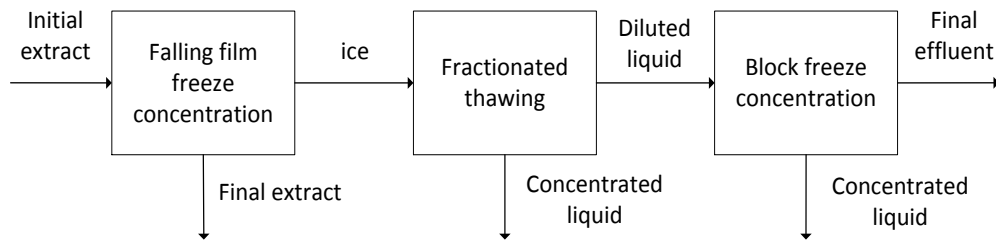
Figure 8.1. Flowchart of freeze concentration tests

Falling film freeze concentration tests

The FFFC tests were developed in a multi-plate freeze concentrator shown in Fig 8.2(a). The equipment included a freezing chamber, a freezing system, and a hydraulic system. The freezing unit consisted of two cooling plates with dimensions of 0.8 m width and 0.6 m height in a closed chamber. The hydraulic system spreads the coffee extract by means of two distributors with several holes 3 mm in diameter. The coffee extract flows in a descending film over the cooling plates, and it was collected in a collector tank and recirculated by a centrifugal pump. The ice growth on the surface of the freezing plates was then removed in a batch operation.

The freezing system consisted of refrigeration cycle using the primary refrigerant R-507 with a compressor (Tecumseh Europe, La Verpilliere, France), a condenser and an expansion valve. The evaporation of the refrigerant occurred in the interior of the cooling plates, transferring the energy through the walls of the plate. Consequently, this process

produces layer crystallisation in which the ice forms in thin layers on the surface of the heat exchanger.

All the stages of FFFC started with 40 kg of coffee extract. The stage ended when the ice achieved an average width of 25-35 mm. After that, the ice was removed, and the concentrated liquid fraction was used in the next stage. The initial mass in the next stage was obtained adding extract prepared at the concentration of the extract used in the previous stage. A total of seven stages of FFFC were developed. The mass of the concentrated fractions and the ice was measured on a PS 60-KB scale with 1 g precision (Gram Precision, Spain). The solid concentration percentage (Cs) was measured by refractometry (Atago Pal 100, Japan). The relationship between Brix degrees and Cs is represented by the equation CS=0.87*°Brix reported by Moreno et al. (2014) for the same coffee used in the present study.

Figure 8.2. Experimental setup for freeze concentration tests.

a) Falling film freeze concentration; b) Fractionated thawing; c) Block freeze concentration

Coffee solids recovery by partial thawing tests

Thawing tests were performed according to the method described by Gulfo et al. (2013). Cylindrical samples with a diameter of 60 mm, thickness from 25 to 35 mm and weight between 65 and 75 g were taken from the ice obtained at each of the seven stages of

FFFC to study the solute recovery for fractionated thawing. A drill equipped with a puncher (Esgarret, Spain) was used to obtain six samples homogeneously distributed in each of the six ice sheets, for a total of 36 samples. Samples were taken in a refrigerated chamber to avoid melting the ice.

The samples were subjected to thawing tests in the setup shown in Fig. 8.2(b). The setup consisted of a cubic isolated chamber with 0.48 m sides. The chamber has a temperature control system (Pie Electro Dit, model 11 551, 0 to 300 W) and a 4-channel data logger (Testo 177-T4, Germany). The thawing was carried out at 20 +/- 1 °C in a vertical position, similar to the position that the ice layers had in the freeze concentrator. The dripping of the melting ice is collected by a funnel connected to a container on a scale (Ohaus PA3102, USA) with a precision of 0.01 g to measure the mass. Ten thawing fractions of equal mass were separated, and the solid concentration was measured by refractometry. The average concentration was calculated from the data of the six samples of ice from each stage.

Block freeze concentration tests

Based on the results of the fractionated thawing tests, the diluted fractions of this stage (fractions where the concentration index was less than 1) were mixed and freeze-concentrated by the total block technique. The conditions of the FC test were as follows: cooling temperature -10 °C, thawing temperature 20 °C and thawing direction opposite to the freezing direction according to the best results reported by Moreno et al. (2014).

The block freeze concentrator is shown in Fig. 2(c). 160 g of the coffee sample were placed into a cylindrical double jacked container measuring 5.2 cm in diameter and 8.5 cm in height. The heat exchange fluid was a mixture of ethylene glycol and water (53% w/w) coming from two baths (Polystat, Cole Parmer, USA) with temperature control (-35 °C to 150 °C +/- 0.01 °C).

The cooling fluid temperature was settled at -10 °C. After the fluid reached that temperature, it was circulated to the internal jacket to freeze the inner solution. The ice growth occurred from the centre to the external wall of the container. When the sample was completely frozen, the sample was thawed by pumping heating fluid through the external jacket at 20 °C. A valve located on the bottom of the container and close to the external wall was opened, and the liquid fraction was separated in a collector vessel on a scale (Ohaus PA3102, USA) with a precision of 0.01 g for mass measurement. Ten liquid fractions of the same mass were collected. The solid concentration of each fraction was measured by refractometry (Atago Pal 100, Japan). Test were performed in triplicate

Data analysis

Solute Yield (Y)

Solute yield represents the amount of solute or coffee solids recovered from the original solution. *Y* 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., 2013; 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.

Concentration Index

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 mass percentage in the freeze-concentrated liquid, and $C_{s\ 0}$ is the solid mass percentage in the initial solution.

Thawing fraction

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

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

Where, *f* is the thawing fraction, m_{liq} is the freeze-concentrated liquid mass, and m_0 is the initial mass

Concentration efficiency

The concentration efficiency indicates the increase in the concentration of the solution in relation to the amount of solids remaining in the ice (Hernández et al., 2010; Sánchez et al., 2010). Efficiency was calculated by Eq. 4:

$$Eff = (C_{s\ liq} - C_{s\ ice})/ C_{s\ liq} *100 \quad (4)$$

Where, *Eff* is the concentration efficiency (%), $C_{s\ liq}$ is the solid mass percentage in the freeze-concentrated liquid, and $C_{s\ ice}$ is the solid mass percentage in the ice (or diluted fraction).

Statistical analysis

The experimental results obtained from this study were fit to different mathematical models using the statistical software SPSS 20.0. The fit was evaluated by the determination coefficient.

8.4. Results and Discussion

8.4.1. Falling film freeze concentration

The total solid concentration in the freeze-concentrated liquid for the seven FFFC stages is shown in Fig. 3. The concentration progressed linearly according to Eq. 6:

$$C_{s\ liq} = 3.9\ n + C_0 \qquad R^2 = 0.991 (6)$$

where $C_{S\ LIQ}$ represents the solid percentage in the freeze-concentrated extract, *n* is the stage number, and C_0 is the solid concentration of the initial extract, which corresponds to 5% in these tests. Linear behaviour was also obtained for orange, apple and pear juices by Hernández et al. (2010) and Sánchez et al. (2011b, 2010). The results indicate that the solid concentration increased 3.9%, and the concentration index increased from 1.1 to 1.7 in each stage.
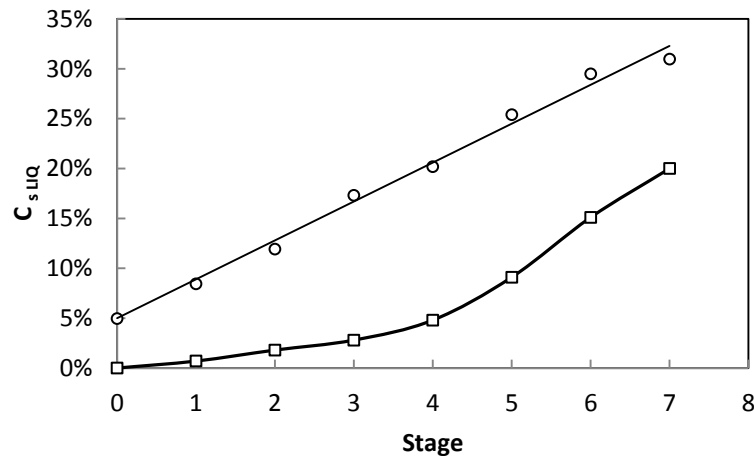
Figure 8.3. Solid concentration in liquid (○) and ice (□) at each stage of falling film freeze concentration.

On the other hand, the solid concentration of the ice evolved according to a quadratic function. The occluded solids in the ice increased approximately linearly between the first and fourth stages. From this point, when the solution had 20.2% of solids, the solid retention in the ice increased. The increasing solid occlusion can be explained by several effects. First, the higher amount of solids in the extract produced an increased interaction between solids and water molecules (Chen et al., 1998). Second, the solution is more

viscous (Hernández et al., 2010) and washing the concentrated liquid fractions from the falling film was more difficult. In addition, the ice tends to grow in dendritic form at higher solid concentrations, trapping more solids inside (Butler, 2002; Yee et al., 2003).

As a consequence of the higher solid occlusion, the concentration efficiency decreased linearly with the solid concentration in each stage, as shown in Table 1. A linear decrease in concentration efficiency was also reported by Hernández et al. (2009), (2010) and Raventós et al. (2007) for freeze concentration of must, fruit juices and sugar solutions, respectively.

The final solid concentration over seven stages of FFFC was 31%, corresponding to a concentration index of 6.25, as shown in Table 1. The ice fraction obtained in each stage (f_{ICE}) is presented in the same table. The ice mass obtained decreased in each stage. When the solid concentration of the extract increased, the amount of water that had to be removed to increase the concentration was lower. In addition, the freezing point decreased with the solid concentration, and the cooling capacity of the equipment limited the ice production. The ice in the last stage was less consistent due to the increased amount of solids.

In Table 8.1, the solute yield of each stage (Y_{STAGE}) is presented. The values began at 95% and decreased through the following stages. Moreover, the accumulated solute yield in the seven stages was 0.42 based on the total amount of solids in the initial extract. This means that 42% of the coffee solids present in the initial extract were in the final extract. A large amount of solids was recovered in the ice due to the amount of ice, despite the lower concentration of these solids.

Table 8.1. Initial coffee solid concentration (C $_{s0}$), concentration index (CI), solute yield at each stage (Y $_{STAGE}$), ice fraction (f $_{ice}$) and concentration efficiency (Eff) of falling film freeze concentration tests

Stage	C $_{s0}$ (%)	CI	Y $_{STAGE}$	f $_{ICE}$	Eff (%)
1	5.0	1.70	0.95	0.44	91.7
2	8.4	2.40	0.87	0.39	84.9
3	11.9	3.49	0.96	0.34	83.8
4	17.3	4.07	0.78	0.33	76.2
5	20.2	5.12	0.89	0.30	64.2
6	25.4	5.95	0.78	0.33	48.8
7	29.5	6.25	0.78	0.26	35.4

The results indicated that falling film freeze concentration can be used to obtain a final extract with a solid concentration that meets industrial requirements. However, a large amount of solids remained occluded in the ice, and it is necessary to find a technique to recover them. For this reason, fractionated thawing tests were performed.

8.4.2. Coffee solids recovery by fractionated thawing

The ice obtained in the seven stages of FFFC tests was thawed in ten mass fractions to study the solid recovery. The concentration index (*CI*), calculated as the ratio between the solid concentration in the thawed fraction and the average solid concentration of the ice, is shown in Fig. 8.4. The *CI* began with values higher than 1 and descended throughout all stages of the thawing process. This indicated that the concentrated extract was collected in the first fractions, and the thawing procedure can be used for solid recovery in the ice. Gulfo et al. (2013); Miyawaki et al. (2012) and Yee et al. (2003) reported similar behaviour of the concentration in solute recovery in the thawing of sugar solutions.

The solid concentrations of the first fractions were higher than the average mainly due to two phenomena. First, the concentration of the external faces of the ice is higher than the concentration in the internal portion; the external faces were the first thawed portions. In the face in contact with the cooling plate, the nucleation at supercooling temperatures increased the concentration of the liquid fraction trapped when the ice front grew (Scholz et al, 1993). In the face in contact with the falling fluid film, the dendritic growth of the ice trapped the concentrated extracts of the falling film (Sánchez et al., 2010). Second, and possibly more important, there was solute diffusion from the concentrated liquid occluded in the ice to the thawed drops. When the water drops melted, there was enough time for solute diffusion to the drops, increasing the solid concentration and allowing the recovery of a concentrated liquid (Nakagawa et al., 2009). If the ice is partially thawed, the concentrated fraction trapped in the ice crystals can flow freely and be separated. This phenomenon is known as sweating, and it is very important in the solute recovery (Guardani et al., 2001).
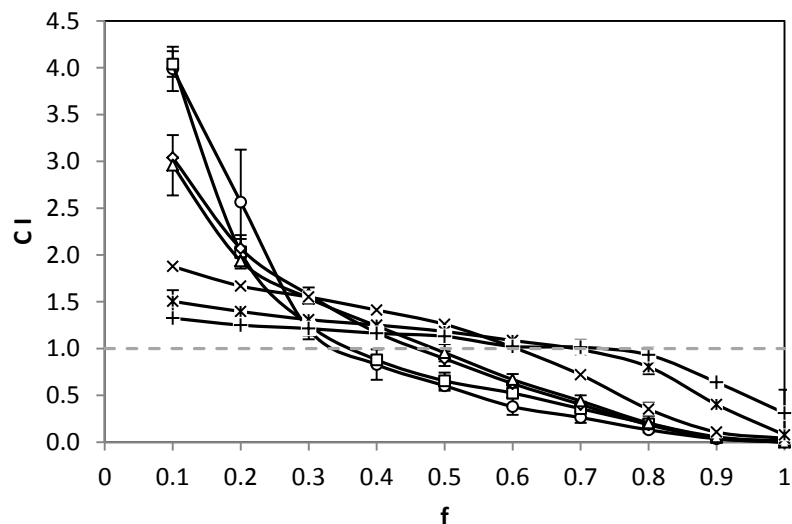
Figure 8.4. Concentration index as a function of the thawing fraction.

(○) stage 1; (□) stage 2; (◊) stage 3; (Δ) stage 4; (x) stage 5; (✶) stage 6; (+) stage 7

Fig. 8.4 shows that the concentration index decreased with f, and there was a thawing fraction in which the CI was less than one. From this point, the concentration of the following fractions was less than the average; consequently, the thawing process should be stopped at this point to avoid dilution of the recovered extract. At this fraction (*f* at *CI*=1), two products are obtained, the initial fractions with *CI*>1 (concentrated fraction) and the final fractions with *CI*<1 (diluted fraction).

The values of *f* at *CI*=1 between 0.3 and 0.7 were obtained as shown in Table 8.2. These values depended on the initial solid concentration of the ice (*C* $_{s\ 0\ ice}$). A small amount of ice had to be thawed to recover the solids in the first stages, in which the ice had a lower solid concentration. In contrast, in last stages, a higher amount of ice had to be thawed. The concentration of the thawing fraction was more homogenous (flatter curve in Fig. 4). In addition, the movement of the solids is more difficult in high solid concentrations because of the interaction between molecules.

The solid concentrations of the diluted (*C* $_{s\ dil}$) and concentrated fractions (*C* $_{s\ conc}$) for *f* at *CI*=1 are shown in Table 8.2. Thawing fractions where *CI*=1 are also shown. These are the fractions in which high solid recovery is achieved without excessive dilution of the sample. With this strategy, a concentration index between 1.3 and 2.5 was obtained. The CI was highest in the first stages. Similar results were reported by Gulfo et al. (2013) for sugar solutions. The *CI* can be calculated from the concentrations reported in Table 2. The *CI* decreased with the initial solid concentration in the ice, as shown in Fig. 8.5. The behaviour can be described by Eq. 7:

CI= 50.35•C$_{s0}$^{2} – 16.98•C$_{s0}$ + 2.61   R^2= 0.94 (7)

Table 8.2. Concentration of the diluted (C $_{s\ dil}$) and concentrated fractions (C $_{s\ conc}$) of the recommended thawing fraction (f at CI=1).

Stage	f at CI=1	C $_{s\ 0\ ice}$ (%)	C $_{s\ conc}$ (%)	C $_{s\ dil}$ (%)
1	0.3	0.7 ± 0.1	1.8 ± 0.4	0.2 ± 0.0
2	0.3	1.8 ± 0.2	4.5 ± 0.6	0.7 ± 0.0
3	0.4	2.9 ± 0.3	5.7 ± 0.8	1.0 ± 0.1
4	0.4	5.0 ± 0.7	8.6 ± 1.1	1.4 ± 0.3
5	0.5	9.4 ± 0.1	14.5 ± 0.2	4.2 ± 0.1
6	0.7	15.6 ± 1.0	20.4 ± 0.3	8.3 ± 2.9
7	0.7	20.0 ± 1.6	23.2 ± 1.4	12.6 ± 2.2

Average ± standard deviation.
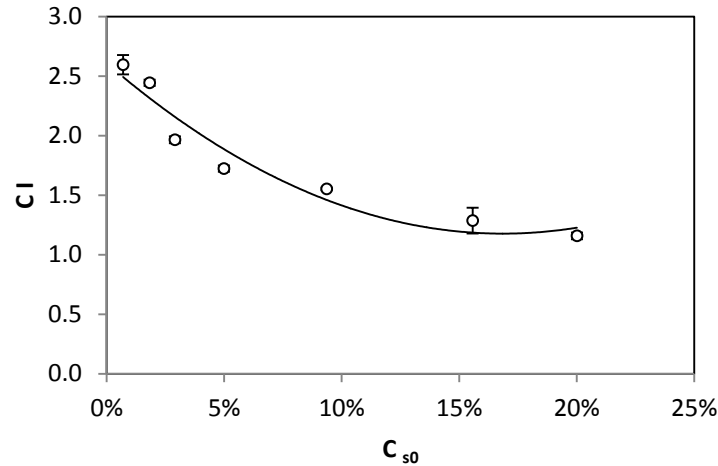
Figure 8.5. Concentration index (CI) at the recommended thawing fraction as a function of the initial solid concentration (C $_{s0}$) of the ice.

Solute yield can be calculated from Eq. 8, which is obtained by combining Eqs. 1, 2 and 3 (Moreno et al., 2014). Solute yields from 73% and 81% were obtained. Miyawaki et al. (2012) reported solute yields above 90% by ice thawing from a tubular progressive freeze concentrator. The solute yield depends on the thawing fraction.

$Y=f*CI$ (8)

The combination of the fractionated thawing process and the FFFC technique resulted in a solute yield of 62%. Although the solid recovery was increased by more than 70%, a large amount of coffee solids remained in the diluted fraction. Another technique needed to be integrated to the process to increase the solid recovery. Block FC was studied for this purpose.

8.4.3. Block freeze-concentration

The diluted fractions from the fractionated thawing tests were mixed and freeze-concentrated by the block technique to recover the solids from this fraction. Ten fractions were obtained in the first stage, and the solute yield (*Y*) and concentration index (*CI*) were calculated. The diluted fractions (according to the *CI* values) obtained in the first stage were mixed and freeze-concentrated in a second stage. The results of the two stages are shown in Fig. 8.6.

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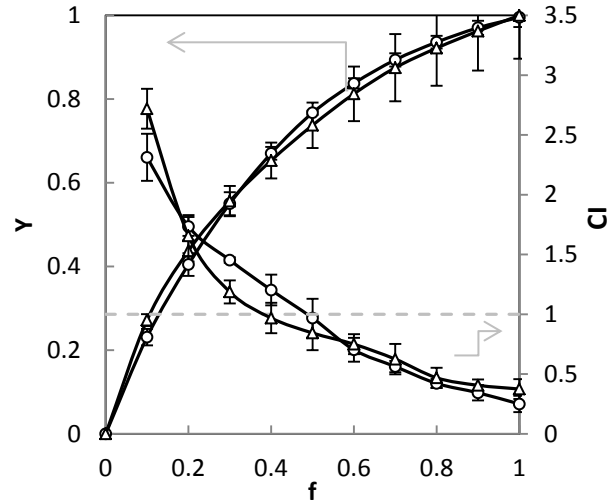
Figure 8.6. Solute yield (Y) and concentration index (CI) after block freeze concentration.

(○) stage 1; (Δ) stage 2.

Maximal *CI* values of 2.3 and 2.7 were obtained in the first thawing fraction. These results were obtained because the sample was frozen from the centre and thawed from the exterior of the container. With this control of the thawing direction, the solids moved to the growing freezing front by elution when the ice crystals formed. The last fraction frozen was the first to be thawed. This fraction had the highest solid content. The solid elution was possible because of the low freezing rate achieved by the cooling temperature of -10 °C; at this temperature the average freezing rate was 1.84 µm•s^{-1} (Moreno et al., 2014). The lower the freezing rate is, the lower the solid occlusion is. Nakagawa et al. (2010) reported a limit of 8 µm•s^{-1} for freeze concentration in a similar cylindrical device.

The *CI* decreased during the thawing. The highest values were obtained for the firsts thawing fractions due to sweating, similarly to the fractionated thawing test results. Sweating is defined as crystal purification based on partial melting by heating the cooling surface at a temperature close to the freezing point (Jiang et al., 2013). Sweating depends on factors such as temperature, porosity of the ice layer, solid concentration, and thawing rate (Rich et al., 2010). The coffee solids moved to the thawing drops and increased the concentration in the drops; in this way, recovery of the majority of solids was possible in the first fractions. As in fractionated thawing, sweating is of great importance in block freeze concentration (Nakagawa et al., 2009).

The CI decreased until it reached a value of 1. In this thawing fraction (*f* at *CI*=1), it is convenient to stop the thawing stage and to separate two streams, one diluted and one concentrated. For the first stage of block FC with an initial solid concentration of 1.8%, the *CI* was 1 at *f*=0.5. At this point, 77% of coffee solids have been recovered, and a *CI* of 1.54

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has been achieved, as can be calculated from data in Table 3. The mixture of the five diluted fractions had a solid concentration of 0.9%; for this reason, this mixture was freeze-concentrated in a second stage. For the second stage, *CI* was 1 at *f*=0.4. When 40% of the extract was thawed, a solute yield of 66% and a *CI* of 1.6 were achieved. The diluted fraction of the second stage had an average solid concentration of 0.5%, as shown in Table 8.3.

Table 8.3. Results of block freeze concentration.

Thawing fractions when the concentration index (CI) is 1. thawing fraction when CI=1 (f at CI=1); solid concentration of the Initial (C s0 (%));the concentrated (C s conc) and diluted fractions (C s dil), and solute yield (Y)

Stage	f at CI=1	C_{s0} (%)	$C_{s\,conc}$ (%)	$C_{s\,dil}$ (%)	Y
1	0.5	1.9 ± 0.0	2.8 ± 0.1	0.9 ± 0.1	0.78 ± 0.01
2	0.4	0.9 ± 0.1	1.5 ± 0.1	0.5 ± 0.1	0.68 ± 0.02

Block FC was considered to be complete based on the solid concentration of the diluted fraction in the second stage. A third stage could be implemented, but this decision depends on the global process strategy and the desired solid concentration of the final effluent.

8.4.4. Integration of falling film freeze concentration, ice thawing and block freeze concentration

Falling film freeze concentration, fractionated thawing and block freeze concentration can be integrated in a global strategy to establish an industrial process to concentrate coffee extracts. In this process, the objective is to obtain an extract that is as concentrated as possible and to minimise the concentration of the effluent to avoid the coffee solid loss. Two streams, diluted and concentrated, are obtained in each technique. The process is presented in Fig. 8.7. The mass and solid concentration of the extract is presented for each stream. The mass balance was achieved for a basis of calculation of 1000 kg/h of diluted coffee extract entering the process (Feed). Even though the process must be scaled up, mass balance can be applied to analyse the possible results at an industrial level.

The process starts with seven stages of falling film freeze concentration. The solid concentration at the end of each stage was calculated by Eq. 6. The concentrated fraction of each stage entered the next stage. After falling film freeze concentration, the ice is thawed to recover the occluded solids. This thawing can be achieved using the same equipment used for FFFC. The concentration obtained from the thawing process was calculated by Eq. 7. The thawing ended when the f values shown in Table 8.2 were reached. The diluted and concentrated fractions can be separated. At this point, 64% of

the solids retained in the ice were recovered. The diluted fraction of the first thawing stage had 0.24% solids and was considered an effluent. The other diluted fractions can be mixed to obtain 574.8 kg/h of extract with 1.7% of coffee solids. This mixture can be freeze-concentrated by the block technique.
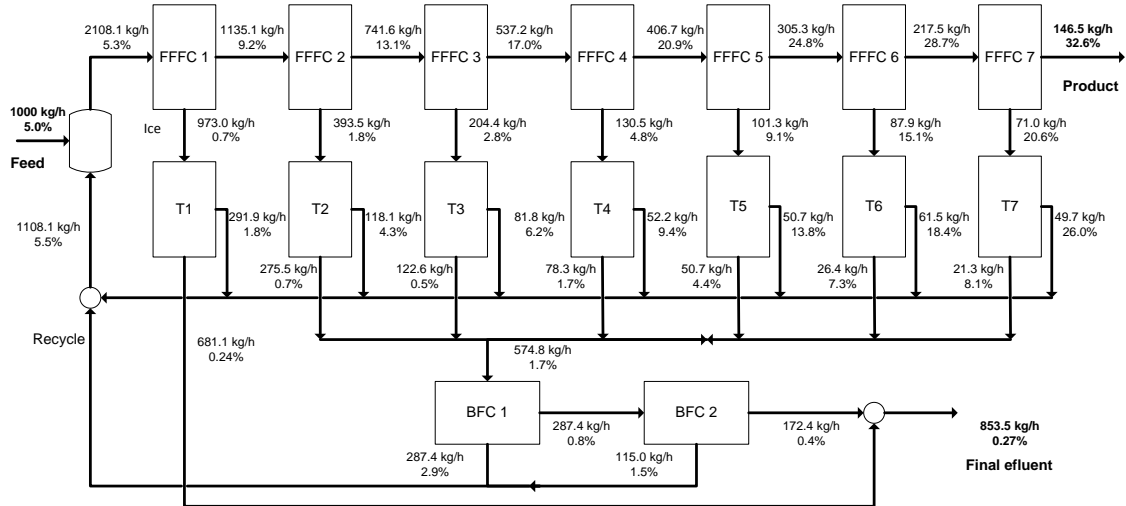
Figure 8.7. Integrated process to freeze-concentrate coffee extract using falling film freeze concentration (FFFC), fractionated thawing (T) and block freeze concentration (BFC).

The results of block FC were calculated from the data reported in Table 8.3. A diluted stream with 0.4% of coffee solids was obtained after two stages of block FC. This stream can be mixed with the diluted fraction of the first thawing stage to obtain an effluent of 853.5 kg/h with 0.27% coffee solids. This final concentration is acceptable according to industrial standards. The concentrated fractions from the thawing stages and block FC can be mixed and re-circulated through the process. A mixture of 1108.1 kg/h with 5.5% of solids was obtained and can be mixed with the feed.

With the proposed process, the concentration of the extract increased from 5% to 32.6%. The concentration of the final effluent was 0.27%, comparable to industrial standards (Van Mil and Bouman, 1990; Van Pelt and Bassoli, 1990). The process results are presented in Table 8.4. Through the combination of the three techniques, the solute yield increased to 95%, the concentration index to 6.5, and the concentration efficiency to 99.2%. The results indicate the convenience of the process to concentrate coffee extract in comparison to FFFC. The process is comparable to the suspension system currently implemented in the coffee industry in terms of the concentration of the product and effluent.

Different variations of the process can be utilised to optimise energy consumption or cost. For example, an alternative process can be proposed by analysing the concentration of the ice in the three last stages of FFFC. These solid concentrations were higher than the

solid concentration of the initial extract, so they can be re-circulated without going through the thawing stage. Applying mass balance, with this alternative only one block FC stage is required to obtain an effluent with a solid concentration less than 0.3%. The process would include seven stages of FFFC, four stages of thawing and one stage of Block FC, reducing costs and time. In the same way, other combinations of strategies can be performed. The technical viability of the current strategy has been shown in terms of the requirements of the final extract and the final effluent solid concentrations. From this point, the optimisation of the process and equipment sizing can be initiated. This process is in development for future studies.

Table 8.4. Final results of the integrated freeze-concentration process.

Technique	Y	CI	Efficiency
Falling Film Freeze concentration (FFFC)	0.43	6.2	90.1%
FFFC + fractionated thawing (T)	0.64	6.4	97.2%
FFFC+ T + Block FC	0.95	6.5	99.2%

8.5. Conclusions

An operative strategy to integrate falling film freeze concentration, fractionated thawing and block freeze concentration was proposed as an alternative to suspension freeze concentration of aqueous coffee extract. Falling film freeze concentration is effective for increasing the solid concentration of the extract to levels reported by industry. However, a large amount of solid is occluded in the ice. Fractionated thawing allows the recovery of the solids occluded in the ice. Block freeze concentration is able to obtain a final effluent with low solid content, reducing solids loss.

Falling film freeze concentration increased the concentration of the coffee extract 6.2 times. With fractionated thawing, 64% of the solids retained in the ice were recovered. By block freeze concentration, a high-purity effluent was obtained. Through the process, the coffee extract was concentrated from 5% to 32.5% with an effluent with 0.27% solids. The concentration efficiency increased to 99.2% and the solute yield to 95%. The process is an alternative to the industrial freeze concentration systems based on suspension technology, with the advantage of the simplicity of the falling film and block freeze concentration equipment.

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9. MAIN RESULTS OF THIS DISSERTATION

This final chapter presents a summary of the main results achieved in this dissertation. From the main question of the research, *what is the effect of the operational variables of block and falling-film freeze concentration on separation efficiency and quality of coffee extract*, the most important results are highlighted.

- *The coffee mass fraction of the extract significantly affected the separation achieved during block and falling-film freeze concentration.*

Separation is more difficult when the concentration of coffee solids increases as a result of the concentration process due to the combined effect of several phenomena. First, the diffusion rate of solutes elution to the ice front decreases by cause of the interactions between molecules. Second, viscosity of the coffee solution increases, and consequently, liquid fraction movement is slower in the freezing and thawing stages. In addition, the volume of water that can be frozen and separated is lower for higher concentrations. Finally, increasing solute concentration decreases the freezing point and produces the constitutional supercooling phenomenon, trapping more quantity of solutes in the ice front. The combination of these effects explains why the efficiency of separation decreases with solid concentration.

- *Controlling freezing direction was useful to recover solutes during block freeze-concentration.*

Commonly, the thawing of the ice block is achieved from the same front where it was frozen. However, when the thawing direction was controlled in such a way that it was opposite to the freezing direction, a higher amount of solutes were recovered. Solute recovery was increased when the last frozen fractions were thawed first. Solute elution to the freezing front was obtained; consequently, solutes were accumulated in the fractions farthest from the cooling wall. Solute recovery was increased when these fractions were thawed. This effect was dependent on initial coffee mass concentration.

- *The sweating phenomenon during the thawing stage increased solute recovery*

The sweating phenomenon was observed during the thawing stage in block freeze-concentration and during the fractionated thawing of the ice sheets in falling-film freeze concentration. A highly concentrated liquid was recovered in the first fractions. Solutes diffused from the concentrated liquid fractions to the droplet of water that had melted during thawing. This phenomenon is highly important in solute recovery.

- *The behaviour of block freeze-concentration was determined by response variables such as solute recovery ratio and the area under the curve of solute recovery.*

The effect of the operational variables of freeze concentration on separation efficiency was evaluated through response variables proposed in the present work. The comparative analysis of block freeze-concentration is difficult because solute recovery depends on the thawing fraction. The area under the curve of solute recovery and the solute recovery ratio can be used for this purpose. In addition, these variables were useful to determine the thawing fractions at which completion of the thawing stage was convenient. These variables are a contribution to the state of the art of the research on block freeze-concentration.

- *The implementation of microwave thawing and vacuum assisted separation increased separation efficiency in block freeze-concentration.*

Several aids can be used during the thawing and separation stages of block freeze-concentration. Microwave energy accelerated thawing around the channels of concentrated liquid trapped between ice crystals. These concentrated liquid fractions absorbed the microwave energy before the ice. On the other hand, vacuum separation increased the hydrodynamic movement of the concentrated liquid fraction between ice crystals, increasing solute recovery. The aids had a synergic effect on the increase of solute recovery. The viability of the use of these strategies depends on operational costs and equipment requirements, and thus, thawing and separation aids should continue to be studied.

- *The main physical properties of coffee extract were determined at temperatures close to freezing.*

Viscosity, density, freezing point, and coffee mass fraction of coffee extract were determined as a function of temperature and solid concentration at temperatures close to freezing. The properties were mathematically modelled within the typical intervals of solid content and temperature of freeze concentration. The information forecasted with the models is useful in freeze concentration modelling.

- *Average ice growth rate, fluid film velocity, and coffee mass fraction affected the average distribution coefficient of the ice obtained in the falling-film freeze concentrator.*

Low ice growth rate, high fluid film velocity, and low coffee mass fraction decreased solute occlusion in the ice during falling-film freeze concentration. These three variables were related according to the Chen and Chen model. Parameters to estimate the average distribution coefficient were obtained. A model to predict the concentration index, the solute yield and the average distribution coefficient in successive stages of falling-film

freeze concentration was generated. This model can be used to identify the number of stages required to obtain a specific concentration of the coffee extract.

- *Block and falling-film freeze concentration preserved the content of bioactive compounds and the antioxidant activity of the coffee extract.*

The major bioactive compounds with functional interest in coffee extract, chlorogenic acids and caffeine, were distributed proportionally in the ice and liquid fraction. A higher concentration of the bioactive compounds was obtained in the liquid fraction due to the higher total solid content in this fraction than in the ice. A significant correlation between bioactive compounds and antioxidant activity was found. Results indicated that freeze concentration preserves the functional quality of the beverage. These results show the potential of freeze concentration to concentrate extracts with biological activity in the biotechnology industry.

- *Block and falling-film freeze concentration preserved volatile compounds concentration and sensory quality of the coffee extract.*

Eight major volatile compounds were identified in the coffee extract. The same compounds were present after freeze concentration in the liquid and ice fractions. In general, the relative concentration of the volatile compounds was preserved when using both techniques thanks to the low processing temperatures. Most of the coffee extract attributes were preserved after block and falling-film freeze concentration. No differences in sensory attributes between ice and liquid fractions were found. As a general result, the sensory properties of the freeze-concentrated coffee extract were preserved. These results show the convenience of both techniques to preserve the sensory quality of the beverage.

- *Morphology of the ice crystals produced during freeze concentration affected the amount of solutes retained in the ice*

Ice crystals obtained using block and falling-film freeze concentration were characterised through image analysis. The morphology of ice cells and freeze-concentrated liquid channels was observed. The size of ice crystals decreased and solute occlusion increased when the freezing rate increased. The relationship between ice morphology, the operational variables of freeze concentration, and solute retention is an interesting parameter of study aiming to increase separation efficiency. The image analysis technique is a tool that can be used in ice crystal characterisation during freeze concentration.

- *Falling-film freeze concentration was effective to increase coffee extract concentration.*

The concentration of the coffee extract was increased 6.2 times when using the falling-film freeze concentration technique. This is a fast and flexible technique to obtain extract

concentrations comparable to industrial standards of the suspension technique. Nevertheless, part of the solutes remains trapped in the ice sheets and need to be subsequently recovered.

- *Fractionated thawing was useful to recover the solutes retained in the ice produced in a falling-film freeze concentrator.*

Sixty-four percent of the solutes retained in the ice produced in a falling-film freeze concentration were recovered through partial thawing. The sweating phenomenon contributed to recovering a highly concentrated liquid in the first thawing fractions. This technique is useful to increase solute yield in falling-film freeze concentration.

- *Block freeze-concentration was effective to produce a pure ice fraction with low solid content in the final effluent.*

The block technique as a final stage of freeze concentration efficiency produced a final effluent with 0.3% solids. The solid content of this effluent is consistent with the industrial requirements. Pure ice blocks were obtained thanks to the low freezing rate. In addition, aids can be used in the thawing and separation stages to increase separation efficiency in block freeze-concentration.

- *An operative strategy to integrate falling-film freeze concentration, fractionated thawing, and block freeze-concentration fulfilled the industrial requirements on the final concentration of coffee extract and effluent.*

A process to concentrate coffee extract that takes advantage of each studied technique was proposed. A final concentration of the extract and the effluent consistent with industrial requirements can be obtained. Concentration efficiency was increased to 99.2%. This process is an alternative to the industrial freeze concentration systems based on suspension technology, and it is an advance in the state of the art on the development of new freeze concentration techniques.

10. CONCLUSIONS AND SUGGESTIONS

The purpose of the current study was to determine the effect of the operational variables of block and falling-film freeze concentration on separation efficiency and quality of coffee extract. The following conclusions have been obtained.

This study has shown that the concentration of coffee extract can be incremented with high freezing temperatures and a thawing direction opposite to the freezing direction in block freeze-concentration. On the other hand, low solute occlusion in the ice and high concentration efficiency can be obtained at low solid concentrations, low freezing rates, and high falling fluid velocities for falling-film freeze concentration. The relevance of extract solute concentration is clearly supported by the current findings. The study of the operational variables of freeze concentration makes several contributions to the current literature.

The equipment designed and built to study block and falling-film freeze concentration showed to be efficient in controlling the main operational variables. This equipment may be used to systematically study freeze concentration technology.

The behaviour of the average distribution coefficient in the ice produced in falling-film freeze concentration can be predicted through the Chen and Chen model. The number of stages needed to reach a specific concentration of coffee extract can be predicted through the mathematical model proposed in the present study.

The results of this investigation show that solute yield in block freeze-concentration can be mathematically described by the monomolecular model. In addition, the area under the curve of solute yield can be used to compare the behaviour of block freeze-concentration under different operational conditions.

This study has demonstrated, for the first time, that block and falling-film freeze concentration techniques are effective in the preservation of the functional and sensory quality of coffee extract. The major bioactive and volatile compounds are preserved in the freeze-concentrated liquid using both techniques. Consequently, antioxidant activity and most of the attributes of sensory quality are preserved with block and falling-film freeze concentration.

The integration of block freeze-concentration, falling-film freeze concentration, and fractionated thawing is an alternative to the current freeze concentration systems. Falling-film freeze concentration is effective to increase the solute concentration of the extract

from 5% to 32%. With fractionated thawing, up to 64% of the solutes retained in the ice sheet can be recovered. Block freeze-concentration has the ability to produce a final pure effluent with 0.3% solids.

The process proposed to freeze-concentrate coffee extract is a technically viable alternative to obtain an extract and an effluent with a solute concentration according to industrial requirements. The process is an alternative to the industrial freeze concentration systems based on suspension technology, with the advantage of the simplicity of the falling film and block freeze-concentration equipment.

Finally, the study has made some progress towards enhancing our understanding of freeze concentration and contributing to the state of the art with five research papers published in indexed journals and five participations in scientific events. Returning to the research question, it is now possible to state that freeze concentration is an applicable technology to concentrate coffee extract preserving the quality of the beverage. This technology is an alternative to extract purification in the food and biological industries.

This research has given rise to several suggestions in need of further investigation:

Further research could explore the energetic optimization of the proposed process to establish the viability of its industrial implementation. The technical viability was demonstrated in terms of concentration requirements, but the economic viability of the energetic, initial, and maintenance costs must be established in contrast to other concentration systems.

Future work is needed to design and scale-up equipment required to implement the integrated process of block and falling-film freeze concentration. This equipment needs to keep the simplicity and flexibility of the techniques in order to ensure the comparative advantages of other concentration techniques.

Further research on the role of ice crystals morphology on solute retention would be interesting. More information on the influence of operational conditions on crystals morphology would help increase the degree of separation achieved.

Another possible area of future research is to investigate mathematical models to describe phenomena such as occlusion and sweating in the ice as a function of the morphometric parameters of ice crystals.

Finally, it is suggested to research the application of freeze concentration to recover components from extracts of biological materials in future studies in order to take advantage of this technology.

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12. APPENDIXES

APPENDIX A: Published papers

List of publications

1. Moreno, F.L., Raventós, M., Hernández, E., & Ruiz, Y. (2014). Block freeze-concentration of coffee extract: effect of freezing and thawing stages on solute recovery and bioactive compounds. Journal of Food Engineering, 120, 158-166

2. Moreno, F.L., Robles, C. M., Sarmiento, Z., Ruiz, Y., & Pardo, J. M. (2013). Effect of separation and thawing mode on block freeze-concentration of coffee brews. Food and Bioproducts Processing, 91(4), 396-402

3. Moreno, F.L., Hernández, E., Raventós, M., Robles, C., & Ruiz, Y. (2014). A process to concentrate coffee extract by the integration of falling film and block freeze-concentration. Journal of Food Engineering, 128, 88-95.

4. Moreno, F.L., Raventós, M., Hernández, E., Ruiz, Y. (2014). Behaviour of falling-film freeze concentration of coffee extract. Journal of Food Engineering 141, 20-26.

5. Moreno F.L., Raventós M., Hernández E., Santamaría N., Acosta J., Pirachican O., Torres L. and Ruiz Y. (2014) Rheological behaviour, freezing curve and density of coffee solutions at temperatures close to freezing. International Journal of Food Properties. DOI: 10.1080/10942912.2013.833221

List of works presented in scientific congresses

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3. Moreno, F. L., Raventós, M., Hernández E., Gulfo R., Ruiz, Y. (2014) Technical, energetic and economic comparative of three concentration systems in a fruit juice industry: Case of study. In: Congreso Iberoamericano de Ingeniería de Alimentos CIBIA 9. Valencia, España.

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Block freeze-concentration of coffee extract: Effect of freezing and thawing stages on solute recovery and bioactive compounds

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ABSTRACT

Coffee extract was freeze-concentrated using the total block technique. The effects of four parameters were evaluated: the initial coffee mass fraction (5 and 15% w/w), the cooling temperature (−10 and −20 °C), the heating temperature (20 and 40 °C) and the freezing direction (parallel and counter-flow to the thawing direction). The solid concentration was measured during the thawing stage to quantify the solute recovery and the concentration index for one stage of freeze concentration. The coffee mass fraction, the freezing direction and the cooling temperature significantly influenced the solute recovery. A concentration index between 1 and 2.3 was obtained in one cycle. The effect of block freeze concentration on the bioactive compound concentration and the antioxidant activity was measured. The coffee bioactive compounds were distributed in proportion to the total solid content in the ice and liquid. Therefore, block freeze concentration is an effective technique to preserve functional properties of coffee extracts.

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1. Introduction

Coffee is the most traded food in the world, and its production has great economic and social importance worldwide (Esquivel and Jiménez, 2012; Vignoli et al., 2011). For the consumer, the value of coffee is provided by its sensory and functional properties; for this reason, technologies that promote quality preservation are highly valued in coffee processing. In the production of freeze-dried coffee, freeze concentration (FC) technology is used to remove water from coffee extracts to increase the solid content and reduce the time and cost of the freeze-drying process. At the same time, the sensory properties of the product are preserved using low temperatures (Boss et al., 2004; Joët et al., 2010; Sánchez et al., 2009).

Water removal in FC is achieved by cooling the solution until the ice crystals form and separate (Miyawaki et al., 2005). Three techniques are used according to the ice crystal growth: suspension FC, film FC (progressive or falling film FC) and block FC (total or partial) (Aider and de Halleux, 2009; Sánchez et al., 2009). Suspension FC is a unique technique implemented at the industrial level. Different techniques, such as falling film FC (Chen et al., 1998; Sánchez et al., 2011), progressive FC (Miyawaki et al., 2005) and block FC (Aider and Ounis, 2012; Nakagawa et al., 2010a), are being developed to reduce operational costs.

In the block FC method, also known as freeze–thaw concentration, the solution to be concentrated is completely frozen and then partially thawed to recover a fraction of liquid with a higher concentration (Aider and de Halleux, 2009; Nakagawa et al., 2010b). Block FC consists of three stages: freezing, thawing and separation of the concentrated liquid fraction (Moreno et al., 2013). These stages define the separation efficiency (Nakagawa et al., 2009). Additionally, the process can be repeated in successive cycles to increase the concentration index (Aider and Ounis, 2012).

The technical viability of the block FC method has been proposed recently by several researchers (Gao et al., 2009; Nakagawa et al., 2010a; Aider and Ounis, 2012; Boaventura et al., 2012; Miyawaki et al., 2012; Petzold et al., 2013). During the freezing stage, heat and mass transfer phenomena can modify the solute occlusion, which should be as low as possible. Chen et al. (2001) reported that the solute elution in the freezing front in FC depends on the molecular size of the compounds. Certain authors have reported that the solute separation is controlled by the thawing stage (Nakagawa et al., 2010b). For coffee solutions, Moreno et al. (2013) studied the use of aids in the separation stage. These authors reported the influence of the FC protocol and solution type on solute recovery and the concentration index; for this reason, there is no agreement on the significance of the process variables. The effects of the process variables of block FC on the separation efficiency of coffee extracts have not been reported.

Coffee can be considered to be a functional beverage due to its radical scavenging capabilities (Cheong et al., 2013; Esquivel and

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Nomenclature

CI	concentration index	$m_{s\,liq}$	solute mass in the liquid fraction
CI_{cum}	cumulative concentration index	m_0	initial mass
C_{FCL}	concentration of bioactive compounds in the freeze-concentrated liquid	m_{liq}	collected liquid mass
		T_C	cooling temperature
C_{RI}	concentration of bioactive compounds in the residual ice	T_H	heating temperature
		$X_{s\,0}$	coffee mass fraction in the initial solution
f	thawing fraction	X_S	coffee mass fraction
F_D	freezing direction	$X_{s\,liq}$	coffee mass fraction in the freeze-concentrated liquid fraction
IL	ice loss percentage		
$m_{s\,0}$	initial solute mass	Y	solute yield

Jiménez, 2012). Several studies have reported the health benefits of coffee consumption related to the components with antioxidant activity, such as the group of chlorogenic acids and caffeine. Chlorogenic acid (3-caffeoylquinic acid), cryptochlorogenic acid (4-caffeoylquinic acid), neoclorogenic acid (5-caffeoylquinic acid) and caffeine are the major bioactive compounds present in coffee (Ferruzzi, 2010; Fujioka and Shibamoto, 2008; Sopelana et al., 2013; Vignoli et al., 2011). The block FC method has been shown to retain nutritional and functional properties of the product using low processing temperatures (Belén et al., 2013; Boaventura et al., 2012); however, this effect has not been tested for coffee extracts.

The aim of the present study was to evaluate the effect of the initial coffee mass fraction, the cooling temperature, the heating temperature and the freezing direction on the solute yield and concentration index of block freeze-concentrated coffee extracts. Additionally, the impact of the technique on bioactive compound concentration and the antioxidant activity of the coffee extract was tested.

2. Materials and methods

2.1. Materials

Coffee solutions were prepared from freeze-dried soluble coffee supplied by the company Buencafé Liofilizado de Colombia (Colombian Coffee Growers Federation, Colombia) for the FC tests. The coffee was added to distilled water at 35 °C and mixed for 20 min. The samples were stored at 4 °C for 12 h. The solid concentration is expressed as the coffee mass fraction (X_S), which is defined as the mass of coffee solids per unit of coffee solution mass. The relationship between Brix degrees and X_S is represented by the equation $X_S = 0.0087$ °Brix ($R^2 = 0.991$). This expression was obtained by preparing coffee solutions at 10, 20, 30, 40 and 50 °Brix and by measuring coffee mass fraction using the weight loss technique in the oven at 103 °C for 4 h according to technical standard NTC4602 (Icontec, 2009). The measurements were performed in triplicate. The coffee mass fraction of the solutions was ascertained immediately before the FC tests by refractometry (Atago Pal 100, Japan). A liquid coffee extract was used for the measurement of bioactive compounds. This extract belonged to the same batch of soluble coffee and was also provided by Buencafé Liofilizado de Colombia.

2.2. Methods

2.2.1. Freeze concentration protocol

The effects of the initial coffee mass fraction (X_S), cooling temperature (T_C), heating temperature (T_H) and the freezing direction (F_D) were studied. A full factorial design with four factors and

two levels was used for a total number of 16 tests (Table 1). The coffee solutions were subjected to one cycle of freezing, thawing and separation to study the effect of process variables on solute yield after one cycle of FC.

The block FC device is shown in Fig. 1. In total, 160 g of the coffee sample was placed into a cylindrical container (1) measuring 52.5 mm in diameter and 85 mm in height. The container is a double jacket device for the flux of cooling and heating fluids. The internal jacket is 19 mm in diameter (2). The cooling/heating fluid was a mixture of ethylene glycol and water (53% w/w) coming from two circulated baths (4 and 5) (Polystat, Cole Parmer, USA). The baths were temperature controlled (6 and 7) at an interval from −35 °C to 150 °C ± 0.01 °C. The baths pumped the heat exchange fluid to the jackets through a system of ducts and valves (7).

During the tests, the heat exchange fluid temperature was settled in one bath. After the fluid reached the temperature, it was circulated to the jackets to freeze the solution inside. The heat transfer was in the radial direction from the internal wall (for freezing parallel to thawing) or from the external wall (for freezing in counter-flow to thawing). Meanwhile, the heating temperature of the second bath was settled. When the sample was frozen and the temperature was approximately constant, the thawing stage was begun by pumping the heating fluid through the external jacket. The exit valve (9) was opened and the liquid fraction was separated in a collector vessel (10) on a scale (11) (Ohaus PA3102, USA) with a capacity of 3100 g and a precision of 0.01 g for weight measurement. During the thawing stage, the temperature of the internal jacket was maintained one Celsius degree below the

Table 1
Experimental design.

Test	X_S	T_C	T_H	F_D
1	0.05	−10	20	1
2	0.05	−10	20	−1
3	0.05	−10	40	1
4	0.05	−10	40	−1
5	0.05	−20	20	1
6	0.05	−20	20	−1
7	0.05	−20	40	1
8	0.05	−20	40	−1
9	0.15	−10	20	1
10	0.15	−10	20	−1
11	0.15	−10	40	1
12	0.15	−10	40	−1
13	0.15	−20	20	1
14	0.15	−20	20	−1
15	0.15	−20	40	1
16	0.15	−20	40	−1

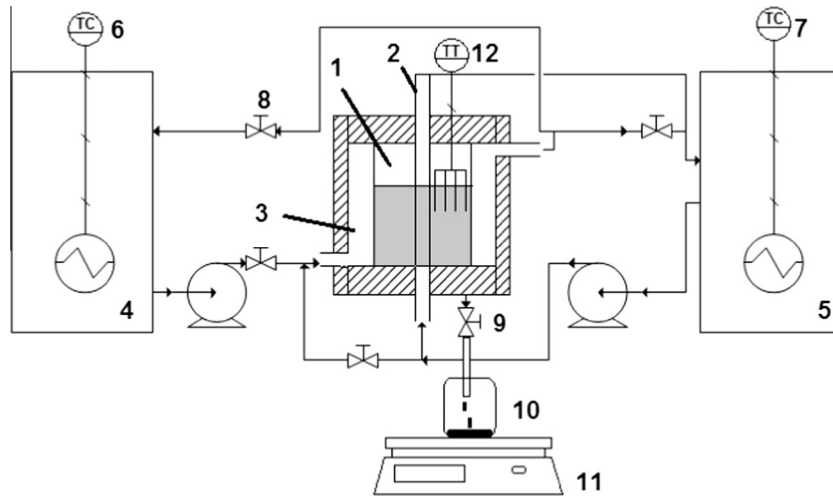F_D + 1: counter-flow to thawing; F_D-1: parallel to thawing.

Fig. 1. Experimental set up for block freeze concentration.

freezing point of the coffee solution to avoid thawing the internal side and to preserve unidirectional thawing. Ten liquid fractions of the same mass were collected. Lastly, the coffee mass fraction (X_S) was measured by refractometry (Atago Pal 100, Japan).

2.2.2. Temperature profile

The FC device seen in Fig. 1 has four temperature sensors (12) inside of the container to measure the temperature profile during one test. These sensors were used during the temperature measuring tests but not during the FC tests. The sensors PT100-IP65 (Testo, Germany) had a 2 mm diameter and a measuring interval of −50 to 300 °C ± 0.01 °C and were placed equidistant from the centre of the container (sensor 1) and the external wall (sensor 4). The sensors were connected to a datalogger 176 T2 (Testo, Germany) connected to a PC for data collection.

2.2.3. Data analysis

2.2.3.1. Thawing fraction (f).
A thawing fraction (f) was used to follow the development of the process. The f was measured as the ratio between the thawed mass and the mass of the original solution, defined by the following equation (Miyawaki et al., 2012; Nakagawa et al., 2010a):

$$f = m_{liq}/m_0 \tag{1}$$

where f is the thawing fraction, m_{liq} the collected liquid mass, m_0 is the initial mass.

2.2.3.2. Solute yield (Y).
Solute yield was calculated for analysing the solute recovery. Y was defined as the relationship between the mass of solute present in the separated liquid and the mass of solute present initially in the original solution, as seen in the following equation (Moreno et al., 2013; Nakagawa et al., 2010a):

$$Y = m_{sliq}/m_{s0} \tag{2}$$

where Y is the solute yield, $m_{s\,liq}$ the solute mass in the liquid fraction, m_{s0} is the initial solute mass.

2.2.3.3. Concentration index.
The concentration index (CI) was used to express the concentration of solutes reached after the FC process. CI was defined as the relationship between the solid concentration in the liquid fraction and the solid concentration in the initial solution. CI is also known as relative concentration (Nakagawa et al., 2009):

$$CI = X_{sliq}/X_{s0} \tag{3}$$

where CI is the concentration index, $X_{s\,liq}$ the coffee mass fraction in the freeze-concentrated liquid fraction, X_{s0} is the coffee mass fraction in the initial solution.

When the CI is calculated using the mixture of the thawed fractions at a given time, Eq. (3) can be expressed as the cumulative index (CI_{cum}). Cumulative CI is the relationship between X_S in the accumulated liquid fraction and X_S in the initial solution.

Eq. (4) was obtained by combining Eqs. (2) and (3):

$$Y = CI_{cum}^* f \tag{4}$$

2.2.3.4. Area under curve Y vs. f.
During the thawing stage of FC, the graph Y against f represents the percentage of coffee solids that was recovered from the initial solution for each thawed liquid fraction. The behaviour of a freeze concentration test can be represented by Fig. 2, as proposed by Nakagawa et al. (2010a).

The diagonal line represents the case in which the thawed liquid fraction had the same concentration as the initial solution; therefore, there was no FC. A higher curve from the diagonal indicates the amount of recovered solute for a given f and the efficiency of the separation were greater. An ideal situation would be a curve very close to the y-axis in which all of the solute was recovered at the beginning of the thawing stage. Therefore, the area under the curve Y vs. f can be used as a single parameter to compare the efficiency of the separation process and to examine the effect of the studied factors.
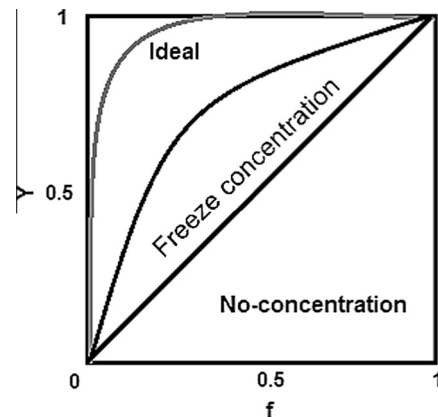

Fig. 2. Solute yield during freeze concentration tests. Adapted from Nakagawa et al. (2009).

The area under the curve represents the integral of the function Y vs. f. The area value is bounded between 0 when the solutes are not recovered and by 1 when all the solutes are recovered instantaneously and there is no solute occlusion. The diagonal line of no-concentration has an area of 0.5. An area value closer to one indicates a better result of the FC process. The area under the curve can be understood as the sum of the solute yield achieved in a thawing fraction during the FC. The area under curve Y vs. f was used as an identifying parameter of the effect of each studied variable.

2.2.3.5. Freezing front growth rate. The average freezing front growth rate was calculated by measuring the distance from the cooling surface to the front of the ice during the freezing stage with a calliper. The average of the ratios of distance to time was used as the rate. The rate was expressed in micrometres per second.

2.2.4. Bioactive compound measurement

The major bioactive compounds of coffee extract, chlorogenic acid (CGA), cryptochlorogenic acid (c-CGA) and caffeine, were measured for the initial solution, the freeze-concentrated liquid recovered at a f value of 50% and for the residual ice at the same f as a comparative parameter. The measurements were performed for tests 1 and 16 (Table 1), which correspond to the extreme values of X_S, T_C, T_H and total process time. The measurements were performed in triplicate.

The concentration of bioactive compounds was determined by reversed-phase high performance liquid chromatography (RP-HPLC) as described by Fujioka and Shibamoto (2008) and Owen et al. (2003) with modifications. The RP-HPLC apparatus, LaChrom (Merck-Hitachi, Germany–Japan), was equipped with a quaternary pump, degasification system and a diode array detector (UV/VIS). The separation was achieved in a Gemini column C-18 (Phenomenex, USA) measuring 250 mm * 4.6 mm and 5 µm at 25 °C. The mobile phase used was acetic acid 2% (A) and methanol (B). The gradient was adjusted as follows: 0–10 min, A/B 96/4; 65 min, 85/15; 75 min, 75/25; and 85 min, 25/75 at a flow rate of 1 mL min^{-1}. CGA and c-GCA were detected at 325 nm, and caffeine was detected at 276 nm. The injection volume was 5 µL. The concentrations of bioactive compounds were calculated using a regression equation of their concentrations and the peak area obtained from pattern grade HPLC (Sigma–Aldrich, USA).

The loss of bioactive compounds in the residual ice due to FC was calculated using the following equation (Ramos et al., 2005):

$$IL = C_{RI}/(C_{RI} + C_{FCL}) * 100 \tag{5}$$

where IL is the ice loss, C_{RI} the concentration of bioactive compounds in the residual ice, C_{FCL} is the concentration of bioactive compounds in the freeze-concentrated liquid.

2.2.5. Antioxidant activity

The antioxidant activity of coffee samples was determined by the ABTS (2,20-azinobis (3-ethylbenzothiazoline-6-sulphonic acid assay) and DPPH (2,2-diphenyl-1-picrylhydrazyl assay) methods.

2.2.6. ABTS methodology

Antioxidant activity was estimated in terms of radical scavenging activity using the procedure described by Vignoli et al. (2011) with modifications. Briefly, ABTS radical cations (ABTS$^+$) were produced by reacting 3.5 mM ABTS stock solution with 12.5 mM potassium persulphate prepared in a 10% phosphate buffer solution at a pH of 7.4 in distilled water. The solution was stored in the dark at room temperature for 12 h. Before the analysis, the solution was settled at 0.8 ± 0.2 nm. Lastly, 50 µL of the coffee sample was added to 200 µL of ABTS + solution and the absorbance was read after 30 min of incubation in complete darkness using an

iMark Microplate Reader spectrophotometer (Bio-Rad, USA). The same procedure was conducted for calibration with ethanol solutions containing known concentrations of Trolox between 3 and 15 µL mL^{-1}. The results were expressed in g of Trolox per 100 g of coffee (dry matter). The experiments were performed in triplicate.

2.2.7. DPPH methodology

The DPPH technique was performed according to Vignoli et al. (2011). A DPPH solution was prepared at 0.6 mM of methanol. The absorbance was settled to 1.1 nm before the tests. For the analysis, 50 µL of DPPH solution was added to 75 µL of each coffee sample. The absorbance was measured at 515 nm after 30 min of incubation at room temperature in complete darkness. The calibration was performed with Trolox at concentrations between 3 and 15 µL mL^{-1}. The antioxidant activity was expressed as mg of Trolox/mL. The experiments were performed in triplicate using methanol as a blank.

2.3. Statistical analysis

All the tests were performed in triplicate. The area under the curve of Y vs. f was obtained by a spline regression procedure. A response surface regression procedure was used to determine the effect of each studied factor listed in Table 1 on the area under the curve with a confidence interval of 95%. One-way analysis of variance (ANOVA) was applied to the results of the area under the curve followed by a LSD test with a level of significance of 95%. For the bioactive compound measurement, the mean values were calculated and a correlation analysis was performed by comparing the Pearson coefficients. All statistical analysis were performed using the SAS 9.2 software package.

3. Results and discussion

3.1. Temperature profiles

The temperature profiles during FC tests for tests 1 and 8 described in Table 1 are shown in Fig. 3. These tests corresponded to the lowest and highest overall process time; therefore, the other tests were within this time interval. Temperature sensor 1 was located beside the internal wall of the container and sensor 4 was located in the external wall. In test 1, the freezing was achieved from the centre and the thawing from the external wall. For this reason, the temperature dropped first in sensor 1 and last in sensor 4, as can be seen in Fig. 3a; during the thawing stage, the order was reversed.

Point "a" shows the nucleation phenomenon that caused a temperature increase due to the latent heat of the phase change. The latent heat released from the portion of liquid closest to the centre (line 1) caused a temperature increasing of the external portion before it was frozen (line 4). For this reason, a temperature increasing in the interval 0 °C to 5 °C was observed. After that, the whole solution was frozen and the temperature tended to be constant. A similar behaviour was reported by Nakagawa et al. (2010b).

When the temperature was stable, the thawing phase began (point b). A change in the temperature was observed in the opposite order than it was in the freezing stage. For test 1, the thawing time was 180 min and the average freezing growth rate was 1.84 µm s^{-1}. Alternatively, in test 8 (Fig. 3b), the freezing and the thawing were both achieved from the external wall in parallel. The first portion that was frozen and thawed corresponded to sensor 4, which was located beside the external wall. A freezing time of 45 min and an average ice growth rate of 7.17 µm s^{-1} were obtained.
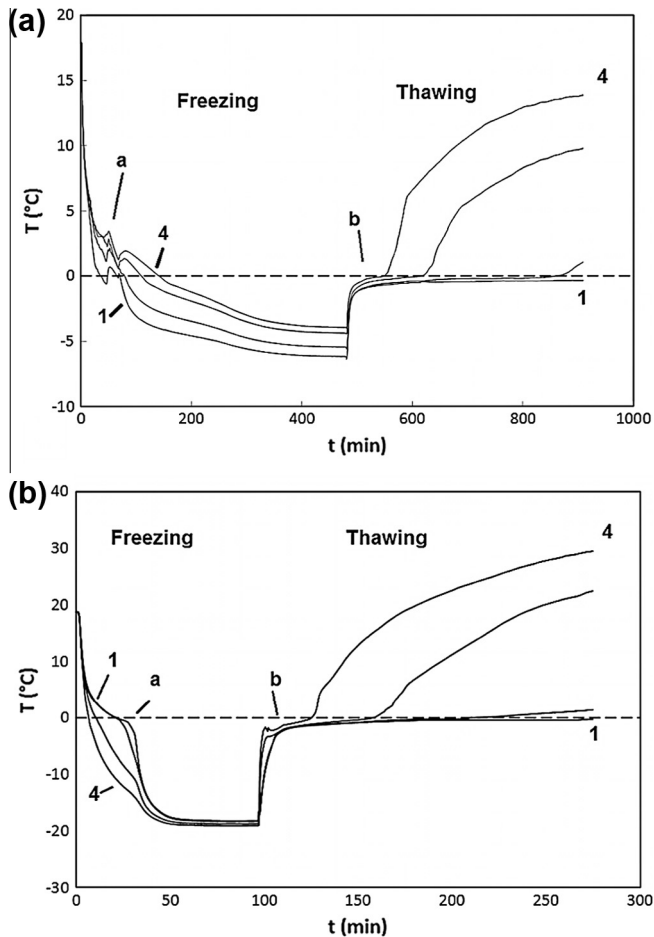
Fig. 3. Temperature profile during freezing and thawing stages. (a) Test 1. $T_C = -10\,°C$, $T_H = 20\,°C$; (b) Test 8 $T_C = -20\,°C$, $T_H = 40\,°C$. 1: Temperature sensor 1 (interior) and 4: temperature sensor 4 (exterior).

3.2. Freeze-concentration tests

The results of the block FC tests are shown in Table 2 in descending order of the area under the curve of Y vs. f. The greatest area was obtained for test 1, which corresponded to the lowest coffee mass fraction, the greatest cooling temperature, the lowest heating temperature and freezing direction in counter-flow to

the thawing. The treatments showed significant differences at $p < 0.05$. The LSD test indicated differences among treatments for X_S 0.05. Differences in F_D and T_C can be observed. On the contrary, the tests with the highest X_S did not show significant difference because the solid concentration is predominant over the effect of the other factors.

The values for Y and f when the CI was equal to one are shown in Table 2. At this value of f, solute yields between 67% and 83% were obtained. At this point, the cumulative CI values were between 1.10 and 1.67. A CI of 1.8 for one cycle of FC was reported by Aider and Ounis (2012). For falling film FC, a CI between 2 and 3 was reported by Sánchez et al. (2011) and Belén et al. (2012). Miyawaki et al. (2005) reported a CI between 2 and 3 for progressive FC. However, all of these authors reported that the results depended on the fluid being concentrated, the type and size of the equipment and the process time.

The maximum CI obtained was 2.38 for test 8. The maximum CI for each test was reached in the first thawing fractions and these values descended during the thawing stage. The concentrated fraction percolates through the frozen matrix (Petzold et al., 2013) and its concentration descended until values close to zero during the thawing stage. It therefore was possible to know the f value at which the CI reached a value of 1. This situation corresponded to the moment at which it becomes convenient to separate the thawing fraction to avoid a cumulative concentration decrease. The f values are shown in Table 2 (f at CI = 1) and varied from 0.5 to 0.8. The f value at which the thawing stage has to be stopped depends on the process conditions.

Freezing front growth rates from 1.8 to 7.5 μm s^{-1} were obtained. The values depended on the cooling temperature, the heat transfer area and the initial coffee mass fraction. The area under the curve tended to be higher for lower freezing rates. The result is more evident at low solid concentrations. For high solid concentrations the effect of freezing rate was not observed because of the effect of solid interactions. No concentration was obtained for a freezing rate of 7.5 μm s^{-1}. At this rate, the ice occluded solutes during the freezing stage. A critical rate value was also obtained by Nakagawa et al. (2010a). The authors reported that for velocities higher than 8 μm s^{-1}, the freezing was too fast to expect a considerable separation of the concentrated solution phase.

3.3. Effect of each operational factor on solute recovery

A regression analysis was performed to determine the statistical significance of the factors of the study on the area under the curve of Y vs. f. The result is shown in Table 3. The analysis showed a

Table 2
Freeze concentration tests in descending order of area under the curve.

TEST	X_S	T_C	T_H	F_D	Area under curve	f at CI = 1	Y at CI = 1	Cumulative CI at CI = 1	CI max	Freezing front growth (μ s^{-1})
1	0.05	−10	20	1	0.802[a]	0.5	0.83	1.67	2.22	1.84
3	0.05	−10	40	1	0.778[a,b]	0.5	0.78	1.56	1.49	1.83
5	0.05	−20	20	1	0.777[b,c]	0.5	0.81	1.62	1.89	2.87
2	0.05	−10	20	−1	0.762[b,c,d]	0.5	0.82	1.64	2.26	3.71
4	0.05	−10	40	−1	0.746[e,c,d]	0.6	0.91	1.51	2.23	3.71
7	0.05	−20	40	1	0.741[e,d]	0.5	0.73	1.47	1.87	2.87
6	0.05	−20	20	−1	0.736[e,d]	0.6	0.88	1.47	1.79	7.17
8	0.05	−20	40	−1	0.735[e]	0.6	0.90	1.50	2.38	7.17
9	0.15	−10	20	1	0.657[f]	0.7	0.81	1.16	1.25	1.19
10	0.15	−10	20	−1	0.653[f]	0.7	0.81	1.16	1.29	5.10
11	0.15	−10	40	1	0.652[f]	0.7	0.78	1.12	1.17	1.19
14	0.15	−20	20	−1	0.647[f]	0.7	0.80	1.14	1.32	7.53
16	0.15	−20	40	−1	0.646[f]	0.8	0.89	1.11	1.23	7.53
13	0.15	−20	20	1	0.644[f]	0.6	0.67	1.12	1.22	2.58
15	0.15	−20	40	1	0.640[f]	0.7	0.77	1.10	1.18	2.58
12	0.15	−10	40	−1	0.635[f]	0.7	0.78	1.11	1.16	5.10

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

Table 3
Significance analysis of surface response for freeze concentration factors.

Parameter	Estimator	Pr > |t|
Intercept	0.917	<0.001
X_S	−1.617	0.0002[*]
T_C	0.004	0.039[*]
T_H	−0.001	0.077
F_D	0.037	0.010[*]
$T_C \cdot X_S$	−0.020	0.049[*]
$T_H \cdot X_S$	−0.006	0.184
$T_H \cdot T_C$	−0.001	0.545
$F_D \cdot X_S$	−0.133	0.019[*]
$F_D \cdot T_C$	0.001	0.141
$F_D \cdot T_H$	0.001	0.358

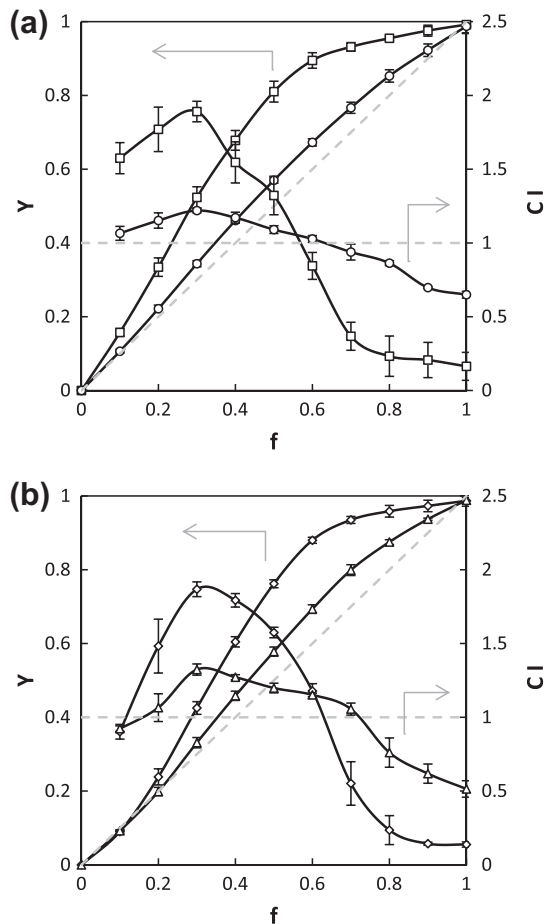[*] Statistically significant at $\alpha < 0.05$.

Fig. 4. Effect of coffee mass fraction on solute yield and the concentration index. (a) Test 5, X_S = 5% (□); Test 13, X_S = 15% (○); (b) Test 6, X_S = 5% (◇); Test 14, X_S = 15% (△).

good fitting of the experimental data (R^2 = 0.9874 and RMSE = 0.0123). The parameters with a Pr < 0.05 significantly affected the area under the curve. The main effects X_S, T_C and F_D and the interaction terms $T_C \cdot X_S$ and $F_D \cdot X_S$ significantly affected the freeze concentration.

The coffee mass fraction had the greatest influence with a negative correlation; in other words, the grade of concentration achieved with the block FC decreased with the increase in X_S. The second main effect was the freezing direction followed by the cooling temperature. The interactions between X_S and the other two mean factors were also significant, indicating the influence of these variables. Alternatively, the T_H did not significantly
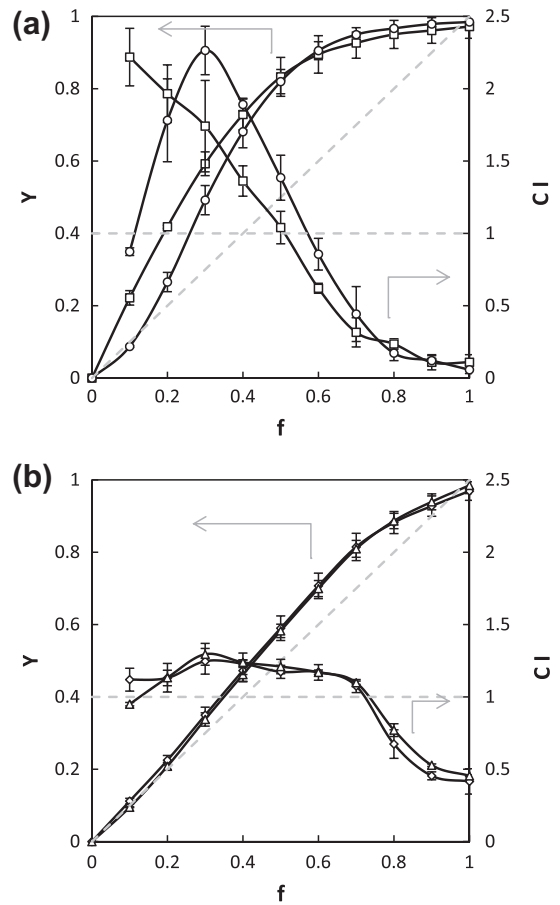

Fig. 5. Effect of freezing direction on solute yield and the concentration index. (a) Test 1, F_D = +1 (□); Test 2, F_D = −1 (○); (b) Test 9, F_D = +1 (◇); Test 10, F_D = −1 (△).

affect the studied intervals. Nakagawa et al. (2010b) and Moreno et al. (2013) reported that the T_H influenced the solute yield when lower thawing temperatures were compared. This result depended on the FC protocol and the level of T_H.

3.3.1. Effect of initial coffee mass fraction (X_S)

The curves Y against f and CI against f for tests 5 and 13 are shown in Fig. 4. These test had different values of X_S, but the other factors were constant. A higher solute recovery was obtained for X_S = 0.05. This result was the same for all of the tests. Comparing the curve with the diagonal line of no-concentration, the area under the curve was higher for the lowest X_S.

This result can be explained by different factors. First, during the freezing stage, the ice grows by the diffusion of water molecules to the ice surface and the counter-diffusion of solutes to the liquid phase (Petzold and Aguilera, 2009). The diffusion rate of solutes decreases when the solid concentration increases due to the interactions between molecules; consequently, the achieved concentration decreases. The same result was reported by Chen et al. (2001) and Hindmarsh et al., 2005. Second, the coffee solution viscosity increases with X_S; this factor can cause the separation of the liquid phase during the thawing stage to be difficult (Raventós et al., 2007). Additionally, the ice tends to grow in dendritic form for high solid concentrations, occluding higher amounts of solutes (Yee et al., 2003). Lastly, the volume of water that can be frozen and separated is lower for higher concentrations (Aider and de Halleux, 2008a). The combination of these four effects explains why X_S was the factor with the greatest effect on Y and CI.

In the CI vs. f curve, the value at which the CI crossed the horizontal line of CI = 1 is shown in Figs. 4–7. This intersection
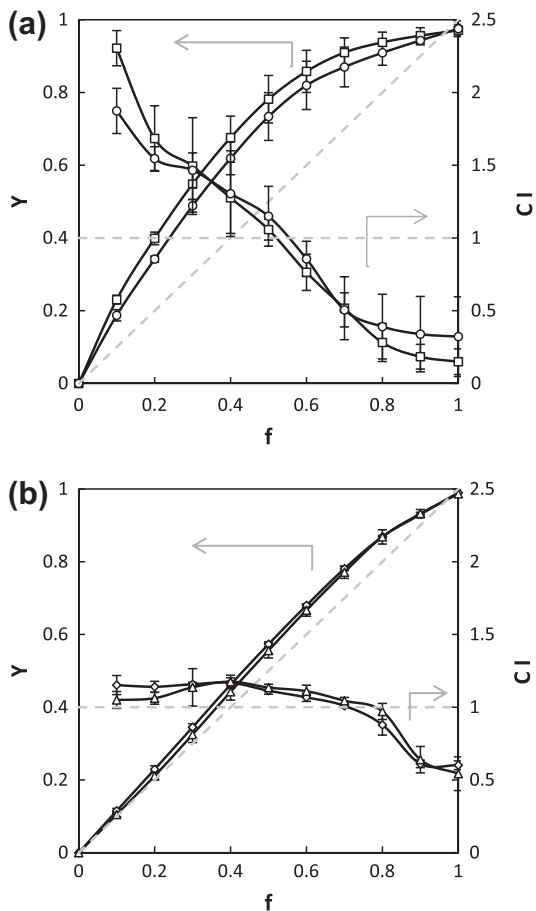
Fig. 6. Effect of cooling temperature on solute yield and the concentration index. (a) Test 3, T_C = −10 °C (□); Test 7, T_C = −20 °C (○); (b) Test 11, T_C = −10 °C (◇); Test 15, T_C = −20 °C (△).

Fig. 7. Effect of heating temperature on solute yield and the concentration index. (a) Test 2, T_H = 20 °C (□); Test 4, T_H = 40 °C (○); (b) Test 10, T_H = 20 °C (◇); Test 12, T_H = 40 °C (△).

corresponded to the moment at which the thawing stage has to be completed to avoid a sample dilution and to recover as much solute as possible. For test 1, at f = 0.5, 83% of the coffee solids had been recovered and the cumulative CI was 1.67. These results indicate a good separation efficiency.

3.3.2. Effect of freezing direction (F_D)

Tests 1 and 2 are shown in Fig. 5a. Tests 9 and 10 are shown in Fig. 5b. Table 2 shows the differences in freezing direction. A better FC was obtained for the tests in which the freezing and thawing directions were opposite.

For the F_D during counter-flow, the CI began in maximum values and descended during the thawing. This result indicates that the solutes moved during the freezing stage to the farthest zone from the container centre, which was the last area frozen and the first area thawed. Additionally, the lower heat transfer area in the internal wall compared to the external wall facilitated the solute elution due to the slower ice front growth. Alternatively, the initial CI was lower than the CI for the tests when the F_D was in parallel. The solutes moved from the external region of the container, as evidenced by the smaller X_S compared to the initial X_S. This finding can be explained by the elution phenomenon, in which a movement of the solutes was produced by counter-diffusion during ice crystals formation that expelled the solutes to the liquid fraction. This result was also observed by Nakagawa et al. (2009). Moreover, Chen et al. (2001) reported that elution depends on the molecular size of the solutes. The effect is smaller with increasing initial solute contents.
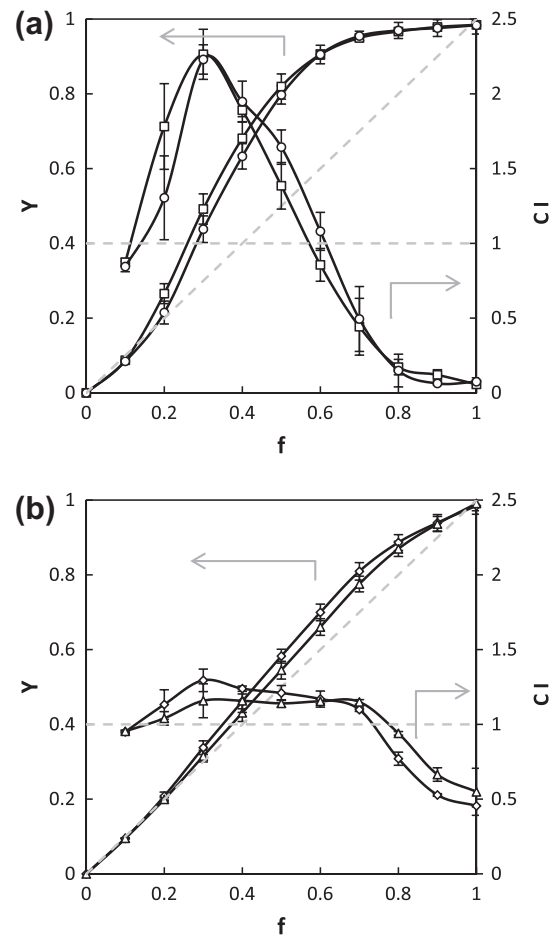
For the tests when the F_D was in parallel, the CI was lower than counter-flow direction at the beginning, and then it increased at f values from 0.2 to 0.4. This result could have occurred because the solutes diffused from the concentrated liquid fractions to the droplet of water that had melted during thawing. This phenomenon is known as sweating. This result was also reported by Nakagawa et al. (2009). Likewise, the concentrated portions were the first fractions to be thawed and separated due to the difference in densities, as reported by Yee et al. (2003). The results show the freezing direction as a variable of interest in the study of block FC to promote the intensification of solute recovery.

3.3.3. Effect of cooling temperature (T_C)

Fig. 6 shows the tests comparing the effect of T_C. Better outcomes were obtained at −10 °C. The heat transfer rate was slower at higher cooling temperatures. The ice crystals were able to grow in a more ordered pattern that occluded a smaller amount of solutes. For the elution to occur, the solutes mass transfer rate must be greater than the ice growth rate (Caretta et al., 2006; Petzold and Aguilera, 2009). In addition, the ice crystal size depends on the cooling rate, which can affect the level of occlusion (Pardo et al., 2002). Certain authors have reported that the cooling temperature is not a significant factor impacting block FC (Aider and de Halleux, 2008b; Gao et al., 2009). These reports suggest that the effect of T_C depends on the FC protocol during both the freezing and thawing stages and depends on the separation mode of the liquid phase.
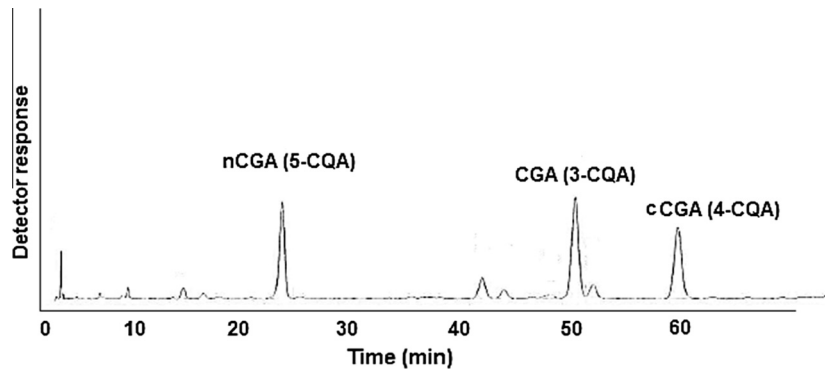
Fig. 8. Typical chromatogram of a coffee solution sample: Test 1.

Table 4
Changes in bioactive compounds and the antioxidant activity of coffee during freeze concentration.

Test	Compound	C_0 (mg/mL)	C_{FCL} (mg/mL)	C_{RI} (mg/mL)	% Ice loss	% Ice loss (dry basis)	C_{FCL}/C_0
1	CGA	0.29 ± 0.01	0.48 ± 0.04	0.09 ± 0.02	16.03 ± 4.05	48.68 ± 0.37	1.66 ± 0.14[a]
	c-CGA	0.20 ± 0.00	0.33 ± 0.03	0.06 ± 0.01	16.28 ± 3.89	49.21 ± 0.79	1.66 ± 0.12[a]
	Caffeine	1.21 ± 0.01	2.02 ± 0.17	0.39 ± 0.08	16.07 ± 3.83	48.79 ± 0.77	1.67 ± 0.13[a]
	Total solids	0.05 ± 0.00	0.08 ± 0.01	0.01 ± 0.00	16.87 ± 4.30	50.0 ± 0.00	1.60 ± 0.14[a]
	DPPH[a]	2.61 ± 0.39	4.01 ± 2.42	1.17 ± 0.25	27.10 ± 13.5	61.50 ± 19.82	1.58 ± 1.00
	ABTS[a]	24.02 ± 2.64	58.22 ± 22.70	12.63 ± 1.97	18.84 ± 5.97	53.10 ± 10.40	2.47 ± 1.08
16	CGA	0.93 ± 0.01	1.07 ± 0.02	0.76 ± 0.01	41.50 ± 0.74	49.62 ± 0.77	1.16 ± 0.03[b]
	c-CGA	0.63 ± 0.01	0.73 ± 0.01	0.52 ± 0.01	41.65 ± 0.70	49.79 ± 0.70	1.17 ± 0.12[b]
	Caffeine	3.93 ± 0.03	4.56 ± 0.08	3.28 ± 0.03	41.81 ± 0.68	49.96 ± 0.58	1.16 ± 0.03[b]
	Total solids	0.15 ± 0.00	0.17 ± 0.01	0.12 ± 0.00	41.86 ± 0.43	50.0 ± 0.00	1.15 ± 0.01[b]
	DPPH[a]	53.15 ± 3.99	72.90 ± 9.01	33.5 ± 2.97	30.77 ± 0.51	37.92 ± 0.32	1.41 ± 0.31
	ABTS[a]	136.90 ± 9.01	171.31 ± 1.50	114.8 ± 8.20	39.52 ± 2.25	47.32 ± 2.08	1.27 ± 0.13

Different letters indicate statistically significant differences ($p < 0.05$).
[a] Expressed as mg Trolox/mL.

3.3.4. Effect of heating temperature (T_H)

A slightly higher solute recovery was obtained at a T_H of 20 °C (Fig. 7). The average temperature in the empty region of the container after each liquid fraction separation during the thawing was 10 °C (Fig. 3). The treatments with the lowest T_H allowed for a slower thawing and avoided the dilution of the concentrated phase. However, the effect was not significant at the studied levels. The T_H may be significant at different levels, as reported by Moreno et al. (2013) where the tested heating temperatures were closer to the freezing point.

3.4. Bioactive compounds and the antioxidant activity of coffee

The concentrations of the major bioactive compounds in coffee solutions were determined for the initial solution (C_0), the liquid freeze-concentrated liquid (C_{FCL}) and the residual ice (C_{RI}) obtained for a thawing fraction of 50%. A typical chromatogram is shown in Fig. 8. Chlorogenic acids were the major component in the solutions. The bioactive compounds concentration and the ice loss percentage are shown in Table 4.

The ice loss percentage was approximately 16% for the lowest X_S and 41% for the highest X_S. This factor was related to the concentration index. When the ice loss (IL) was calculated on a coffee dry matter basis, the result was approximately 50%. This result indicates that the functional compounds were equally distributed in the ice and liquid fractions. There was a greater amount of bioactive compounds in the liquid phase because the concentrated liquid had a higher X_S. The results correspond to tests 1 and 16 (Table 1), which had extreme values of X_S, T_C, T_H and total process time. All of the other tests were inside the intervals of tests 1 and 16.

Table 5
Correlations between antioxidant activity and bioactive compounds concentration.

	CGA	cCGA	CAFFEINE	ABTS	DPPH
CGA	1	1.00[**]	1.00[**]	0.557[*]	0.913[**]
cCGA	1.00[**]	1	1.00[**]	0.561[*]	0.915[**]
CAFFEINE	1.00[**]	1000[**]	1	0.561[*]	0.914[**]
ABTS	0.557[*]	0.561[*]	0.561[*]	1	0.744[**]
DPPH	0.913[**]	0.915[**]	0.914[**]	0.744[**]	1

[*] The correlation is significant $p < 0.05$ (bilateral).
[**] The correlation is significant $p < 0.01$ (bilateral).

The CI of total coffee solids for tests 1 and 16 at $f = 0.5$ were 1.60 and 1.15, respectively as seen in Table 4. These values were statistically equal to the CI for the bioactive compounds, according to the LSD test. A higher significant correlation (1.00) was found ($p < 0.01$) between X_S and the concentrations of CGA, 4-CQA and caffeine. The same correlation between CI and %Li was found. Consequently, the amount of bioactive compounds was maintained in proportion to the amount of total coffee solids. Therefore, the concentration of bioactive compounds was enhanced through freeze concentration and the bioactive compounds of the beverage were preserved by block FC.

Highly significant correlations ($p < 0.01$) between antioxidant activity measured by DPPH and the concentrations of CGA, c-CGA and caffeine were demonstrated, as seen in Table 5. The correlations of the ABTS measurements were significant ($p < 0.05$). These results confirm that the antioxidant activity of coffee depends on the CGA and caffeine content, as reported by Fujioka and Shibamoto (2008).

A ratio between the antioxidant activity of the liquid fraction and the initial solution was calculated to represent the antioxidant activity relative index (C_{FCL}/C_0) (Table 4). There was no significant difference between the antioxidant activity relative index and the CI of the total coffee solids. The antioxidant activity was increased until 2.4 in one FC cycle. The increase of the antioxidant activity of mate extract was also reported by Boaventura et al. (2012) using block freeze concentration. This finding suggests block FC is an effective technique to preserve the functional properties of coffee extracts.

4. Conclusions

Coffee extract was freeze-concentrated by the total block technique. A significant effect of the initial coffee mass fraction, freezing direction and cooling temperature on solute recovery was found. The highest solute recovery was achieved at the lowest coffee mass fraction, when the freezing direction was in counter-flow to the thawing direction and at the highest cooling temperatures. The thawing fractions at which completion of the thawing stage was convenient were found between the values of 0.5 and 0.8. The initial coffee mass fraction was the factor with the highest influence on the solute yield and the concentration index. Using a freezing direction in counter-flow to the thawing direction represents an interesting alternative to increase solute recovery due to solute elution. Furthermore, the coffee bioactive compounds were distributed in the ice and liquid phase in proportion to the total solid content. Very significant correlations between the antioxidant activity and chlorogenic acid and caffeine contents in the freeze-concentrated extract were found. Consequently, the freeze concentration method increased the bioactive compound concentration and the antioxidant activity of the coffee extract. The block freeze concentration method is a potential technique to remove water and preserve the functional properties of coffee extracts.

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Effect of separation and thawing mode on block freeze-concentration of coffee brews

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ABSTRACT

Coffee brews were freeze-concentrated using block technique to evaluate the effect of thawing temperature, thawing mode and separation mode on solute yield. Samples were frozen and solute recovered using different thawing and separation conditions. Three thawing temperatures (20, 4 and 1 °C), two thawing modes (microwave assisted and free thawing) and two liquid fraction separation modes (gravitational and vacuum assisted) were tested. Solute yield was evaluated as a function of thawing ratio. Data were fitted to a monomolecular model to compare separation quality by means of the solute recovery ratio for each treatment. A combination of microwave assisted thawing and vacuum separation showed the best results in terms of solute recovery ratio. On the other hand, applying microwave assisted thawing or vacuum separation individually did not significantly enhance the solute recovery ratio. Additionally a thawing temperature effect on the solute recover ratio was also found. These results show that it is possible to improve the separation quality of Block FC by combining this technology with vacuum-assisted separation microwave heating. These results suggest that block freeze-concentration has potential industrial application.

1. Introduction

Freeze-concentration (FC) is a technology used to remove water at low temperatures preserving the quality of the original material (Miyawaki et al., 2005). Water remotion is achieved once water ice crystals are formed, leaving behind a more concentrated fluid (Sánchez et al., 2009). Moreover, FC allows to reduce processing time during the industrial freeze drying (Boss et al., 2004).

FC techniques can be classified in three groups: suspension crystallization (Huige and Thijssen, 1972), film freeze concentration (Sánchez et al., 2009) and freeze-thaw method, known also as block freeze concentration (Aider and de Halleux, 2009; Sánchez et al., 2011a). For suspension crystallization a scraped surface heat exchanger is used to form a suspension of ice crystals that can be subsequently separated (Miyawaki et al., 2005; Habib and Farid, 2006). In Film FC a single crystal layer is formed by contact with a refrigerated surface (Raventós et al., 2007; Sánchez et al., 2011b). Freeze-thaw FC

can be achieved using two different techniques: total or partial block (Nakagawa et al., 2010a). In the partial block technique, the solution is partially frozen and the remaining concentrated liquid is separated after a pre-determined time (Burdo et al., 2008). On the other hand, the total block technique consists of completely freezing the sample with a subsequent thawing until the desired amount of solute has been recovered (Aider and de Halleux, 2009). Consequently, block FC comprises three important steps: freezing, thawing and separation.

Increasing ice purity is a big challenge for block FC (Aider and de Halleux, 2008). Although, it is clear that the mass of the collected liquid increases with the collection time, increasing it until collection of the entire original solution will lead to no overall concentration effect. Therefore, it is important to determine the mass of the collected sample in which solute recovery and concentration are high enough in order to stop the process at this point. In the same way, it is important to establish the thawing conditions or aids in separation stage to recover as much solute as possible.

1. Frozen solution container
2. Collectionvessel
3. Scale
4. Vacuum pump
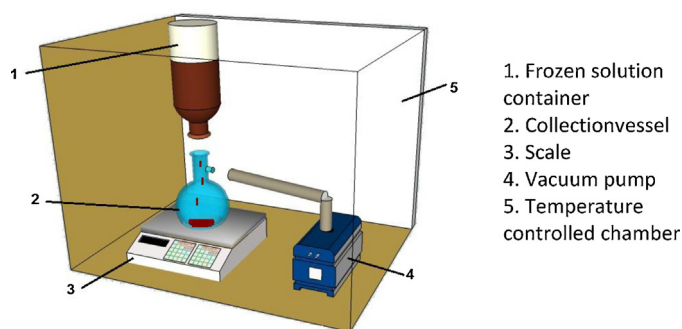5. Temperature controlled chamber

Fig. 1 – Experimental setup.

The block FC method has been recently studied as a way to improve solute yield (Gao et al., 2009; Okawa et al., 2009; Nakagawa et al., 2010a; Miyawaki et al., 2012). Furthermore, microwave assisted and gravitational thawing have been studied for milk whey (Aider et al., 2008) and for maple sap (Aider and de Halleux, 2008). It is worth noting that there are no reported studies about vacuum application and its relationship with process variables during the thawing and separation stages of block FC.

Meanwhile, coffee is the most traded food commodity worldwide (Esquivel and Jiménez, 2012). The functional and organoleptic properties of coffee are highly important for its processing and trading. Coffee processing technologies play a large role in defining the quality of the beverage (Joët et al., 2010), therefore, in the soluble coffee industry, technologies that preserve the initial characteristics of the brew are useful. Currently, suspension FC is the unique technique that is being used by coffee industry. This technique shows a high efficiency and purity of separated ice crystals, however, it is recognized as an expensive method for food concentration (Aider and de Halleux, 2009). Therefore, the use of this separation process is restricted to large-scale processing plants. For this reason, the block FC technique has been proposed in order to reduce cost and maintain high crystal purity (Aider and de Halleux, 2009), including different modes to increase solute recovery in thawing and separation stages, looking forward to implement this technique at different industrial scales.

In this paper, the total block FC of coffee brews is studied, analysing the effect of separation mode (gravitational and vacuum assisted), thawing temperature (1 °C, 4 °C and 20 °C) and thawing mode (natural convection and microwave assisted) on solute yield.

2. Materials and methods

2.1. Materials

Coffee solutions were prepared from commercial soluble coffee, (Aroma brand, Colombia) and distilled water at 20 °C. An initial concentration of 4.3 g of dissolved solids/100 g of solution (5 °Brix) was used. Concentration was measured using a refractometer (Abbe refractometer model RL3 Polskie Zaklady Optyczne Warszawa, Poland), together with a calibration equation in order to account for the deviation caused by the mixture of solids present in coffee. The calibration equation was obtained by preparing solutions at 10, 20, 30, 40 and 50 °Brix and measuring their solid contents using an oven drying procedure at 103 °C for four hours according to (NTC 4602, 1999). Measurements were performed in triplicate. The following equation was obtained: $X_s = 0.0087$ °Brix ($R^2 = 0.99$). Due to

the precision of refractometer (±0.5 °Brix), uncertainty in solid fraction measurement corresponded to ±0.00438. It is clear from other reports that the initial concentration affects the results of freeze concentration (Aider et al., 2008). However, in these experiments initial solid content was used as a constant parameter for the experiment to observe the effect of the other factors.

2.2. Methods

2.2.1. Freeze concentration protocol

Samples were frozen in cylindrical containers (200 mL) at −12 °C and then stored during 72 h at the same temperature. Afterwards, samples were thawed and the concentrated fraction was separated under different conditions. As shown in Fig. 1, frozen samples (1) were placed in a chamber with controlled temperature (5) and drops of liquid fraction were collected by gravity in an external collection vessel (2). The chamber consisted of an upright freezer with thermostat (Haceb 87L, Colombia) for the two lowest temperatures and an incubator chamber (Selecta Celmag-L, Spain) for the highest temperature level. Below the vessel was a scale (3). (Mettler Toledo AB 204 S, Switzerland. Precision ±0.1 g), used to record weight changes during thawing. The collection vessel was removed approximately every time that 7% of liquid was collected in order to measure the liquid concentration. The thawing procedure was performed at three different thawing temperatures (TT) fixed in the chamber (1 °C, 4 °C and 20 °C ±1 °C), two thawing modes (TM) and two separation modes (SM) as shown in Table 1 following a complete factorial design.

Table 1 – Experimental design.			
Treatment	Thawing temperature (°C) (TT)	Thawing mode (TM)	Separation mode (SM)
1	20	−1	Gravitational
2	4	−1	Gravitational
3	1	−1	Gravitational
4	20	+1	Gravitational
5	4	+1	Gravitational
6	1	+1	Gravitational
7	20	−1	Vacuum
8	4	−1	Vacuum
9	1	−1	Vacuum
10	20	+1	Vacuum
11	4	+1	Vacuum
12	1	+1	Vacuum

+1: microwave assisted thawing.
−1: free thawing (without microwaves).

Thawing and separation modes are explained in Sections 2.2.2 and 2.2.3. All experiments were performed in triplicate.

2.2.2. Thawing mode

For some samples, as it is shown in Table 1, the thawing stage was initiated by applying a microwave pulse (+1) and for others thawing was freely developed under a settled external temperature (−1). Therefore, half of samples were exposed to 5.1 kJ of microwave energy that was delivered in one minute by a microwave oven (Haceb Arezzo-0.7, China). This energy pulse was made of three short pulses of 2 s at 1.7 kJ, leading to an average power delivery of 85 Watts during one minute. Afterwards, the thawing and separation procedure was carried out at the settled thawing temperature following the procedure described in Section 2.2.1.

2.2.3. Separation mode

Two different separation modes were carried out: gravitational and vacuum assisted. The first consisted of drop collecting under gravity without any interference. In the second, a vacuum pressure of 1 kPa (74.7 kPa abs) was applied using an aspirator (Büchi model B-169, Switzerland) to route and increase the movement of the liquid fraction that was trapped inside the frozen portion. Thawing and separation procedures were carried out as described in Section 2.2.1. The vacuum pump was disconnected in order to measure mass and solid concentrations and reconnected after collecting the sample.

2.3. Data analysis and modelling

2.3.1. Thawing fraction

A thawing fraction (f) was defined to follow the development of the process. f was measured as the ratio between thawed mass and that of the original solution, defined by Eq. (1) (Nakagawa et al., 2010b; Miyawaki et al., 2012):

$$f = \frac{m_{liq}}{m_0} \tag{1}$$

where, f is the thawing fraction, m_{liq} is the collected liquid mass, m_0 is the initial mass.

2.3.2. Solute yield

Solute yield is defined as the fraction of recovered solute, calculated by the relation between mass of solids present in the separated liquid and the mass of solute present initially in the original solution (Nakagawa et al., 2010a):

$$Y = \frac{m_{s\,liq}}{m_{s\,0}} \tag{2}$$

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

2.3.3. Concentration factor

A concentration factor was defined as the relation between the solid concentration in the liquid fraction and the solid concentration in the initial solution:

$$CF = \frac{X_{s\,liq}}{X_{s\,0}} \tag{3}$$

where, CF is the concentration factor, $X_{s\,liq}$ is the solid fraction in freeze concentrated liquid fraction, $X_{s\,0}$ is the solid fraction in initial solution.

Additionally, Y can be obtained as shown in Eq. (4) by combining Eqs. (1)–(3):

$$Y = CF * f \tag{4}$$

2.3.4. Mathematical model

Both solute yield (Y) and thawing fraction (f) vary between 0 and 1. It is important to note that a diagonal line with slope equal to one in the plot Y against f represents a process without concentration and is considered a process with a perfect solute inclusion (Nakagawa et al., 2010a). Therefore, at any point on the diagonal line, the concentration of solids in the portion sample is that of the initial sample as seen from Eq. (5).

$$\text{If } Y = f \Rightarrow \frac{m_{s0}}{m_0} = \frac{m_{s\,liq}}{m_{liq}} \tag{5}$$

It can be inferred from the Y–f plot that the further a point is from the diagonal line, the higher the concentration of the sample. It is worth pointing out that the behaviour of the FC process in this plot is a curve bounded between the points (0,0) and (1,1). This relationship can be represented by a "monomolecular" model Eq. (6), which is frequently used in the statistical analysis of nonlinear relationships (Nothnagl et al., 2004).

$$\frac{dY}{df} = r(1 - Y) \tag{6}$$

where, Y is the solute yield, f is the thawing fraction, r is the solute recovery ratio (constant for each condition).

Eq. (7) is obtained by solving the differential equation and transforming it into a linear equation using natural logarithms:

$$\ln\left(\frac{1}{1-Y}\right) = r \cdot f \tag{7}$$

Therefore, the constant r is the slope of straight line calculated from Eq. (7) and is not directly related with time. Furthermore, it represents the solute yield per thawed liquid fraction and can be named "solute recovery ratio". The higher the slope r, the less ice that should be melted to recover a defined amount of solute. Thus r can be used as an indicator of separation quality. The monomolecular model is an intrinsically linear model with one parameter (r). As CF is the ratio between Y and f according to Eq. (4), the r parameter can be understood as the change of concentration factor in the graph Y vs. f.

2.3.5. Statistic analysis

Parameters of the monomolecular model for each treatment were obtained by a simple linear regression procedure using SAS 9.2. The result was the r value for each of twelve evaluated treatments. A ratio comparison with confidence interval procedure at $p < 0.05$ was used to determine differences of r value between treatments.

Additionally, it is possible to identify the influence of factors TT, TM and SM on the solute recovery ratio (r). The r value can be considered as a functional value, it represents the relationship between Y and f. A multiple linear regression procedure ($p < 0.05$) was applied using SAS 9.2 to this purpose. The significance of the mean and combined effects on the r values was established.

Table 2 – Solute recovery ratio.						
Treatment number	TT (°C)	TM	SM	Solute recovery ratio(r)	R^2	RMSE
11	4	MW	Vacuum	6.74	0.978	0.078 a
10	20	MW	Vacuum	6.42	0.976	0.117 a
12	1	MW	Vacuum	6.26	0.931	0.216 a
6	1	MW	Gravitational	5.61	0.979	0.052 b
9	1	–	Vacuum	5.60	0.980	0.047 c
3	1	–	Gravitational	5.12	0.943	0.419 d
1	20	–	Gravitational	5.01	0.989	0.031 e
4	20	MW	Gravitational	5.00	0.977	0.117 e
7	20	–	Vacuum	4.74	0.990	0.018 e
2	4	–	Gravitational	4.32	0.984	0.041 f
5	4	MW	Gravitational	3.37	0.968	0.106 g
8	4	–	Vacuum	3.04	0.963	0.030 h

Treatments with the same letter do not differ significantly.

3. Results and discussion

The solute recovery ratio (r), defined in Eq. (7), was obtained for each treatment and these values are presented in decreasing order in Table 2. In this table, the best conditions for solute recovery in freeze concentration correspond to those with the highest r values. There, it can be seen that regression coefficients vary between 0.93 and 0.99, showing a good fit to the model. The majority of treatments were statistically different from each other, except for the treatments 10, 11 and 12 that showed statistically the same values (95% confidence) as well as treatments 1, 4 and 7.

Fig. 2 shows the comparison between the $\hat{Y}$ values that were estimated using Eq. (7) and Y values obtained from experimental data. It is clear that the data points were distributed close and around the continuous line that represents ($\hat{Y} = Y$). Analyzing the slope of predicted and experimental data line ($m = 0.999$) and regression coefficient ($R^2 = 0.94$), it can be inferred that predicted values tend to be similar to experimental values. This result confirms the good fit of experimental data to the monomolecular model.

At this point, it is important to highlight the usefulness of parameter r in FC quality analysis. As discussed earlier,
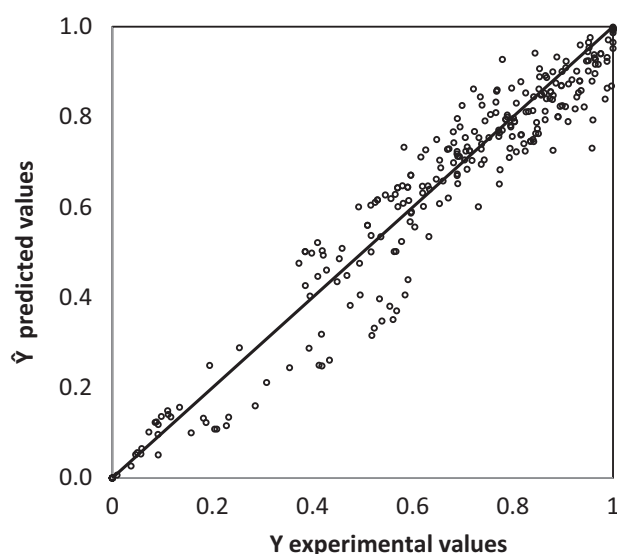

Fig. 2 – Parity plot: ex**perimental Y values against predicted $\hat{Y}$ values.**
Regression line obtained: $y = 0.999 \cdot x$; $R^2 = 0.94$.

the r value represents the amount of sample that needs to be melted in order to recover a defined amount of solids. It can be seen from experimental data (Table 2), that solute recovery ratios vary from 3.04 to 6.74. Thus, these r values are showing that under some experimental conditions (treatment 8), it is necessary to thaw nearly half of the sample in order to recover 75% (Y = 0.75) of the solids. On the other hand, in the best case scenario (treatment 11), it will be necessary to thaw only 20% of the sample in order to recover the same amount of solute. Furthermore, the concentration of recovered liquid X_{liq} can be calculated using r values and, Eqs. (1), (2) and (7).

$$X_{liq} = \frac{Y \cdot m_{s0}}{f \cdot m_0} = \frac{Y \cdot X_0}{f} \qquad (8)$$

where, X_0: initial solids concentration in the sample.

If Eq. (7) is included the resulting expression is a function of r:

$$X_{liq} = \frac{Y \cdot X_0 \, r}{\ln\left(1/(1 - Y)\right)} \qquad (9)$$

Therefore, using experimental data which have r values between 3.04 and 6.74, it can be estimated that to recover 75% of solids, the concentration of solids in the liquid samples will vary between 0.08 and 0.18 depending on the procedure selected. This information, combined with information on mass transfer speed, is a useful tool to define block FC processing strategies. Therefore, modelling heat and mass transfer kinetics should be part of the future work.

A regression analysis was used to quantify the effect of each parameter on the solute recovery ratio (Table 2). The experimental design selected for this work, made it possible to obtain linear main effect and linear combined effect of the evaluated parameters. These results are presented in Table 3. Two parameters showed a significant effect on solute recovery ratio: thawing temperature (both TT and TT × TT) and the combination of separation mode with thawing mode (SM × TM).

The thawing temperature had a significant effect on solute yield as illustrated in Fig. 3. The trend was not linear because of the significant influence of TT × TT (Table 3). Therefore, TT = 1 °C is better than TT = 20 °C and better than TT = 4 °C for all separation and thawing conditions where the combination of MW-Vacuum is not present.

The significance of thawing temperature can be explained by changes in ice structure. The solute recovery depends on

Table 3 – Effect of TT, TM and SM on solute recovery ratio.

Parameter	Standard estimator	$Pr > |t|$
Intercept	6.028	<0.0001
TT	−0.608	0.0028
TM	−0.310	0.6110
SM	−0.186	0.7595
TT × TT	0.027	0.0023
TT × TM	0.018	0.6586
TM × TM	–	–
SM × TT	−0.003	0.9348
SM × TM	2.184	0.004
SM × SM	–	–

the capacity of the separation system to collect concentrated liquid fractions and this is related to the porous structure and density of frozen matrix. Water solutions experience density changes during freezing and thawing (Akyurt et al., 2002). Freezing and thawing temperatures influence freezing and thawing speeds, affecting the ice porous structure (Pardo et al., 2002) and the movement of liquid through it. Moreover, if diffusion of liquid is slower than heat transfer, some ice would be expected to melt and to dilute the solution before it can be recovered. Therefore, the rate of mass transfer affects the solute recovery ratio because at low mass transfer rates, greater portions of the sample should be melted in order to obtain a certain amount of solute. Thus, for this kind of freeze concentration process it is important to find a good balance between thawing speed (heat transfer) and separation speed (mass transfer) not only to optimize processing rate, but also to find the best recovery condition. Meanwhile, TT did not show a linear effect, which was not expected, therefore, further work in order to relate changes of frozen sample's microstructure with processing parameters can lead to a deeper understanding of block FC.

It was seen from experimental data (Table 2) that, the highest solute recovery ratio was obtained for treatments 10, 11

Fig. 4 – Effect of separation mode on solute yield treatments numbered according to Table 1 (1, 4 = gravitational; 7, 10 = vacuum) Lines are modelled by Eq. (7) and parameters in Table 3. Each symbol corresponds to data collected from triplicate experiments.

and 12, in which a combination of microwave thawing and vacuum separation was used. Moreover, temperature did not show a significant effect. This observation is in accordance with the results of regression analysis (Table 3) in which the combined parameter had a bigger standard estimator than TT and TT × TT parameters. Other parameters such as TM and SM had no significant influence when analyzed alone. A similar result, where MW thawing did not show a significant effect on separation efficiency was reported by (Aider and Ounis, 2012).
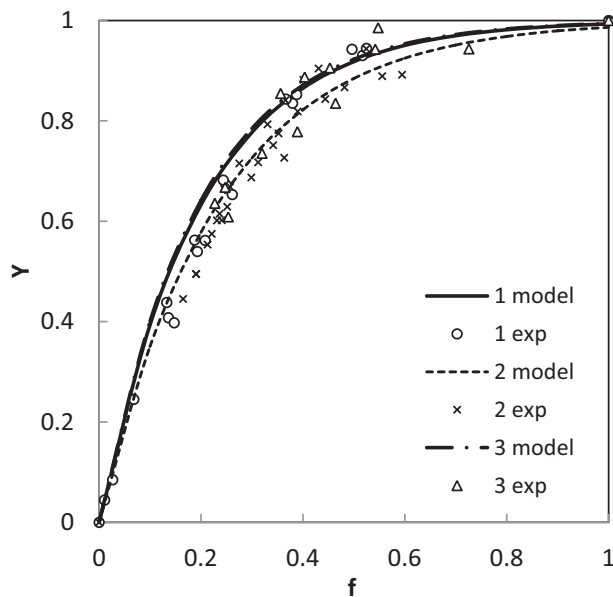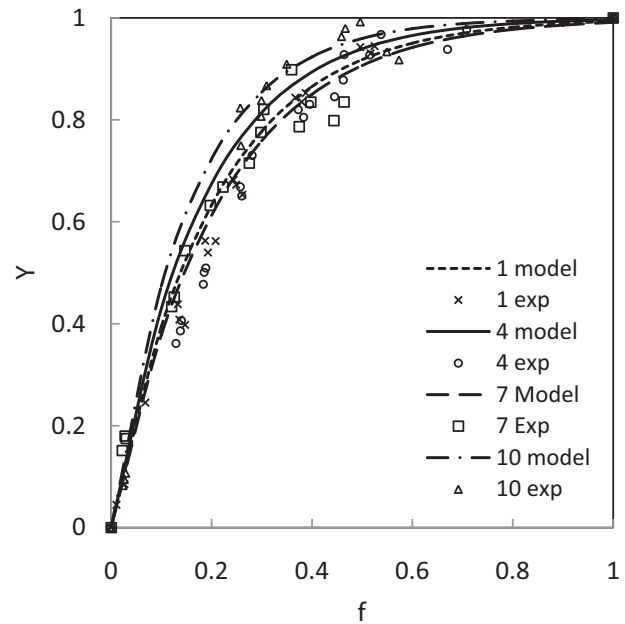

Fig. 3 – Effect of temperature on solute yield treatments numbered according to Table 1 (1, 20 °C; 2, 4 °C; 3, 1 °C). Lines are modelled by Eq. (7) and parameters in Table 3. Each symbol corresponds to data collected from triplicate experiments.
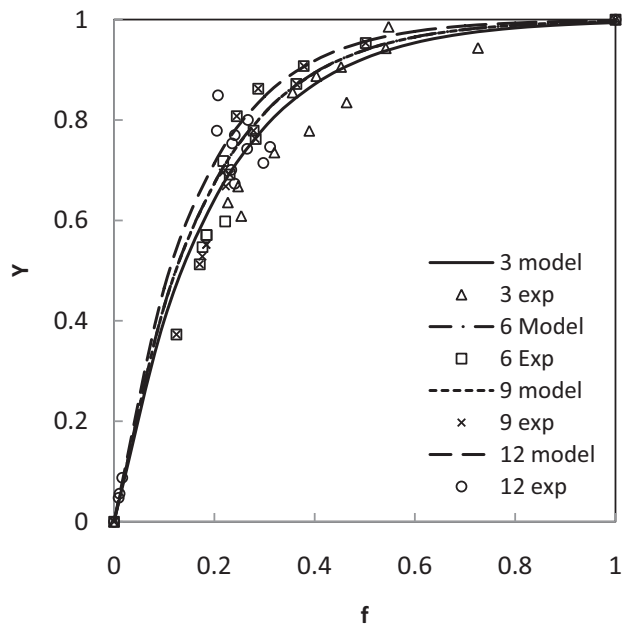

Fig. 5 – Effect of thawing mode on solute yield treatments numbered according to Table 1 (3, 9 = free; 6, 12 = Microwave). Lines are modelled by Eq. (7) and parameters in Table 3. Each symbol corresponds to data collected from triplicate experiments.

Table 4 – Thawing time and concentration factor.[a]						
Treatment	TT (°C)	TM	SM	Thawing time (h) at $f = 0.5$	Y at $f = 0.5$	CF at $f = 0.5$
10	20	1	Vacuum	2.7	0.98 ± 0.03	1.96 ± 0.05
4	20	1	Gravitational	3	0.96 ± 0.05	1.92 ± 0.05
7	20	−1	Vacuum	3	0.90 ± 0.12	1.8 ± 0.11
1	20	−1	Gravitational	3.5	0.94 ± ± 0.07	1.88 ± 0.05
11	4	1	Vacuum	12.5	0.94 ± 0.06	1.88 ± 0.15
5	4	1	Gravitational	25.6	0.84 ± 0.07	1.68 ± 0.11
8	4	−1	Vacuum	31	0.72 ± 0.08	1.44 ± 0.17
3	1	−1	Gravitational	35	0.93 ± 0.05	1.86 ± 0.2
2	4	−1	Gravitational	48.3	0.94 ± 0.07	1.88 ± 0.05
9	1	−1	Vacuum	50	0.93 ± 0.04	1.86 ± 0.55
12	1	1	Vacuum	75	0.95 ± 0.13	1.9 ± 0.34
6	1	1	Gravitational	80	0.94 ± 0.04	1.88 ± 0.55

[a] Values in increasing order of thawing time. Average values with standard deviation.

Figs. 4–6 depict this situation, in which the effect of microwave thawing and vacuum separation is significant only when both of them are present in the treatment.

Experimental results showed that the r value was increased up to two times when MW was combined with vacuum separation. This means that a similar Y can be reached with a lower f, increasing concentration of separated liquid portion. On the other hand, the effect of vacuum was very small without microwave assisted thawing as seen in Fig. 5. Actually, r values decreased when vacuum was present, but Table 3 shows that this effect was not significant when compared with other parameters. This suggests that vacuum separation promotes the separation of concentrated liquid fraction from the ice matrix and increases process efficiency only when microwave thawing is present. Therefore, this synergy when MW and vacuum are combined shows that this operating condition is an appropriate tool to improve separation quality in block FC.
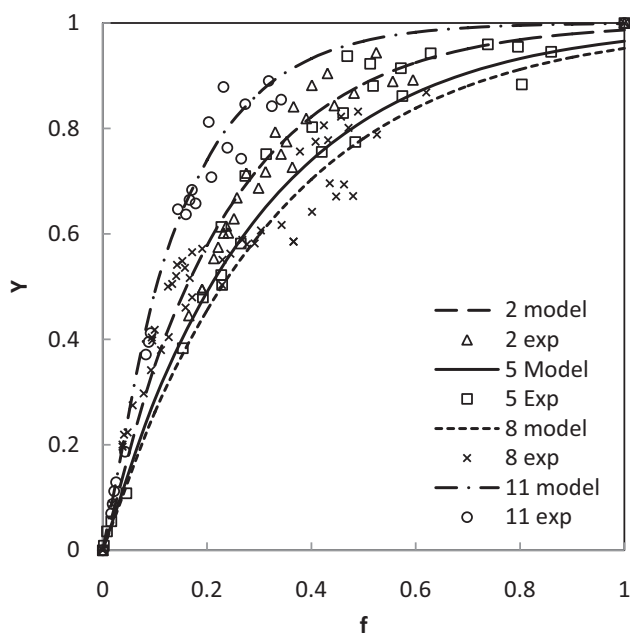

Fig. 6 – Effect of thawing mode on solute yield treatments numbered according to Table 1 (2, 8 = free; 5, 11 = Microwave). Lines are modelled by Eq. (7) and parameters in Table 3. Each symbol corresponds to data collected from triplicate experiments.

This synergistic behaviour can be explained using two different mechanisms: accelerated internal thawing and hydrodynamic movement of molten portions of the sample. As it is known, the absorbed microwave energy is related to the loss factor of the material. Thus, substances with a high loss factor will readily absorb microwave energy, while those with a low loss factor are either reflecting or transparent to microwave energy (Wu et al., 2004; Wang et al., 2011). It is important to highlight that the loss factor of liquid water is greater than that of ice (Ryyniinen, 1995). Microwaves can penetrate the frozen layer and reach the unfrozen liquid (Rattanadecho, 2004). Therefore, it would be expected that during a microwave pulse, liquid pockets will be formed in regions with higher concentration of solids and lower melting points. However, these liquid pockets cannot be easily separated from the sample because of the tortuosity of the paths inside the frozen matrix. Here, vacuum plays a synergistic role because pressure difference helps evacuating the concentrated liquid phase easily promoting liquid movement and separation. Experimental data showed that this hydrodynamic movement enabled by vacuum is a good way to accelerate liquid removal. Therefore, in a future paper, the effect of these parameters on the Block FC process kinetics will be analyzed.

As solute yield indicates the amount of solute recovery but not the process velocity, it is useful to combine this parameter with the analysis of thawing time. The thawing time (t) required to collect 50% of liquid (t at $f = 0.5$) is shown in Table 4 in increasing order. Also, the solute yield (Y) and the concentration factor (CF) at $f = 0.5$ are presented.

The thawing time was lower for treatments 10, 4, 7, and 1, which correspond to TT, 20 °C. Treatments with TT, 4 °C and TT, 1 °C resulted in a 25-fold increase in thawing times. The result is similar for the solute recovery rate, in which TT showed a significant effect. Comparing treatments with the same TT, microwave thawing slightly reduced thawing time.

Vacuum separation helped to reduce t slightly. At the same time, vacuum separation allowed more solute to be recovered. This suggests that vacuum separation promotes the separation of the concentrated liquid fraction from the ice matrix and increases process efficiency, showing this separation mode as an interesting topic in block FC.

The concentration factor (CF) at 50% of thawing is presented for each condition in Table 4. Values between 1.4 and 1.9 were obtained. These values are comparable with those obtained using other concentration techniques. For example, in falling film FC, CF is around 2 for one stage of FC (Raventós et al., 2007), in progressive FC, where CF is around

2.8 (Miyawaki et al., 2005), in Block FC, CF = 1.4 without separation assistance (Nakagawa et al., 2010b) and in microwave assisted thawing Block FC, CF is close to 1.7 (Aider and Ounis, 2012) for one stage.

The highest CF was obtained for treatments with vacuum separation, due to the positive effect of pressure difference on the movement of the concentrated liquid fraction.

On the other hand the shortest thawing time and highest solute recovery rate was obtained for treatment 10 (TT, 20 °C, MW thawing and vacuum separation). This condition gave the best overall is appropriate for the performance of FC, recovering 98% of solute when 50% of mass is thawed and just spending 2.7 h of thawing time.

4. Conclusions

The relationship between solute yield and thawing fraction can be represented using the monomolecular model. Linearization of this model, using slope r which is not related to time, simplifies the analysis in terms of the separation efficiency, and quality of the recovered liquid.

The combination of microwave assisted thawing and vacuum separation exerts a synergistic positive effect on solute recovery ratio. Experimental results showed that this operating condition is an appropriate tool to improve separation quality in block FC.

Thawing temperature has a significant effect on solute recovery ratio; both TT and TT × TT, are highly influential parameters. Therefore, under the experimental conditions used in this work temperature did not show a linear effect on separation quality.

Block freeze-concentration is a potential technology for food concentration. Process alternatives such as, thawing temperature control, microwave thawing and vacuum separation are helpful to increase solute recovery and should be taken into account when scaling up this technology.

Acknowledgements

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A process to concentrate coffee extract by the integration of falling film and block freeze-concentration

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ABSTRACT

A process to concentrate aqueous coffee extract by freeze concentration is proposed to achieve an industrially viable system. The techniques of falling film freeze concentration, fractionated thawing and block freeze concentration were studied. Batches of 40 kg of coffee extract with 5% initial solid concentration were freeze-concentrated in seven stages in a falling film multi-plate freeze concentrator. The ice from each stage was fractionally thawed to recover the coffee solids retained in the ice. The diluted fractions of the thawing stage were freeze-concentrated using the block technique. A concentrated extract with 32.6% solids and an effluent with 0.27% solids were obtained through the integration of these techniques. A concentration index of 6.5, a concentration efficiency of 99.2% and a solute yield of 95% were obtained. The integration of these simple techniques results in a concentration index and solute yield comparable to industrial standards in freeze-concentrated coffee extract production.

1. Introduction

Coffee is one of the most consumed beverage worldwide (Esquivel and Jiménez, 2012; Sopelana et al., 2011). Freeze-dried coffee is a high-quality product of the coffee industry because of the flavour preservation due to the low-temperature processing conditions (MacLeod et al., 2006). The process of obtaining freeze-dried coffee begins with the extraction of roasted coffee beans by percolation. Subsequently, the extract is freeze-concentrated to remove part of the water and to obtain a concentrated extract. The concentrated extract may be the final product or may be freeze-dried to remove the remaining water to obtain soluble coffee (Boss et al., 2004). The use of freeze-concentration technology is justified by the reduction of the freeze-drying process costs by 25% (Van Pelt and Bassoli, 1990). In addition, the quality of the product is preserved by low processing temperatures (Rahman et al., 2007).

Freeze concentration (FC) is a technique used to remove water from food fluids by freezing (Sánchez et al., 2009). The solution is cooled below the freezing point to produce and separate ice crystals. Three techniques are used for growth of ice crystals, suspension FC, film FC (progressive or falling film FC) and block FC (also known as freeze–thaw FC) (Aider and de Halleux, 2009; Sánchez et al., 2011a).

The only technique implemented in coffee processing at the industrial level is suspension FC. This is an efficient technique in terms of ice purity and increased concentration (Qin et al., 2007,2006; van der Ham et al., 2004). With this technique, it is possible to concentrate the coffee extract to 32–35% solids and to obtain a high-purity effluent with 0.1% solids (Van Mil and Bouman, 1990; Van Pelt and Bassoli, 1990). However, this technique requires complicated systems of ice separation and many moving parts, which increases the initial and operating costs (Aider and de Halleux, 2009; Miyawaki et al., 2005; Sánchez et al., 2009). For this reason, several other FC techniques have been studied. Recently, the industrial future of freeze concentration has shifted toward the configuration of one-step systems or a combination of systems rather than suspension freeze concentration because of the simpler separation step (Petzold and Aguilera, 2009, 2013).

In falling film freeze concentration (FFFC), the solution to be concentrated is in contact with a cooled vertical plate on which the fluid descends. The ice forms a single layer on the cold surface, and the solution is re-circulated continuously (Sánchez et al., 2011b). FFFC has been studied with several food fluids (Belén et al., 2013; Chen et al., 1998; Hernández et al., 2009, 2010; Raventós et al., 2007; Sánchez et al., 2010). Flesland (1995) proposed multi-stage FFFC coupled to reverse osmosis for water desalination. In that study, water elimination was efficient. Recently, the recovery of solutes of sucrose solutions retained in ice was attempted using fractionated thawing of the ice (Gulfo et al., 2013; Miyawaki et al., 2012).

In contrast, in block freeze concentration (block FC), the whole solution is frozen and partially thawed to recover the concentrated liquid fraction (Aider and de Halleux, 2009). Block FC has been

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used for sucrose solutions, dairy products, syrup, mate extract and fruit juices (Aider and Ounis, 2012; Aider et al., 2009; Boaventura et al., 2012; Nakagawa et al., 2010a,b). For coffee extracts, Moreno et al. (2014) and Moreno et al. (2013) studied the effect of process conditions on the freezing and thawing stages of block FC. The viability of the technique was primarily demonstrated for low solid concentrations.

In some food applications, FC can be used to maximise the final solid content of the solution. However, in the coffee industry, the minimisation of the solid content of the final effluent is also important due to the high value of the product. Currently, there is no plan to use FFFC or block FC to obtain an extract with a high solid concentration and an effluent with a low solid content that comply with industrial requirements.

The aim of the present study was to propose a process to freeze-concentrate coffee extracts through the integration of falling film freeze concentration, which includes coffee solids recovery by fractionated thawing and block freeze concentration techniques.

2. Materials and methods

2.1. Materials

A coffee extract with 5% (w/w) wet basis of total solid content was prepared from freeze-dried soluble coffee supplied by Buencafé Liofilizado de Colombia (Colombian Coffee Growers Federation, Colombia) and water at 35 °C. The solution was stored at 4 °C for 24 h prior to the tests.

2.2. Methods

Three techniques were studied for coffee extract freeze-concentration following the flowchart shown in Fig. 1. First, the initial extract was freeze-concentrated by the falling film technique. Second, the ice formed in the first technique was thawed fractionally to study the recovery of the retained solutes. Finally, the diluted fractions obtained in the thawing stage were concentrated by the block technique to recover the retained solids. Each technique was individually studied. Based on the results, an integration of the techniques in a global process was proposed.

2.2.1. Falling film freeze concentration tests
The FFFC tests were developed in a multi-plate freeze concentrator shown in Fig 2(a). The equipment included a freezing chamber, a freezing system, and a hydraulic system. The freezing unit consisted of two cooling plates with dimensions of 0.8 m width and 0.6 m height in a closed chamber. The hydraulic system spreads the coffee extract by means of two distributors with several holes 3 mm in diameter. The coffee extract flows in a descending film over the cooling plates, and it was collected in a collector tank and recirculated by a centrifugal pump. The ice growth on the surface of the freezing plates was then removed in a batch operation.

The freezing system consisted of refrigeration cycle using the primary refrigerant R-507 with a compressor (Tecumseh Europe,

La Verpilliere, France), a condenser and an expansion valve. The evaporation of the refrigerant occurred in the interior of the cooling plates, transferring the energy through the walls of the plate. Consequently, this process produces layer crystallisation in which the ice forms in thin layers on the surface of the heat exchanger.

All the stages of FFFC started with 40 kg of coffee extract. The stage ended when the ice achieved an average width of 25–35 mm. After that, the ice was removed, and the concentrated liquid fraction was used in the next stage. The initial mass in the next stage was obtained adding extract prepared at the concentration of the extract used in the previous stage. A total of seven stages of FFFC were developed. The mass of the concentrated fractions and the ice was measured on a PS 60-KB scale with 1 g precision (Gram Precision, Spain). The solid concentration percentage (Cs) was measured by refractometry (Atago Pal 100, Japan). The relationship between Brix degrees and Cs is represented by the equation $CS = 0.87*°Brix$ reported by Moreno et al. (2014) for the same coffee used in the present study.

2.2.2. Coffee solids recovery by partial thawing tests
Thawing tests were performed according to the method described by Gulfo et al. (2013). Cylindrical samples with a diameter of 60 mm, thickness from 25 to 35 mm and weight between 65 and 75 g were taken from the ice obtained at each of the seven stages of FFFC to study the solute recovery for fractionated thawing. A drill equipped with a puncher (Esgarret, Spain) was used to obtain six samples homogeneously distributed in each of the six ice sheets, for a total of 36 samples. Samples were taken in a refrigerated chamber to avoid melting the ice.

The samples were subjected to thawing tests in the setup shown in Fig. 2(b). The setup consisted of a cubic isolated chamber with 0.48 m sides. The chamber has a temperature control system (Pie Electro Dit, model 11 551, 0–300 W) and a 4-channel data logger (Testo 177-T4, Germany). The thawing was carried out at 20 ± 1 °C in a vertical position, similar to the position that the ice layers had in the freeze concentrator. The dripping of the melting ice is collected by a funnel connected to a container on a scale (Ohaus PA3102, USA) with a precision of 0.01 g to measure the mass. Ten thawing fractions of equal mass were separated, and the solid concentration was measured by refractometry. The average concentration was calculated from the data of the six samples of ice from each stage.

2.2.3. Block freeze concentration tests
Based on the results of the fractionated thawing tests, the diluted fractions of this stage (fractions where the concentration index was less than 1) were mixed and freeze-concentrated by the total block technique. The conditions of the FC test were as follows: cooling temperature −10 °C, thawing temperature 20 °C and thawing direction opposite to the freezing direction according to the best results reported by Moreno et al. (2014).

The block freeze concentrator is shown in Fig. 2(c). One hundred sixty grams of the coffee sample was placed into a cylindrical double jacked container measuring 5.2 cm in diameter and 8.5 cm in height. The heat exchange fluid was a mixture of ethylene glycol
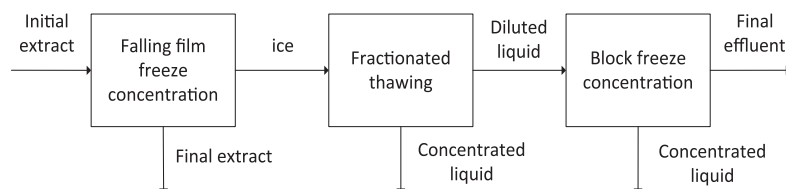

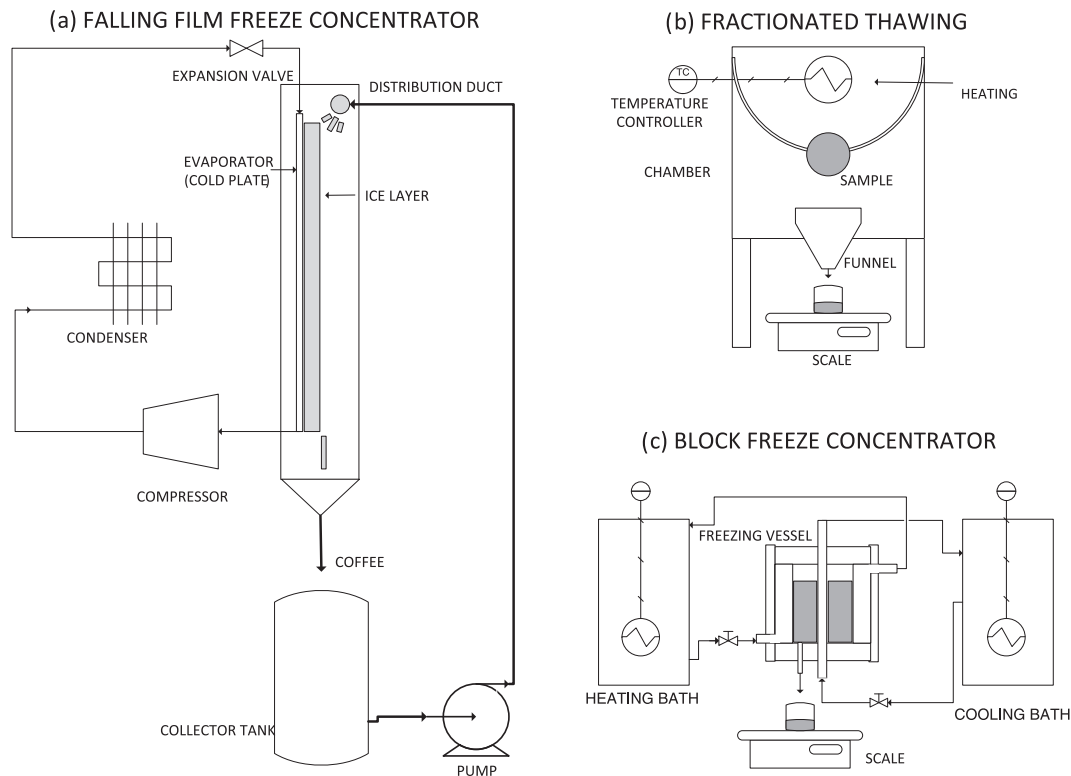**Fig. 1.** Flowchart of freeze concentration tests.

Fig. 2. Experimental setup for freeze concentration tests. (a) Falling film freeze concentration; (b) fractionated thawing and (c) block freeze concentration.

and water (53% w/w) coming from two baths (Polystat, Cole Parmer, USA) with temperature control (−35 to 150 °C ± 0.01 °C).

The cooling fluid temperature was settled at −10 °C. After the fluid reached that temperature, it was circulated to the internal jacket to freeze the inner solution. The ice growth occurred from the centre to the external wall of the container. When the sample was completely frozen, the sample was thawed by pumping heating fluid through the external jacket at 20 °C. A valve located on the bottom of the container and close to the external wall was opened, and the liquid fraction was separated in a collector vessel on a scale (Ohaus PA3102, USA) with a precision of 0.01 g for mass measurement. Ten liquid fractions of the same mass were collected. The solid concentration of each fraction was measured by refractometry (Atago Pal 100, Japan). Test were performed in triplicate.

2.2.4. Data analysis

2.2.4.1. Solute yield (Y).
Solute yield represents the amount of solute or coffee solids recovered from the original solution. Y 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., 2013; Nakagawa et al., 2010a,b):

$$Y = m_{s\,liq}/m_{s0} \qquad (1)$$

where Y is the solute yield, $m_{s\,liq}$ is the solute mass in the liquid fraction, and m_{s0} is the initial solute mass.

2.2.4.2. Concentration index (CI).
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):

$$CI = C_{s\,liq}/C_{s0} \qquad (2)$$

where CI is the concentration index, $C_{s\,liq}$ is the solid mass percentage in the freeze-concentrated liquid, and C_{s0} is the solid mass percentage in the initial solution.

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

$$f = m_{liq}/m_0 \qquad (3)$$

where f is the thawing fraction, m_{liq} is the freeze-concentrated liquid mass, and m_0 is the initial mass.

2.2.4.4. Concentration efficiency.
The concentration efficiency indicates the increase in the concentration of the solution in relation to the amount of solids remaining in the ice (Hernández et al., 2010; Sánchez et al., 2010). Efficiency was calculated by Eq. (4):

$$Eff = (C_{s\,liq} - C_{s\,ice})/C_{s\,liq} * 100 \qquad (4)$$

where Eff is the concentration efficiency (%), $C_{s\,liq}$ is the solid mass percentage in the freeze-concentrated liquid, and $C_{s\,ice}$ is the solid mass percentage in the ice (or diluted fraction).

2.2.4.5. Statistical analysis.
The experimental results obtained from this study were fit to different mathematical models using the statistical software SPSS 20.0. The fit was evaluated by the determination coefficient.

3. Results and discussion

3.1. Falling film freeze concentration

The total solid concentration in the freeze-concentrated liquid for the seven FFFC stages is shown in Fig. 3. The concentration progressed linearly according to Eq. (5):

$$C_{s\,liq} = 3.9\,n + C_0 \quad R^2 = 0.991 \qquad (5)$$

where $C_{s\,liq}$ represents the solid percentage in the freeze-concentrated extract, n is the stage number, and C_0 is the solid

concentration of the initial extract, which corresponds to 5% in these tests. Linear behaviour was also obtained for orange, apple and pear juices by Hernández et al. (2010) and Sánchez et al. (2011b, 2010). The results indicate that the solid concentration increased 3.9%, and the concentration index increased from 1.1 to 1.7 in each stage.

On the other hand, the solid concentration of the ice evolved according to a quadratic function. The occluded solids in the ice increased approximately linearly between the first and fourth stages. From this point, when the solution had 20.2% of solids, the solid retention in the ice. The increasing solid occlusion can be explained by several effects. First, the higher amount of solids in the extract produced an increased interaction between solids and water molecules (Chen et al., 1998). Second, the solution is more viscous (Hernández et al., 2010) and washing the concentrated liquid fractions from the falling film was more difficult. In addition, the ice tends to grow in dendritic form at higher solid concentrations, trapping more solids inside (Butler, 2002; Yee et al., 2003).

As a consequence of the higher solid occlusion, the concentration efficiency decreased linearly with the solid concentration in each stage, as shown in Table 1. A linear decrease in concentration efficiency was also reported by Hernández et al. (2009, 2010) and Raventós et al. (2007) for freeze concentration of must, fruit juices and sugar solutions, respectively.

The final solid concentration over seven stages of FFFC was 31%, corresponding to a concentration index of 6.25, as shown in Table 1. The ice fraction obtained in each stage (f_{ICE}) is presented in the same table. The ice mass obtained decreased in each stage. When the solid concentration of the extract increased, the amount of water that had to be removed to increase the concentration was lower. In addition, the freezing point decreased with the solid concentration, and the cooling capacity of the equipment limited the ice production. The ice in the last stage was less consistent due to the increased amount of solids.

In Table 1, the solute yield of each stage (Y_{STAGE}) is presented. The values began at 95% and decreased through the following stages. Moreover, the accumulated solute yield in the seven stages was 0.42 based on the total amount of solids in the initial extract. This means that 42% of the coffee solids present in the initial extract were in the final extract. A large amount of solids was recovered in the ice due to the amount of ice, despite the lower concentration of these solids.

The results indicated that falling film freeze concentration can be used to obtain a final extract with a solid concentration that meets industrial requirements. However, a large amount of solids remained occluded in the ice, and it is necessary to find a technique
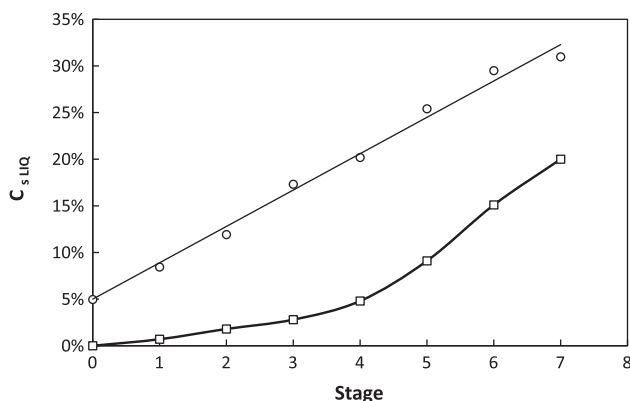
Table 1
Initial coffee solid concentration (C_{s0}), concentration index (CI), solute yield at each stage (Y_{STAGE}), ice fraction (f_{ice}) and concentration efficiency (Eff) of falling film freeze concentration tests.

Stage	C_{s0} (%)	CI	Y_{STAGE}	f_{ICE}	Eff (%)
1	5.0	1.70	0.95	0.44	91.7
2	8.4	2.40	0.87	0.39	84.9
3	11.9	3.49	0.96	0.34	83.8
4	17.3	4.07	0.78	0.33	76.2
5	20.2	5.12	0.89	0.30	64.2
6	25.4	5.95	0.78	0.33	48.8
7	29.5	6.25	0.78	0.26	35.4

to recover them. For this reason, fractionated thawing tests were performed.

3.2. Coffee solids recovery by fractionated thawing

The ice obtained in the seven stages of FFFC tests was thawed in ten mass fractions to study the solid recovery. The concentration index (CI), calculated as the ratio between the solid concentration in the thawed fraction and the average solid concentration of the ice, is shown in Fig. 4. The CI began with values higher than 1 and descended throughout all stages of the thawing process. This indicated that the concentrated extract was collected in the first fractions, and the thawing procedure can be used for solid recovery in the ice. Gulfo et al. (2013), Miyawaki et al. (2012) and Yee et al. (2003) reported similar behaviour of the concentration in solute recovery in the thawing of sugar solutions.

The solid concentrations of the first fractions were higher than the average mainly due to two phenomena. First, the concentration of the external faces of the ice is higher than the concentration in the internal portion; the external faces were the first thawed portions. In the face in contact with the cooling plate, the nucleation at supercooling temperatures increased the concentration of the liquid fraction trapped when the ice front grew (Scholz et al., 1993). In the face in contact with the falling fluid film, the dendritic growth of the ice trapped the concentrated extracts of the falling film (Sánchez et al., 2010). Second, and possibly more important, there was solute diffusion from the concentrated liquid occluded in the ice to the thawed drops. When the water drops melted, there was enough time for solute diffusion to the drops, increasing the solid concentration and allowing the recovery of a concentrated liquid (Nakagawa et al., 2009). If the ice is partially thawed, the concentrated fraction trapped in the ice crystals can flow freely

Fig. 3. Solid concentration in liquid (○) and ice (□) at each stage of falling film freeze concentration.
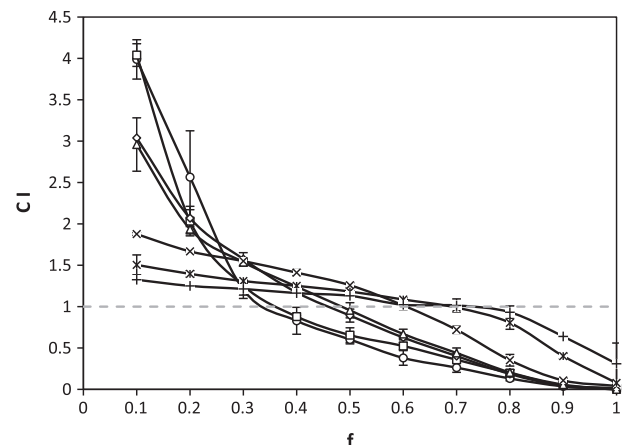

Fig. 4. Concentration index as a function of the thawing fraction. (○) Stage 1; (□) stage 2; (◇) stage 3; (△) stage 4; (×) stage 5; (□) stage 6; (+) stage 7.

and be separated. This phenomenon is known as sweating, and it is very important in the solute recovery (Guardani et al., 2001).

Fig. 4 shows that the concentration index decreased with f, and there was a thawing fraction in which the CI was less than one. From this point, the concentration of the following fractions was less than the average; consequently, the thawing process should be stopped at this point to avoid dilution of the recovered extract. At this fraction (f at $CI = 1$), two products are obtained, the initial fractions with $CI > 1$ (concentrated fraction) and the final fractions with $CI < 1$ (diluted fraction).

The values of f at $CI = 1$ between 0.3 and 0.7 were obtained as shown in Table 2. These values depended on the initial solid concentration of the ice ($C_{S0\,ice}$). A small amount of ice had to be thawed to recover the solids in the first stages, in which the ice had a lower solid concentration. In contrast, in last stages, a higher amount of ice had to be thawed. The concentration of the thawing fraction was more homogenous (flatter curve in Fig. 4). In addition, the movement of the solids is more difficult in high solid concentrations because of the interaction between molecules.

The solid concentrations of the diluted ($C_{s\,dil}$) and concentrated fractions ($C_{s\,conc}$) for f at $CI = 1$ are shown in Table 2. Thawing fractions where $CI = 1$ are also shown. These are the fractions in which high solid recovery is achieved without excessive dilution of the sample. With this strategy, a concentration index between 1.3 and 2.5 was obtained. The CI was highest in the first stages. Similar results were reported by Gulfo et al. (2013) for sugar solutions. The CI can be calculated from the concentrations reported in Table 2. The CI decreased with the initial solid concentration in the ice, as shown in Fig. 5. The behaviour can be described by Eq. (6):

$$CI = 50.35 \cdot C_{s0}^2 - 16.98 \cdot C_{s0} + 2.61 \quad R^2 = 0.94 \tag{6}$$

Solute yield can be calculated from Eq. (7), which is obtained by combining Eqs. (1)–(3) (Moreno et al., 2014). Solute yields from 73% to 81% were obtained. Miyawaki et al. (2012) reported solute yields above 90% by ice thawing from a tubular progressive freeze concentrator. The solute yield depends on the thawing fraction.

$$Y = f * CI \tag{7}$$

The combination of the fractionated thawing process and the FFFC technique resulted in a solute yield of 62%. Although the solid recovery was increased by more than 70%, a large amount of coffee solids remained in the diluted fraction. Another technique needed to be integrated to the process to increase the solid recovery. Block FC was studied for this purpose.

3.3. Block freeze-concentration

The diluted fractions from the fractionated thawing tests were mixed and freeze-concentrated by the block technique to recover the solids from this fraction. Ten fractions were obtained in the first stage, and the solute yield (Y) and concentration index (CI) were calculated. The diluted fractions (according to the CI values)
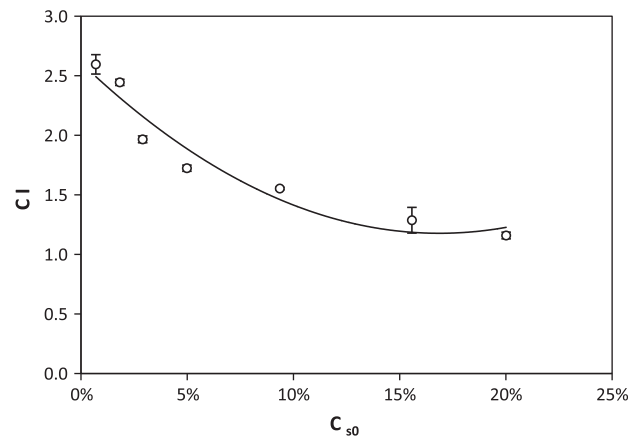

Fig. 5. Concentration index (CI) at the recommended thawing fraction as a function of the initial solid concentration (C_{s0}) of the ice.

obtained in the first stage were mixed and freeze-concentrated in a second stage. The results of the two stages are shown in Fig. 6.

Maximal CI values of 2.3 and 2.7 were obtained in the first thawing fraction. These results were obtained because the sample was frozen from the centre and thawed from the exterior of the container. With this control of the thawing direction, the solids moved to the growing freezing front by elution when the ice crystals formed. The last fraction frozen was the first to be thawed. This fraction had the highest solid content. The solid elution was possible because of the low freezing rate achieved by the cooling temperature of $-10\,°C$; at this temperature the average freezing rate was $1.84\ \mu m\ s^{-1}$ (Moreno et al., 2014). The lower the freezing rate is, the lower the solid occlusion is. Nakagawa et al. (2010a,b) reported a limit of $8\ \mu m\ s^{-1}$ for freeze concentration in a similar cylindrical device.

The CI decreased during the thawing. The highest values were obtained for the firsts thawing fractions due to sweating, similarly to the fractionated thawing test results. Sweating is defined as crystal purification based on partial melting by heating the cooling surface at a temperature close to the freezing point (Jiang et al., 2013). Sweating depends on factors such as temperature, porosity of the ice layer, solid concentration, and thawing rate (Rich et al., 2010). The coffee solids moved to the thawing drops and increased the concentration in the drops; in this way, recovery of the majority of solids was possible in the first fractions. As in fractionated

Table 2
Concentration of the diluted ($C_{s\,dil}$) and concentrated fractions ($C_{s\,conc}$) of the recommended thawing fraction (f at $CI = 1$). Average ± standard deviation.

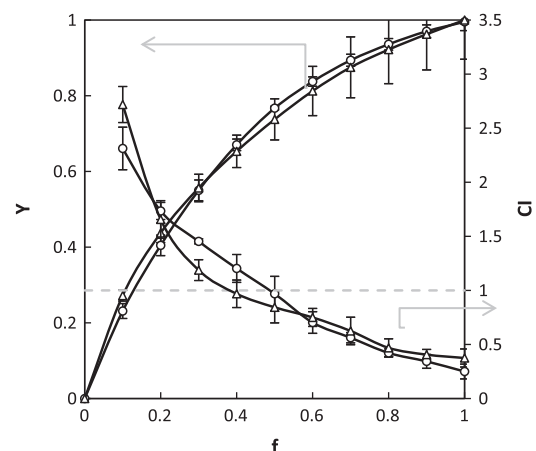| Stage	f at $CI = 1$	$C_{s0\,ice}$ (%)	$C_{s\,conc}$ (%)	$C_{s\,dil}$ (%)
1	0.3	0.7 ± 0.1	1.8 ± 0.4	0.2 ± 0.0
2	0.3	1.8 ± 0.2	4.5 ± 0.6	0.7 ± 0.0
3	0.4	2.9 ± 0.3	5.7 ± 0.8	1.0 ± 0.1
4	0.4	5.0 ± 0.7	8.6 ± 1.1	1.4 ± 0.3
5	0.5	9.4 ± 0.1	14.5 ± 0.2	4.2 ± 0.1
6	0.7	15.6 ± 1.0	20.4 ± 0.3	8.3 ± 2.9
7	0.7	20.0 ± 1.6	23.2 ± 1.4	12.6 ± 2.2

Fig. 6. Solute yield (Y) and concentration index (CI) after block freeze concentration. (○) Stage 1; (△) stage 2.

Table 3
Results of block freeze concentration of the thawing fractions when the concentration index (CI) is 1. Thawing fraction when $CI = 1$ (f at $CI = 1$); solid concentration of the Initial (C_{s0} (%)); the concentrated ($C_{s\,conc}$) and diluted fractions ($C_{s\,dil}$), and solute yield (Y).

Stage	f at $CI = 1$	C_{s0} (%)	$C_{s\,conc}$ (%)	$C_{s\,dil}$ (%)	Y
1	0.5	1.9 ± 0.0	2.8 ± 0.1	0.9 ± 0.1	0.78 ± 0.01
2	0.4	0.9 ± 0.1	1.5 ± 0.1	0.5 ± 0.1	0.68 ± 0.02

thawing, sweating is of great importance in block freeze concentration (Nakagawa et al., 2009).

The CI decreased until it reached a value of 1. In this thawing fraction (f at $CI = 1$), it is convenient to stop the thawing stage and to separate two streams, one diluted and one concentrated. For the first stage of block FC with an initial solid concentration of 1.8%, the CI was 1 at $f = 0.5$. At this point, 77% of coffee solids have been recovered, and a CI of 1.54 has been achieved, as can be calculated from data in Table 3. The mixture of the five diluted fractions had a solid concentration of 0.9%; for this reason, this mixture was freeze-concentrated in a second stage. For the second stage, CI was 1 at $f = 0.4$. When 40% of the extract was thawed, a solute yield of 66% and a CI of 1.6 were achieved. The diluted fraction of the second stage had an average solid concentration of 0.5%, as shown in Table 3.

Block FC was considered to be complete based on the solid concentration of the diluted fraction in the second stage. A third stage could be implemented, but this decision depends on the global process strategy and the desired solid concentration of the final effluent.

3.4. Integration of falling film freeze concentration, ice thawing and block freeze concentration

Falling film freeze concentration, fractionated thawing and block freeze concentration can be integrated in a global strategy to establish an industrial process to concentrate coffee extracts. In this process, the objective is to obtain an extract that is as concentrated as possible and to minimise the concentration of the effluent to avoid the coffee solid loss. Two streams, diluted and concentrated, are obtained in each technique. The process is presented in Fig. 7. The mass and solid concentration of the extract

is presented for each stream. The mass balance was achieved for a basis of calculation of 1000 kg/h of diluted coffee extract entering the process (Feed). Even though the process must be scaled up, mass balance can be applied to analyse the possible results at an industrial level.

The process starts with seven stages of falling film freeze concentration. The solid concentration at the end of each stage was calculated by Eq. (5). The concentrated fraction of each stage entered the next stage. After falling film freeze concentration, the ice is thawed to recover the occluded solids. This thawing can be achieved using the same equipment used for FFFC. The concentration obtained from the thawing process was calculated by Eq. (6). The thawing ended when the f values shown in Table 2 were reached. The diluted and concentrated fractions can be separated. At this point, 64% of the solids retained in the ice were recovered. The diluted fraction of the first thawing stage had 0.24% solids and was considered an effluent. The other diluted fractions can be mixed to obtain 574.8 kg/h of extract with 1.7% of coffee solids. This mixture can be freeze-concentrated by the block technique.

The results of block FC were calculated from the data reported in Table 3. A diluted stream with 0.4% of coffee solids was obtained after two stages of block FC. This stream can be mixed with the diluted fraction of the first thawing stage to obtain an effluent of 853.5 kg/h with 0.27% coffee solids. This final concentration is acceptable according to industrial standards. The concentrated fractions from the thawing stages and block FC can be mixed and re-circulated through the process. A mixture of 1108.1 kg/h with 5.5% of solids was obtained and can be mixed with the feed.

With the proposed process, the concentration of the extract increased from 5% to 32.6%. The concentration of the final effluent was 0.27%, comparable to industrial standards (Van Mil and Bouman, 1990; Van Pelt and Bassoli, 1990). The process results are presented in Table 4. Through the combination of the three techniques, the solute yield increased to 95%, the concentration index to 6.5, and the concentration efficiency to 99.2%. The results indicate the convenience of the process to concentrate coffee extract in comparison to FFFC. The process is comparable to the suspension system currently implemented in the coffee industry in terms of the concentration of the product and effluent.

Different variations of the process can be utilised to optimise energy consumption or cost. For example, an alternative process
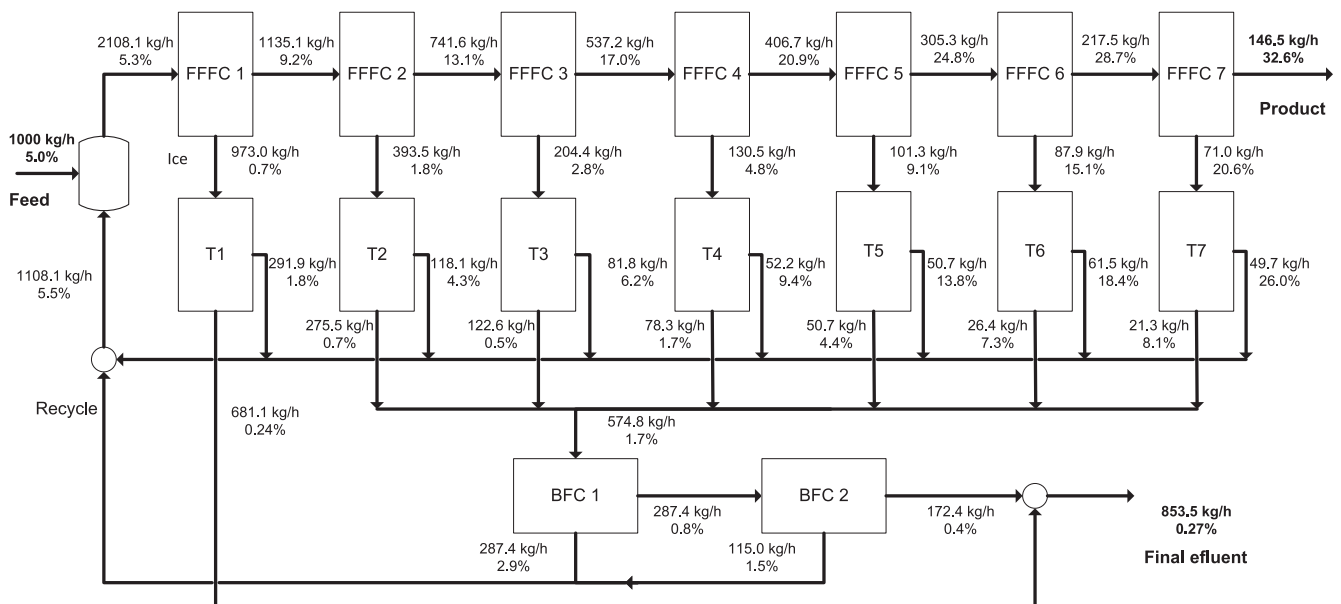

Fig. 7. Integrated process to freeze-concentrate coffee extract using falling film freeze concentration (FFFC), fractionated thawing (T) and block freeze concentration (BFC).

Table 4
Final results of the integrated freeze-concentration process. Solute yield (Y), Concentration index (CI) and concentration efficiency (Eff).

Technique	Y	CI	Eff (%)
Falling film freeze concentration (FFFC)	0.43	6.2	90.1
FFFC + fractionated thawing (T)	0.64	6.2	97.2
FFFC + T + Block FC	0.95	6.5	99.2

can be proposed by analysing the concentration of the ice in the three last stages of FFFC. These solid concentrations were higher than the solid concentration of the initial extract, so they can be re-circulated without going through the thawing stage. Applying mass balance, with this alternative only one block FC stage is required to obtain an effluent with a solid concentration less than 0.3%. The process would include seven stages of FFFC, four stages of thawing and one stage of Block FC, reducing costs and time. In the same way, other combinations of strategies can be performed. The technical viability of the current strategy has been shown in terms of the requirements of the final extract and the final effluent solid concentrations. From this point, the optimisation of the process and equipment sizing can be initiated. This process is in development for future studies.

4. Conclusions

An operative strategy to integrate falling film freeze concentration, fractionated thawing and block freeze concentration was proposed as an alternative to suspension freeze concentration of aqueous coffee extract. Falling film freeze concentration is effective for increasing the solid concentration of the extract to levels reported by industry. However, a large amount of solid is occluded in the ice. Fractionated thawing allows the recovery of the solids occluded in the ice. Block freeze concentration is able to obtain a final effluent with low solid content, reducing solids loss.

Falling film freeze concentration increased the concentration of the coffee extract 6.2 times. With fractionated thawing, 64% of the solids retained in the ice were recovered. By block freeze concentration, a high-purity effluent was obtained. Through the process, the coffee extract was concentrated from 5% to 32.5% with an effluent with 0.27% solids. The concentration efficiency increased to 99.2% and the solute yield to 95%. The process is an alternative to the industrial freeze concentration systems based on suspension technology, with the advantage of the simplicity of the falling film and block freeze concentration equipment.

Acknowledgements

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Behaviour of falling-film freeze concentration of coffee extract

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ABSTRACT

The behaviour of falling-film freeze concentration of coffee extract was studied through determining the solute inclusion in the ice produced in a single-plate freeze concentrator. The effect of the initial coffee mass fraction of the extract, the average ice growth rate and the film velocity were studied. The coffee extract at four coffee mass fractions (0.05, 0.15, 0.25 and 0.35 w/w) was freeze concentrated at three different cooling temperatures (-10, -15 and $-20\,°C$) and three flow rates (5×10^{-5}, 7.5×10^{-5} and $10 \times 10^{-5}\,m^3\,s^{-1}$). The solute inclusion in the ice and the effect of each parameter were determined. The coffee mass fraction, ice growth rate and film velocity affected the average distribution coefficient. The coffee mass fraction had the greatest effect on average distribution coefficient. The Chen model parameters to predict the average distribution coefficient and the concentration index were found. A logistical model was proposed to predict the concentration reached in successive stages, which tended to 35% at the studied intervals. The model showed an adjusted regression coefficient of 0.98 and the experimental values were within the 95% confidence intervals. The model can be used to predict the behaviour of falling film freeze concentration of coffee extract; this technique is an economic and simple alternative to conventional freeze concentration.

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1. Introduction

Freeze concentration (FC) is a technique used to remove water from solutions by cooling the solution until ice crystals are produced and separated (Sánchez et al., 2009). The final liquid fraction has a higher concentration than the initial solution because of the water removed in the form of ice. This technique is used in the food industry due to its ability to preserve sensitive properties in products such as coffee extract.

Depending on the growth of ice crystals, there are three techniques of FC, suspension FC, film FC (progressive or falling-film FC) and block FC (also known as freeze–thaw FC) (Aider and de Halleux, 2009; Boaventura et al., 2013; Sánchez et al., 2011a). Suspension FC is the most implemented technique in the coffee industry. This is an efficient technique to obtain high ice purity despite the high operational costs (Miyawaki et al., 2005; Qin et al., 2006; Sánchez et al., 2011a; Van der Ham et al., 2004).

The falling-film freeze concentration (FFFC) is a simple technique in which the solution to be concentrated is re-circulated on a cooled vertical plate. The fluid descends in a film, and an ice

sheet is produced by freezing. The ice forms a single layer on the cold surface. The solution is collected and re-circulated continuously (Sánchez et al., 2011b). FFFC has been studied with several food fluids (Belén et al., 2013; Chen et al., 1998; Flesland, 1995; Hernández et al., 2009, 2010; Raventós et al., 2007; Sánchez et al., 2010). Coffee extract freeze concentration has been studied using the block technique (Moreno et al., 2013, 2014b) and progressive FC (Miyawaki et al., 2005). Moreno et al. (2014a) studied falling-film freeze concentration to propose an alternative process to concentrate coffee extract.

The solutes retained in the ice sheets determine the concentration efficiency (Raventós et al., 2007). Although the solute can be recovered by partial thawing of the ice (Gulfo et al., 2013), a low amount of solute occluded in the ice is desired. One way to express the level of solid occlusion is the average distribution coefficient. The average distribution coefficient is defined as the ratio between the concentration of solute in the liquid fraction and the concentration of solute in the ice. Chen and Chen (2000) studied the solute occlusion of the ice in falling-film freeze concentration for model solutions. The authors proposed a correlation to evaluate the average distribution coefficient for model solutions and food fluids. The solute inclusion of the ice produced in FFFC has not been studied for coffee extract, and the effect of the ice growth rate and the fluid flow rate has not been determined. This information is useful in the

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Nomenclature

a	width of the ice sheet (m)	$U_{s,\infty}$	fluid film velocity (m s^{-1})
CI	concentration index (unitless)	V_{ice}	average ice growth rate (mm s^{-1})
f	liquid fraction (unitless)	$X_{s\,ice}$	coffee mass fraction in the ice (w/w)
g	acceleration due to gravity (9.8 m s^{-1})	$X_{s\,0}$	coffee mass fraction in the initial solution (w/w)
h	height of the ice sheet (m)	$X_{s\,liq}$	coffee mass fraction in the freeze-concentrated liquid fraction (w/w)
K	average distribution coefficient (unitless)		
m_{ice}	mass of the ice sheet (kg)	Y	solute yield (unitless)
$m_{s\,0}$	initial solute mass (unitless)	η	coffee extract viscosity (Pa s)
$m_{s\,liq}$	solute mass in the liquid fraction (kg)	ρ	coffee extract density (kg m^{-3})
m_0	initial mass (kg)	ρ_c	coffee solids density (kg m^{-3})
m_{liq}	collected liquid mass (kg)	ρ_{ice}	ice density (kg m^{-3})
n	number of stages (unitless)	ρ_w	water density (kg m^{-3})
Q	fluid flow rate (m^3 s^{-1})		
T	temperature (°C)		
t	time of freezing (s)		

design of falling-film freeze concentration systems as a simpler alternative than the suspension technique.

The aim of the present study was to evaluate the behaviour of coffee extract during falling-film freeze concentration at different coffee mass fractions, ice growth rates and film velocities on the plate and to obtain the parameters for average distribution coefficient modelling.

2. Materials and methods

2.1. Materials

Coffee extract was prepared from soluble coffee supplied by Buencafé Liofilizado de Colombia (Colombian Coffee Growers Federation, Colombia). The coffee was added to distilled water at 35 °C and mixed for 20 min. The samples were stored at 4 °C for 12 h.

2.2. Experimental design

The coffee extract was freeze concentrated using a complete factorial design with three variables as shown in Table 1. Four different coffee mass fractions were tested within the typical interval for freeze-concentration processes (Moreno et al., 2014a). Three plate temperatures were tested to achieve different ice growth rates. Finally, three fluid fluxes were adjusted to obtain different film velocities of fluid falling on the ice sheet.

2.3. Freeze concentration tests

In each test, 800 mL of coffee extract was freeze concentrated by the falling-film technique. The experimental setup is shown in Fig. 1. The coffee extract flows in a descending film over the cooling plates, and it was collected in a collector tank and re-circulated by a VGC-400 peristaltic pump (Seditesa, Spain) and a VFD007L2 frequency variator (Seditesa, Spain). The ice growth on the surface of

Table 1
Experimental design.

Variable	Level
X_s[a]	0.05, 0.15, 0.25, 0.35
T_P (°C)	−10, −15, −20
Q (m^3 s^{-1})	5×10^{-5}; 7.5×10^{-5}; 10×10^{-5}

[a] The coffee mass fraction (X_s) was expressed as a fraction (w/w). It can be converted to a percentage by multiplying 100.

the freezing plates was then removed in a batch operation. The plate had dimensions of 25-cm width and 20-cm height.

The coffee mass fraction of the liquid fraction and the ice were measured after one hour of processing by a Pal 100 refractometer (Atago, Japan). The coffee mass fraction is defined as the mass of coffee solids per unit of coffee solution mass. The relationship between Brix degrees and X_s is represented by the equation $X_s = 0.0087$ °Brix reported by Moreno et al. (2014c) for the same product used in the present work.

2.4. Mathematical model

The solid inclusion in the ice is determined by the average distribution coefficient. The concentration of the solute in the solid and liquid fractions can be calculated from this value. The average distribution coefficient is defined as the ratio of the coffee mass fraction of the ice to the coffee mass fraction of the freeze concentrated liquid as shown in Eq. (1).

$$K = \frac{X_{s\,ice}}{X_{s\,liq}} \tag{1}$$

The mathematical model used in the present work was proposed by Chen et al. (1998). The model expressed the average distribution coefficient as a function of the ice growth rate on the plate of a falling-film freeze concentrator and the film velocity of the fluid on the ice sheet produced.
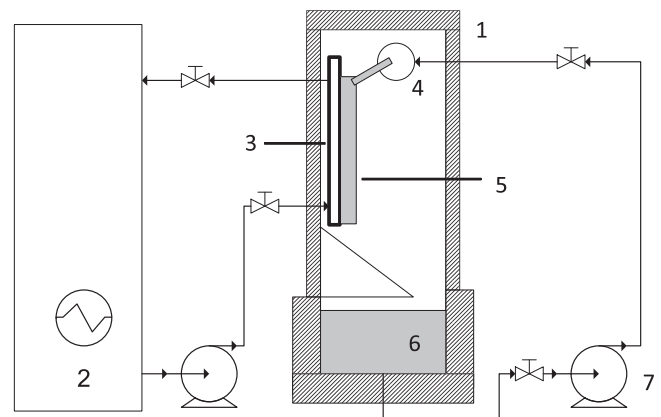

Fig. 1. Experimental setup. (1) Chamber; (2) cooling bath; (3) cooling plate; (4) distribution duct; (5) ice sheet; (6) collector vessel; (7) pump.

The average ice growth rate depends on the heat transfer rate, the degree of supercoiling and the thickness of the ice film, among other variables (Qin et al., 2009). The average ice growth rate is related to the plate temperature. The average ice growth rate was calculated from the mass of the ice sheet at the end of the process, the solid concentration in the ice, the process time, the ice density and the dimensions of the plate, according to the Eq. (2) (Chen et al., 1998).

$$\bar{v}_{ice} = \frac{m_{ice}(1 - X_{s\,ice})}{th a \rho_{ice}} \cdot 10^6 \ (\mu m \, s^{-1}) \tag{2}$$

Meanwhile, the fluid film velocity depends on the fluid flux regulated through the pump, the viscosity and density of the coffee extract and the dimensions of the plate. The film velocity is related to the mass transfer coefficient which is proportional to the fluid velocity to a power of 0.5 (Chen et al., 1998). Consequently, the Chen model includes the average ice growth rate and the falling film velocity to represent heat transfer and mass transfer rates. The fluid film velocity was calculated by Eq. (3). Eq. (3) is valid for films descending on a plate, in laminar flow and without superficial traction forces (Rane and Jabade, 2005; Perry et al., 1992).

$$U_{s,\infty} = \frac{Q}{a\left(\frac{3Q\eta}{\rho a g}\right)^{1/3}} \ (m \, s^{-1}) \tag{3}$$

The viscosity and density of the coffee extract were calculated from the average coffee mass fraction and the average temperature of the extract using Eq. (4) and Eqs. (5)–(7), respectively. Eqs. (4)–(7) were reported by Moreno et al. (2014c) for the same coffee used in the present work and the same temperature and concentrations intervals used in these tests.

$$\log_{10}\eta = 21.3 + 2.1X_{s\,liq} + \left(\frac{30 - T}{91 + T}\right)\left(31.5 - 12.7X_{s\,liq}^{2.53}\right) \tag{4}$$

$$\frac{1}{\rho} = \frac{X_{s\,liq}}{\rho_c} + \frac{(1 - X_{s\,liq})}{\rho_w} \tag{5}$$

$$\rho_c = 1878.1 - 40.76T + 1.035T^2 \tag{6}$$

$$\rho_w = 1000 + 2.30T - 0.11T^2 \tag{7}$$

Once the model variables were calculated, the correlation can be applied for prediction of the average distribution coefficient. This correlation is presented in Eq. (8). The equation proposed by Chen and Chen (2000) is composed of a term related to the coffee mass fraction, a term related to the heat transfer and mass transfer and an independent term.

$$K = A + BX_{s0} + C\frac{\bar{v}_{ice}}{U_{s,\infty}^{0.5}} \tag{8}$$

The assumptions of the model presented in Eq. (8) were the following: The solid distribution in the ice is uniform, the falling-film flows in laminar flow, the ice growth rate is the average of the ice growth rates during the process, the time of one stage is 60 min and the freezing process is developed in vertical plate.

The concentration index, the solute yield and the liquid fraction are variables used to evaluate the behaviour of the freeze concentration process. They can be calculated from the average distribution coefficient. The liquid fraction is the ratio of the mass of the concentrated liquid fraction to the mass of the original solution defined by Eq. (9) (Miyawaki et al., 2012; Nakagawa et al., 2010).

$$f = m_{liq}/m_0 \tag{9}$$

The solute yield was defined as the ratio of the mass of solute present in the separated liquid to the mass of solute present in the original solution and was calculated by Eq. (10) (Moreno et al., 2013; Nakagawa et al., 2010).

$$Y = m_{s\,liq}/m_{s0} \tag{10}$$

The concentration index was used to express the concentration of solutes reached after the FC process. The concentration index, CI, was defined as the ratio of the solid concentration in the liquid fraction to the solid concentration in the initial solution. CI is also known as relative concentration (Nakagawa et al., 2009).

$$CI = X_{s\,liq}/X_{s0} \tag{11}$$

Eq. (12) can be obtained by combination of Eqs. (9)–(11).

$$Y = f * CI \tag{12}$$

Eqs. (13) and (14) were obtained by combining Eqs. (1) and (12) and by the application of mass balance.

$$K = \frac{1 - Y}{CI - Y} \tag{13}$$

$$K = \frac{1 - f * CI}{CI - f * CI} \tag{14}$$

The average distribution coefficient can be predicted from Eq. (8) at different operational conditions of the freeze-concentration process. The amount of solute recovery and the concentration index can be calculated from Eqs. (13) and (14) for different liquid or ice fractions.

2.5. Statistical analysis

The parameters of Eqs. (8) and (16) were fit by the least squares regression method. A multiple regression analysis was performed using the statistical software SAS 9.0. The fit was evaluated by the adjusted regression coefficient. The 95% confidence intervals were calculated.

3. Results

3.1. Effect of the average ice growth rate and the fluid velocity

The effect of the ratio of average ice growth rate to fluid velocity to the power of 0.5 on the average distribution coefficient at different coffee mass fractions is shown in Fig. 2. The average distribu-
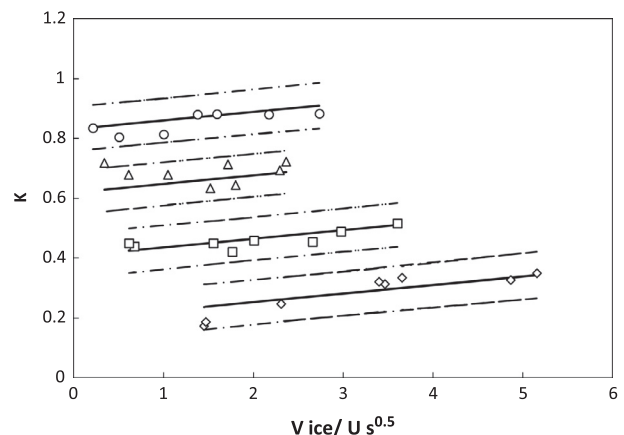

Fig. 2. Effect of the ratio between average ice growth rate and fluid velocity on the average distribution coefficient. Dots represent experimental data (Δ) X_s = 0.05; ($\bigcirc$) X_s = 0.15; ($\square$) X_s = 0.25; ($\Diamond$) X_s = 0.35. Continuous lines represent the predicted data. Segmented lines represent the 95% confidence intervals.

tion coefficient increased with the velocities ratio. A high value of K indicates greater occlusion of solids in the ice sheet and lower concentration efficiency. The ratio of velocities is proportional to the ice growth rate and inverse to the squared root of the fluid velocity. The ratio, and consequently the average distribution coefficient, increased with the ice growth rate and decreased with the fluid film velocity.

This result can be explained by the effect of the growth of the ice front. When the ice growth rate exceeds the velocity at which solids can be expelled from the ice crystals to the ice–liquid interface, the solids stay trapped in the ice sheet (Caretta et al., 2006; Moreno et al., 2014b; Petzold and Aguilera, 2009). On the other hand, a high fluid velocity can remove solids from the ice front to the falling liquid, decreasing the solid occlusion.

The effect of the average ice growth rate was most obvious at low solid concentrations, as reported by Moreno et al. (2014b). For low solid concentration, heat transfer is the controlling phenomenon during freeze concentration. Omran and King (1974) reported that mass transfer controls the FC for solid concentrations higher than 15% for sugar solutions and fruit juices. In the same way, Sánchez et al. (2010) reported values lower than 17% solids when the FC is controlled by heat transfer. In the present work, the effect of the average ice growth rate on the average distribution coefficient was highest for the lowest coffee mass fractions evaluated, which were 5% and 15%. This confirms the observations described by Omran and King (1974) and Sánchez et al. (2010).

The average ice growth rate varied from 0.2 to 4 μm s^{-1}. The highest rates were obtained at the lowest temperatures and concentrations of solids. Moreno et al. (2014b) and Nakagawa et al. (2010) reported that freeze concentration occurs for an ice growth rate lower than 6 μm s^{-1} for the block technique for model solutions. Chen and Chen (2000) studied rates under 2 μm s^{-1} for falling-film freeze concentration of food fluids. Meanwhile, Flesland (1995) reported rates between 0.2 and 2 μm s^{-1} for sucrose solutions FFFC. The use of low supercooling temperatures decrease energy consumption and decrease the ice growth rate (Rane and Padiya, 2011). Low ice growth rates decrease solid occlusion, but, at the same time, the productivity of the process can be affected; as a consequence, both aspects have to be analysed.

On the other hand, the average distribution coefficient decreased slightly with film velocity. Chen et al. (1998) reported a reduction of the average distribution coefficient with the film velocity for sugar solutions. Nevertheless, the effect was low for the studied intervals. In contrast, in the progressive tubular freeze concentration, where the pump provided velocities of 4.8 m s^{-1} (Miyawaki et al., 2005), this variable had a greater influence than FFFC. These results suggest that the film velocity had less influence in FFFC than other techniques because of the low velocity values of the free falling-film. However, the combined effect of the ice growth rate and the film velocity was significant as shown in p-values of the Table 2.

3.2. Effect of solid concentration

Fig. 3 shows the effect of the coffee mass fraction on the average distribution coefficient. K increased linearly with the solid content of the extract. The solid content had the greatest influence on the
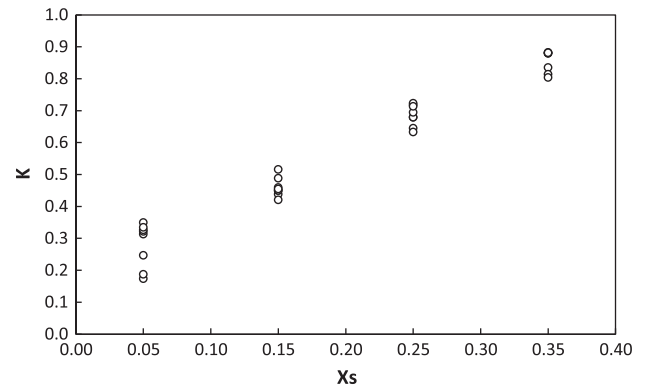

Fig. 3. Effect of coffee mass fraction on average distribution coefficient.

average distribution coefficient according to the slope of the line shown in Fig. 3 and the standardized parameters showed in Table 2. The same result was obtained for block freeze concentration. Moreno et al. (2014b) reported that the solid content of coffee extract primarily affects the separation efficiency (see Table 3).

The solid occlusion was increased with the coffee mass fraction mainly for two reasons. First, the diffusion velocity of solutes from the ice front to the falling-film of fluid decreased with the solid content because of the interaction between solute molecules (Hindmarsh et al., 2005; Petzold and Aguilera, 2009). Secondly, the viscosity of the fluid increased with the solid concentration; consequently, solute movement is slower and is therefore more easily trapped in the ice front (Moreno et al., 2014c; Raventós et al., 2007).

The average distribution coefficient increased from 0.2 to 0.9 when the coffee mass fraction increased from 0.05 to 0.35. This result shows that when the solid extract concentration rises above 35%, the value of K tends to one. At this value of K, the liquid fraction has the same concentration as the ice, and the concentration efficiency tends to zero. A high value of the average distribution coefficient is a problem in terms of the purity of the ice and the concentration efficiency. However, this problem can be solved by fractionated thawing of the ice sheet. Gulfo et al. (2013) proposed a partial thawing of ice sheets to recover the retained solutes. Moreno et al. (2014a) proposed a process to concentrate coffee extract by the integration of the ice thawing with FFFC and block FC. With this strategy, the operational limit of progressive FC can be overtaken, and the concentration efficiency can be increased.

3.3. Mathematical modelling

The parameters of Eq. (3) were obtained from experimental data. A multiple regression analysis was achieved to fit the parameters of the Chen model. The results are shown in Table 2. The parameters of the three variables were statistically significant for a confidence interval of 95%. These results confirm that the coffee mass fraction and the ratio of the average ice growth rate to the fluid velocity affected significantly the average distribution coefficient. An adjusted regression coefficient of 0.98 was obtained. According to these results, the average distribution coefficient in

Table 2
Multiple regression analysis of Eq. (15).

Variable	Estimator of the parameter	Standard error	Pr > |t|	Standardized parameter
Intercept	0.089	0.023	0.0006	0
X_s	2.123	0.067	<.0001	1.069
$V_{ice}/U_{s,\infty}^{0.5}$	0.028	0.006	<.0001	0.161

Table 3
Parameters of Eq. (8) for several food fluids.

Fluid	A	B	C	R^2
Coffee extract (present work)	0.09	2.12	0.03	0.98
Sucrose solution (Chen and Chen, 2000)	−0.14	2.06	0.14	0.96
Orange juice (Chen and Chen, 2000)	−0.12	2.18	0.12	0.98
Milk (Chen and Chen, 2000)	−0.02	0.36	0.08	0.96

FFFC of coffee extract can be calculated as a function of the coffee mass fraction of the extract, the average ice growth rate and the fluid film velocity by Eq. (15).

The smallest average distribution coefficient was obtained for the smallest solid concentration and the smallest ratio of average ice growth rate to film velocity, as shown in Fig 4. Experimental data were compared with the predicted data generated from Eq. (15) in Fig. 5. A good fit was obtained as evaluated by the adjusted regression coefficient.

$$K = 0.089 + 2.123 X_s + 0.028 \frac{\bar{v}_{ice}}{U_{s,\infty}^{0.5}} \quad R^2 = 0.98 \tag{15}$$

The experimental data, the predicted data generated from Eq. (15) and the 95% confidence intervals are shown in Fig 2. The three parameters had significant effect on the average distribution coefficient as shown in Table 2. The parameter with the greatest effect on the average distribution coefficient was the term associated with the coffee mass fraction, according to the standardized parameters presented in Table 2. This confirms the higher influence of solid concentration on the solute occlusion in the ice.

The parameters of Eq. (8) were compared with the parameters for other food fluids obtained by Chen and Chen (2000) in Table 2. The parameters of Eq. (8) for coffee extract were similar to those of orange juice, possibly due to the similar viscosity at low temperatures and similar freezing points (Moreno et al., 2014c; Ibarz et al., 2009). The behaviour of falling-film freeze concentration of orange juice reported by Sánchez et al. (2010) was similar to the FFFC of coffee extract (Moreno et al., 2014a).

3.4. Model for solid concentration prediction in successive stages

The behaviour of falling-film freeze-concentration at can be predicted from the Chen model presented in Eq. (15). A simulation of the process is presented based on the conditions of FFFC of coffee extract reported by Moreno et al. (2014a). The following parameters were used for the simulation: A coffee extract with 5% solids entered the first stage of FFFC. The average ice growth
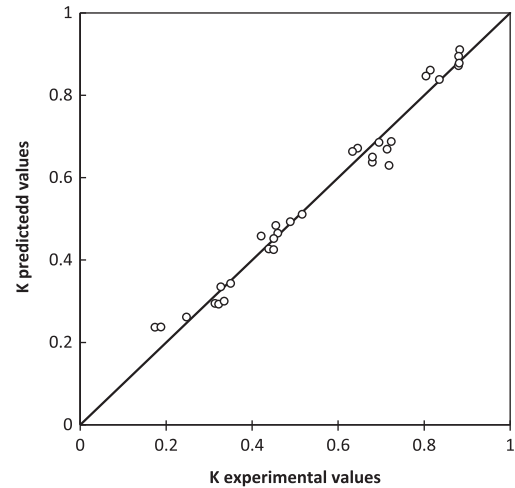

Fig. 5. Parity plot of the average distribution coefficient. Experimental vs predicted data from Eq. (15).

rate was 2 μm s⁻¹, and the film velocity was 0.5 m s⁻¹. The simulation parameters were established to compare them with experimental data reported by Moreno et al. (2014a,b,c) and Auleda et al. (2011) for falling-film freeze concentration of coffee extract and sugar solutions, respectively in a geometrical similar device. In addition, these parameters were all within the intervals tested in the present work.

The average distribution coefficient was predicted from Eq. (15). With this value, the solid concentration in the ice was calculated. After that, a mass balance was achieved assuming an ice fraction between 0.26 and 0.44 according to the data reported by Moreno et al. (2014a). These values were within the results obtained to generate the model in Eq. (15). With the ice fraction, the liquid fraction (f) was calculated. Subsequently, the solid concentrations of the extract were calculated from Eq. (13). This extract can be freeze concentrated again in a new stage, so the calculation process was repeated successively in six stages. The coffee mass fraction of the freeze-concentrated extract at each stage is shown in Fig. 6.

Starting with an extract of 5% coffee solids, the concentration of the freeze-concentrated extract tended to 37% solids at the end of the process. The concentration showed sigmoidal behaviour. The same behaviour was reported by Bayindirli and Ungan (1993) in the freeze concentration of apple juice and by Nonthanum and Tansakul (2008) for lime juice. At the beginning, the concentration

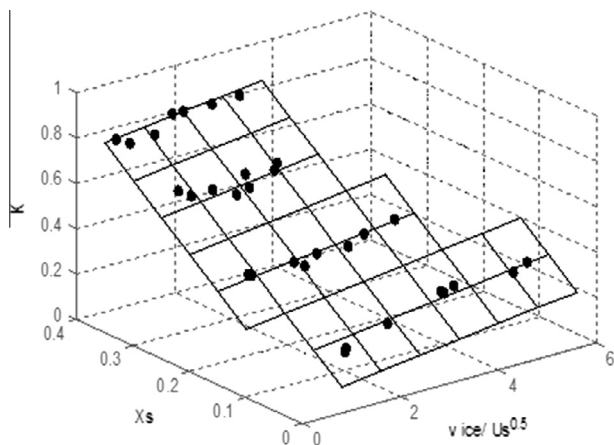**Fig. 4.** Modelling of the partition coefficient as a function of X_s, V_{ice} and U_s. Dots: experimental data; plane: predicted data from Eq. (15).
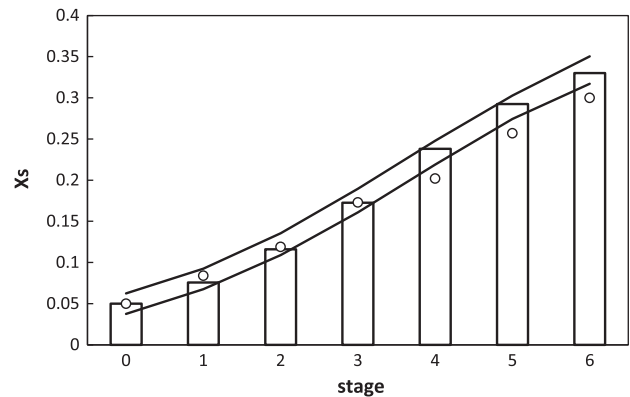

Fig. 6. Predicted values of successive stages of falling film freeze concentration of coffee extract. Bars: predicted data from Eq. (16). Lines: 95% confidence intervals. Dots (○): experimental data reported by Moreno et al. (2014a).

increased linearly. However, at the end, the concentration tends to an asymptotic value due to the thermodynamic limit when the extract was close to the eutectic point concentration.

The Chen model can be applied for one stage of FFFC. A mass balance is needed to calculate the solid concentration in successive stages. However, a model to predict the coffee mass fraction from the number of stages used in FFFC can be adjusted from data generated with Eqs. (13)–(15). The sigmoidal behaviour can be modelled with the logistic model presented in Eq. (16). The model predicts the coffee mass fraction of the concentrated liquid as a function of the initial coffee mass fraction and the number of stages. The parameters of the Eq. (16) were obtained by least squares regression with data generated from the Chen model.

$$X_{s\,liq} = \frac{0.55x_0}{(1.30x_0 + (0.55 - 1.30x_0)\exp(-0.55n))} \quad R^2 = 0.998 \quad (16)$$

The concentration reached after successive stages of FFFC can be predicted by Eq. (16). Fig. 6 shows the predicted data from Eq. (16) (bars), the 95% confidence intervals (lines), and the experimental data of FFFC of coffee extract reported by Moreno et al. (2014a). The experimental data presented a good fit with the models with an adjusted regression coefficient of 0.998. The generated parameters were significant for alpha 0.05. According to the simulation, after six stages of FFFC, a coffee extract of 31.8% solids was obtained. The concentration tended to 35%. Moreno et al. (2014a) reported an extract with 30.4% solids after six stages of FFFC starting with a 5% coffee extract. The results show that the Chen model accurately predicts the behaviour of falling-film freeze concentration of coffee extract. Likewise, the logistic model fit the data accurately for the first stages. A slight deviation of experimental data was observed for the three last stages. The differences can be attributed to the difference in the scale of the device reported by Moreno et al. (2014a,b,c) and those used in the present work. However, the model showed a trend for the solid concentration increasing. The logistic model is useful to predict the solid concentration in terms of the number of stages used in FFFC.

4. Conclusions

This study showed that the mass fraction of solids and the ratio of the average growth rate of the freezing front to the velocity of the fluid film affected significantly the average distribution coefficient of the ice produced during the falling-film freeze concentration of coffee extract. The greatest effect was obtained for the coffee mass fraction of the extract. The parameters of the Chen model were obtained for the prediction of average distribution coefficient of coffee extract. A logistic model was adjusted to predict the behaviour of successive stages of falling-film freeze concentration. In successive stages of falling-film freeze concentration, the coffee mass fraction tends to 35% at the studied conditions. From this information, it is possible to predict the coffee mass fraction of concentrated liquid and ice during falling-film freeze concentration at different operational conditions. The models properly fit the experimental data.

Acknowledgements

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Rheological Behaviour, Freezing Curve, and Density of Coffee Solutions at Temperatures Close to Freezing

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The physical properties of coffee solutions were determined for temperatures close to the freezing point. Rheological behaviour, freezing curve, density, and their relationship between coffee mass fraction and Brix degrees were determined for coffee mass fractions between 5 and 50% (wet basis) in the −6 to 20°C temperature interval. Values of viscosity varied from 1.99 to 1037 mPa·s and values of density from 1000 to 1236 kg·m⁻³. The freezing curve was generated using the undercooling method, giving values within freezing curves for food fluids. The results were used to generate mathematical models to predict viscosity, freezing point depression, and density as a function of coffee mass fraction and temperature.

Keywords: Coffee, Properties, Rheology, Freezing, Modeling, Freeze-concentration.

INTRODUCTION

Coffee is the second most traded commodity in the world after petroleum and one of the most consumed food beverages worldwide.[1,2] In the coffee industry, preservation of quality is highly important; for this reason, low temperature technologies are commonly implemented. Technologies, such as freeze-concentration and freeze-drying, are used to produce soluble coffee thanks to the flavour preservation promoted for using low temperatures.[3−5]

The measurement of physical properties of food fluids at low temperatures is relevant in the designing of processes and equipment for freezing technologies. The freezing curve of food fluids represents the state of food as a function of solid concentration and temperature. The state diagram is useful for process condition's selection in freezing technologies.[6] Flux behaviour comprehension

at temperatures just above the freezing point of fluids is required for sizing freeze-concentration equipment, such as falling film or tubular systems. In a similar way, determining of the viscosity and density is important to establish the power requirements for pumping during fluid processing.[7] Determining of mathematical models for physical properties and rheological behaviour at low temperatures and at different mass fractions allows applying calculation methods for designing and sizing equipment for freeze concentration.[8]

The coffee mass fraction or solid content can be measured by gravimetric techniques; however, °Brix determination can be a faster technique. There is no coincidence between °Brix and solid content because the darker colour of coffee solutions and the minimum fraction of sediments of coffee extract can affect the diffraction of light. A relationship between °Brix and coffee mass fraction has not been described.

There are several mathematical models for viscosity prediction of food fluids.[9−12] However, few studies report mathematical modeling of food fluids viscosity at low temperatures. In this sense, viscosities for sugar solutions, fruit juices, and dairy emulsions at low temperatures were reported by Falguera et al.,[13] Ibarz et al.,[14] Ruiz et al.,[15] Tavares et al.,[16] and Gabriele et al.[17] In the case of coffee solutions, viscosity and some physical properties have been reported by Sobolik et al.[18] and Telis-Romero et al.[19] for temperatures ranging from 20 to 80°C. The freezing curve of coffee extract was obtained by Thijssen[20] and Pardo et al.;[21] nevertheless, the authors report the dependence of data on the type of coffee and extraction methods. Additionally, Telis-Romero et al.[22] studied the physical properties of coffee extract. However, there are no reports of coffee solution's viscosity and physical properties for temperatures below 0°C. The modeling of viscosity and other physical properties at temperatures close to the freezing point could contribute to the design of processes and equipment for freezing technologies, such as freeze concentration, freeze drying, and coffee extract handling, in the coffee industry. The aim of the present work was to measure and model the relation of coffee mass fraction and °Brix, freezing curve, rheological behaviour, and density of coffee solutions at temperatures close to the freezing point.

MATERIALS AND METHODS

Materials

Colombian freeze-dried coffee (Buencafé, Buencafé Liofilizado de Colombia) provided by the Colombian Coffee Growers Federation was used to prepare aqueous solutions at different coffee mass fractions. Soluble coffee granules were dissolved in distilled water at 30°C to obtain samples at different concentrations.

Relationship between Coffee Mass Fraction and °Brix

Coffee solutions were prepared at different coffee mass fractions: $Xs = 0.10, 0.20, 0.30, 0.40$, and 0.50. The solutions were stored at 20°C. °Brix and index refraction were measured by refractometry (Atago Pal 100, Japan) at 20°C $\pm$ 1°C. The total dry matter was measured by weight-loss after oven drying at 103°C $\pm$ 1°C for 4 h according to technical standards.[23] Measurements were performed in quadruplicate.

Freezing Curve

The method of undercooling reported by Auleda et al.,[24] Ayel et al.,[25] and Jie et al.[26] was used to determine the freezing point of coffee solutions. Coffee solutions at $Xs = 0.10, 0.20, 0.30, 0.40$, and 0.50 were tested. The method consisted of cooling the sample by immersion in a cooling bath.

Four test tubes with 10 mL of the sample were immersed in a cooling bath (Polystat, Cole Parmer, USA). The cooling fluid was a mixture of ethylene glycol and water (53% w/w). The bath was temperature controlled at an interval from −35 to 150°C ± 0.01°C. The temperature of the bath was settled at −13°C ± 0.01°C. The test tubes were immersed after the bath reached the temperature. The test tubes contained a PT100-IP65 temperature sensor (Testo, Germany) located in the centre of the sample. The sensor had a 2-mm diameter and a precision of ±0.01°C, and it was connected to a 176 T2 datalogger (Testo, Germany). The temperature profile was stored in a PC. The freezing points were determined based on the cooling curves. The highest temperature reached after the undercooling due to nucleation corresponded to the freezing point. All of the experiments were performed in quadruplicate.

The method was previously standardized by measuring the freezing curve of sucrose solutions and comparing it with reported data.[10,24] The solutions were prepared with sucrose of analytic grade (Panreac Química, Colombia) at solid concentrations of 10–50% w/w and distilled water at 40°C. The solutions were stored and then freezing points were determined. The technique was accepted when the difference between experimental and theoretical data was within 5%. This difference may be attributed to the solute inclusion in ice.[27]

Rheological Measurements

Coffee solutions were prepared at $Xs = 0.05, 0.20, 0.35$, and 0.50. The solid content was verified by refractometry (Atago Pal 100, Japan) at 20°C ± 0.05°C using the equation obtained in the °Brix and coffee mass fraction measurements. The rheological behaviour of the samples was determined using a viscometer of coaxial cylinders (FungiLab Viscostar L, Barcelona, Spain) equipped with a device for low viscosity measurements, which is able to measure viscosities from 0 to 2000 mPa•s. The 18-mL sample of coffee solution was placed on the device with a concentric inside spindle. The device was immersed in a cryostat (Polysience Model 9505, USA, temperature range: −30 to 150°C; temperature stability ±0.5°C; readout accuracy: ±0.5°C). The viscometer was connected to a PC for data storing. The sample temperature was verified using a thermocouple type K (Precision ±0.5°C; measurement range: −50 to 1000°C) connected to a Datalogger (Testo 174 T4, Spain). Viscosity was measured after the sample reached the desired temperature.

The measurements were performed varying shear rate, sample temperature, and coffee mass fraction. Four shear rates were adjusted for each sample, from 5 to 120 s^{-1}, depending on the solution's viscosity. The limit was established by the maximum torque of the viscometer. Shear rates were calculated using an equation given by the viscometer to convert rotational speed into shear rate, $\gamma = 1.2236 * \omega$. Different temperatures above freezing point were tested (−6, −4, −2, 0, 2, and 4°C) depending on Xs, such that the solution remained in a liquid state. Four different coffee mass fractions (0.05, 0.20, 0.35, and 0.50) were tested. Experiments were performed in triplicate. The rheological behaviour of coffee solutions was modeled using the power law shown in Eq. (1):

$$\sigma = K \cdot \gamma^n. \tag{1}$$

An Arrhenius type equation (Eq. 2) was used to describe the effect of temperature on the viscosity of coffee solutions:[14]

$$\eta = k_0 \exp\left(\frac{E_a}{RT}\right). \tag{2}$$

Activation energy and frequency factor were fitted to the Xs dependent model[9] shown in Eqs. (3) and (4):

$$k_0 = a \exp (b * x_s), \tag{3}$$

$$E_a = c \exp (d * x_s). \tag{4}$$

Two general models to predict viscosity of coffee solutions as a function of temperature and coffee mass fraction simultaneously were fitted. Mathlouli and Genotelle (cited by [10]) proposed a general model for sucrose solutions shown in Eq. (5):

$$\log_{10} \frac{\eta}{\eta^*} = a_1 + a_2 x + \varphi \left(b_1 + b_2 x_s^{c_1} \right), \tag{5}$$

where

$$\varphi = (30 - T) / (91 + T). \tag{6}$$

Moreover, Sobolik et al.[18] proposed a model applied to coffee solutions at room temperatures and higher, as shown in Eq. (7):

$$\eta = exp \left(a_3 + a_4 x + a_5 x_s^2 + \frac{a_6 + a_7 x_s^2}{T + 273.15} \right). \tag{7}$$

Density

The density of coffee solutions at $Xs = 0.10$, 0.20, 0.30, 0.40, and 0.50 was determined by using a pycnometer at temperatures of 0, 5, 10, 15, 20, and $25°C \pm 0.01°C$. The pycnometers with the samples were immersed in a cooling bath at the settled temperature (Polystat Cole Parmer, USA). One blank sample had a PT100-IP65 temperature sensor (Testo, Germany) immersed to check the temperature. After the sample reached the temperature, the pycnometers were closed and weighed in an analytical scale (Mettler Toledo, USA). The measures were performed in triplicate.

Statistical Analysis

The average and the standard deviation of all data were calculated by SPSS 20.0 software. The unknown parameters of the models shown in Eqs. (1) to (10) were adjusted from experimental results using a linear regression fitting procedure with SPSS 20.0 for Eqs. (2) to (4) and a non-linear regression procedure for the other intrinsically non-linear models. The goodness of model fit was based on coefficient of determination (R^2), defined by the ratio between the regression sum of square and the total sum of squares. For the best fit, the R^2 value should be high.

RESULTS AND DISCUSSION

Relationship between Coffee Mass Fraction and °Brix

The °Brix are a measure of the soluble solid content of sugar solutions. The relationship between °Brix and coffee mass fraction is presented in Table 1. A linear relation was obtained as seen in Eq. (8). The equation allows measuring coffee mass fraction by refractometry. The equation can be modified to %Solids = 0.87·°Brix, in order to obtain solid percentage. Similar relationships are used in the coffee industry.[28] The refractive index was also measured and its relation with Xs is presented in Table 1. The relationship was fitted in Eq. (9). The models allowed calculating coffee mass fraction using a quick technique, such as refractometry.

TABLE 1
Xs and refractive index as a function of °Brix for coffee solutions

°*Brix*	Xs	*Refractive index*
11.3	0.094	1.3500
10.7	0.095	1.3488
11.4	0.103	1.3499
11.4	0.100	1.3499
22.8	0.183	1.3685
23.0	0.204	1.3661
21.3	0.191	1.3674
22.0	0.154	1.3680
33.2	0.305	1.3870
33.7	0.308	1.3890
34.3	0.297	1.3864
32.9	0.303	1.3870
41.3	0.381	1.4024
45.3	0.396	1.4087
44.5	0.393	1.4112
45.7	0.396	1.4080
55.4	0.494	1.4317
56.2	0.496	1.4428
60.3	0.493	1.4241
51.9	0.459	1.4290

$$Xs = 0.0087 \cdot °\text{ Brix}, \qquad R^2 = 0.991; \qquad (8)$$

$$nD = 1.334 + 0.155Xs + 0.092Xs^2, \qquad R^2 = 0.984. \qquad (9)$$

Freezing Curve

The cooling curves of coffee solutions were determined in quadruplicate as shown in Fig. 1. The super-cooling can be observed by the temperature decrease until the nucleation process begins. Subsequently, a temperature increase was produced due to the latent heat of the phase change. The highest temperature reached corresponded to the freezing point of the sample.[24] From the cooling curves at different *Xs*, an average freezing point was calculated and the freezing curve for coffee solutions was obtained (Table 2). Data correspond to average and standard deviation. The values are comparable to those reported by Thijssen[20] and Thaler[29] for different types of coffee. The difference with the freezing point of water (0°C) corresponded to the freezing point depression. Data were fitted to Eq. (10) for freezing point depression prediction as a function of coffee mass fraction. The regression coefficient obtained was 0.998, showing a good fitness.

$$FPD = 35.01 \bullet Xs^2 + 2.05 \bullet Xs, \qquad R^2 = 0.998. \qquad (10)$$

The freezing curve of coffee is between the freezing curves of glucose and sucrose, within the typical region of food fluids proposed by Auleda et al.[24] This can be attributed to the polysaccharides content of coffee extract, which varies from 20 to 75% dry basis,[29–31] depending on coffee variety, roasting, and extracting processes.
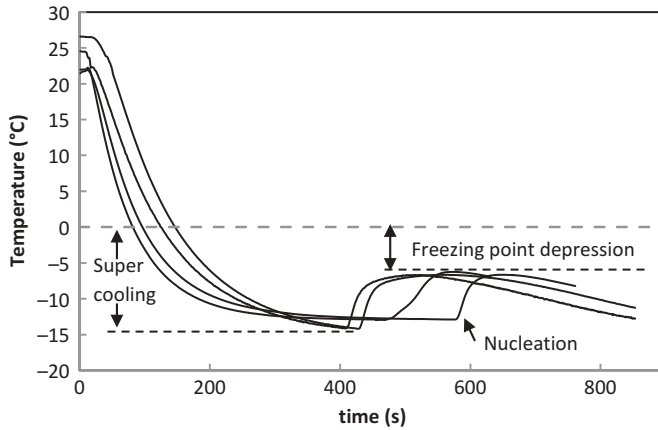
FIGURE 1   Cooling curves of coffee solutions. $Xs = 0.40$.

TABLE 2
Freezing point of coffee solutions as a function of coffee mass fraction

Xs	Freezing point (°C)
0.1	-0.76 ± 0.04
0.2	-1.92 ± 0.08
0.3	-3.45 ± 0.06
0.4	-6.54 ± 0.19
0.5	-9.79 ± 0.24

Rheological Measurements

Rheological behaviour

The rheograms of coffee solutions at Xs 5, 20, 35, and 50% and temperatures between -6 and 4°C are presented in Fig. 2, where shear stress (σ) as a function of shear rate (γ) is plotted. The dots correspond to experimental data and the lines were generated from parameters of Eq. (1), shown in Table 3. For this regression, coefficients of determination between 0.95 and 1.00 were obtained, suggesting good fitness of the models. A Newtonian behaviour was obtained with a flow index close to 1. Exponents of power law were less than 1 for high Xs and low temperatures, showing a slightly pseudoplastic behaviour. However, this result is not significant according to standard deviation. The Newtonian behaviour was reported by Sobolik et al.[18] for concentrated coffee solutions at higher temperatures in the interval from 0 to 1574 s^{-1}. Moreover, the consistency coefficient of Eq. (1) was increased with Xs and decreased with temperature, as indicated by several researchers.[7,32] Assuming a Newtonian behaviour, the values of viscosity of coffee solutions at the tested shear rates are presented in Table 2. As expected, the viscosity increased with increasing Xs and decreasing temperature. It was observed that influence of Xs on viscosity is greater than influence of temperature. These results are comparable with those obtained for other food solutions[15] and for coffee solutions at higher temperatures.[18,19]

Viscosity mathematical modeling

The viscosity dependence on temperature is presented in Table 4. As expected, viscosity increased with Xs and decreased with temperature. Data was fitted to Eq. (2) and the parameters
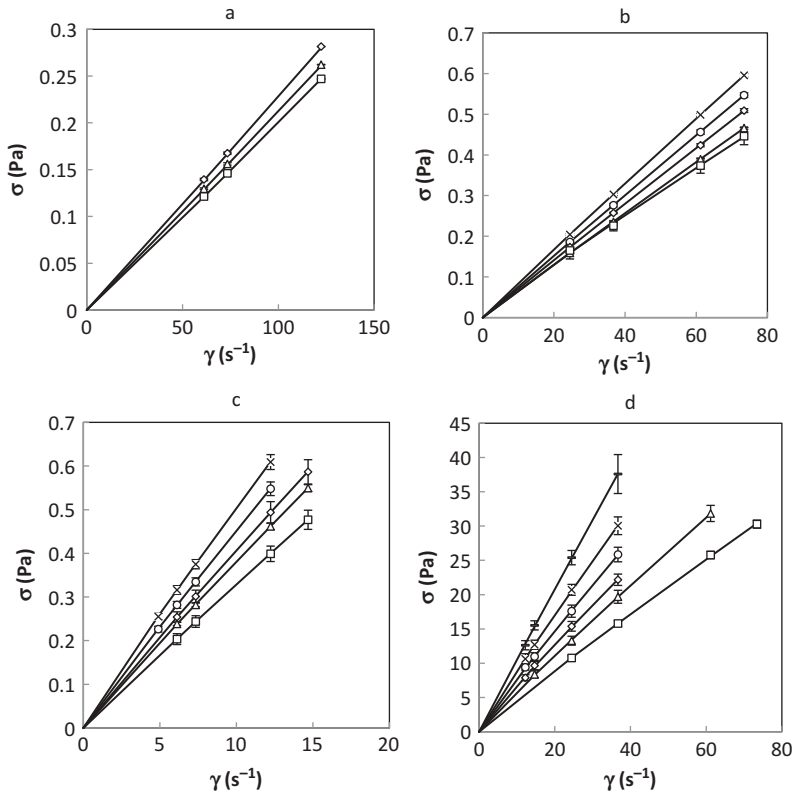
FIGURE 2 Rheogram of coffee solutions at 4°C ($\square$), 2°C ($\triangle$), 0°C ($\lozenge$), −2°C ($\circ$), −4°C ($\times$), and −6°C (—). (a) $Xs = 0.05$, (b) $Xs = 0.20$, (c) $Xs = 0.35$, (d) $Xs = 0.50$. Lines are calculated values using parameters given in Table 3.

for coffee solutions are presented in Table 5. The activation energy was increased with Xs, similarly to the result obtained by Telis-Romero et al.[19] for coffee solutions at temperatures between 20 and 80°C. On the other hand, Ko values decreased with Xs. A good fit between experimental and modeled data was obtained. The results are comparable with those reported for other food solutions at temperatures close to freezing.[13−15]

E_a for sucrose solutions was reported by Galmarini et al.,[33] for sucrose concentration of 35% with a value of 22.0 kJ·mol^{-1} between 20 and 34°C. For fruit juices, activation energy of 42 kJ·mol^{-1} is reported by Chin et al.[7] Likewise, the reported activation energy of untreated sugar cane juice is 36.79 kJ·mol^{-1}.[34] E_a value for mandarin juice at low temperatures is 33 kJ·mol^{-1}.[13] It is important to remember that E_a for water is 14.4 kJ·mol^{-1} and this value can be increased until 60 kJ·mol^{-1} with solid concentration.[35] E_a for coffee solutions obtained in the present study varied from 22.0 to 51.3 kJ·mol^{-1}, giving values within the range for food fluids.

General models. The regression analyses were performed for four different models of viscosity prediction as a function of Xs and temperature. Parameters of models, standard deviation, and coefficients of determination are given in Table 6. Values are comparable with those reported by Ibarz et al.,[9] Longinotti and Corti,[10] and Sobolik et al.,[18] although there are some differences in values due to specificity for coffee solutions at the present conditions. Equation (11) had the highest

TABLE 3
Parameters of power law (Eq. 1) for different coffee mass fractions and temperatures

Xs	T ($°C$)	K	n	R^2
0.05	0	$2.10*10^{-3} \pm 0.90*10^{-3}$	1.01 ± 0.01	0.99
	2	$1.91*10^{-3} \pm 0.10*10^{-3}$	1.01 ± 0.01	1.00
	4	$1.80*10^{-3} \pm 0.10*10^{-3}$	1.03 ± 0.01	0.99
0.20	−4	$9.14*10^{-3} \pm 0.40*10^{-3}$	0.97 ± 0.01	0.99
	−2	$8.02*10^{-3} \pm 0.60*10^{-3}$	0.98 ± 0.02	0.99
	0	$7.52*10^{-3} \pm 0.40*10^{-3}$	0.98 ± 0.01	0.99
	2	$6.90*10^{-3} \pm 0.20*10^{-3}$	0.98 ± 0.01	0.99
	4	$0.81*10^{-3} \pm 2.70*10^{-3}$	0.93 ± 0.08	0.95
0.35	−4	$5.67*10^{-2} \pm 0.47*10^{-2}$	0.95 ± 0.04	0.98
	−2	$4.92*10^{-2} \pm 0.40*10^{-2}$	0.96 ± 0.03	0.98
	0	$4.48*10^{-2} \pm 0.47*10^{-2}$	0.96 ± 0.04	0.98
	2	$4.20*10^{-2} \pm 0.14*10^{-2}$	0.96 ± 0.01	0.99
	4	$3.52*10^{-2} \pm 0.37*10^{-2}$	0.97 ± 0.04	0.98
0.50	−6	1.10 ± 0.29	0.98 ± 0.08	0.95
	−4	1.01 ± 0.18	0.94 ± 0.05	0.97
	−2	0.91 ± 0.16	0.93 ± 0.05	0.97
	0	0.79 ± 0.14	0.92 ± 0.05	0.97
	2	0.65 ± 0.12	0.94 ± 0.04	0.98
	4	0.53 ± 0.06	0.94 ± 0.03	0.99

TABLE 4
Viscosity of coffee solutions at different temperatures (T) and coffee mass fractions (Xs) (mPa·s)

	Xs			
T ($°C$)	*0.05*	*0.20*	*0.35*	*0.50*
4	1.99 ± 0.02	5.84 ± 0.08	32.9 ± 1.68	425.84 ± 16.94
2	2.13 ± 0.02	6.41 ± 0.07	36.8 ± 1.98	543.03 ± 44.73
0	2.29 ± 0.02	6.99 ± 0.09	40.7 ± 1.95	633.43 ± 54.68
−2		7.51 ± 0.18	45.6 ± 2.23	734.54 ± 58.74
−4		8.22 ± 0.12	51.1 ± 2.58	849.11 ± 74.89
−6				1037.24 ± 94.90

TABLE 5
Parameters of Arrhenius equation (Eq. 2) for coffee solutions at different Xs

Xs	Ko *(mPa·s)*	E_a *(kJ·mol^{-1})*	R^2
0.05	$1.39*10^{-4} \pm 0.82*10^{-4}$	22.0 ± 1.35	0.974
0.20	$7.60*10^{-5} \pm 3.10*10^{-5}$	25.9 ± 0.91	0.984
0.35	$1.20*10^{-5} \pm 1.40*10^{-5}$	34.1 ± 2.56	0.933
0.50	$9.27*10^{-8} \pm 0.00*10^{-8}$	51.3 ± 3.57	0.934

R^2 value; thus, this model seems to be capable of adequately describing viscosity of coffee solutions at different temperatures ($°C$) and coffee mass fraction at the investigated conditions:

$$\log_{10}\eta = 21.3 + 2.1Xs + \left(\frac{30 - T}{91 + T}\right)\left(31.5 - 12.7Xs^{2.53}\right). \tag{11}$$

TABLE 6
Parameters of mathematical models for prediction of coffee solution's viscosity

Equations	Parameters	R^2
(3), (4)	$a = 8.1 * 10^{-3} \pm 3.0 * 10^{-5}$ $b = -15.8 \pm 1.43$ $c = 18.9 \pm 1.93$ $d = 1.87 \pm 0.27$	0.955
(5), (6)	$a_1 = 21.3 \pm 1.18$ $a_2 = 2.10 \pm 0.34$ $b_1 = 31.5 \pm 1.76$ $b_2 = -12.7 \pm 0.65$ $c_1 = 2.53 \pm 0.21$	0.999
(7)	$a_3 = -7.03 \pm 19.5$ $a_4 = 1.01 \pm 9.48$ $a_5 = -38.7 \pm 79.8$ $a_6 = 2.16 * 10^3 \pm 5.31 * 10^3$ $a_7 = 1.60 * 10^3 \pm 2.1 * 10^4$	0.992

The other two models tested presented a slightly lower regression coefficient, but the adjustment was also satisfactory. Consequently, it is assumed that all models properly describe the viscosity of coffee solutions in the temperature and coffee mass fraction intervals evaluated in this study.

The parameters of Eq. (7) for coffee solutions at temperatures between 0 and 80°C were reported by Sobolik et al.[18] It is possible to compare a coincident point between the reported model and the model fitted in the present work. The viscosity of a coffee solution at Xs 0.20 and $T = 0$°C, generated by the model reported by Sobolik et al.[18] is 0.0085 Pa s and the corresponding value obtained in this work is 0.0069 Pa s, showing a difference of 18%. Sobolik et al.[18] compared their results with those obtained by Weisser in a previous work and found a maximum difference of 15%. This difference is attributed by the authors to the fact that viscosity depends on the type of coffee and its processing. The generation of parameters of this model at temperatures close to freezing expands the range of application of the model to sub-zero temperatures.

A plot of viscosity values as a function of temperature and Xs was generated using the parameters of Eq. (11) (Fig. 3). This figure showed that viscosity increased with Xs and decreased with temperature. The same result was reported by Diaz-Ocampo et al.[36] The curve on the surface represents the freezing point curve of coffee solutions using values obtained by Eq. (10). The viscosity values beyond the line do not have physical significance because they are below the freezing point. A higher dependence of viscosity on Xs than on T is evident in the studied interval.

Density

The density of coffee extract as a function of coffee mass fraction and temperature is shown in Table 7. As expected, density increases with Xs and decreases with temperature.[37] Values between 1036 and 1277 kg·m^{-3} were obtained. The results are similar to those reported by Telis-Romero et al.[22] between 1000 to 1200 kg m^{-3} for the same Xs intervals and higher temperatures. The density evidences a stronger dependence on solid content than on temperature. Density can be expressed as an average of coffee solids density and water density;[18] in turn, density of these components is dependent on temperature. The model fitted is shown in Eqs. (12) to (14). The regression coefficient was $R^2 = 0.989$, showing a good data fitting.
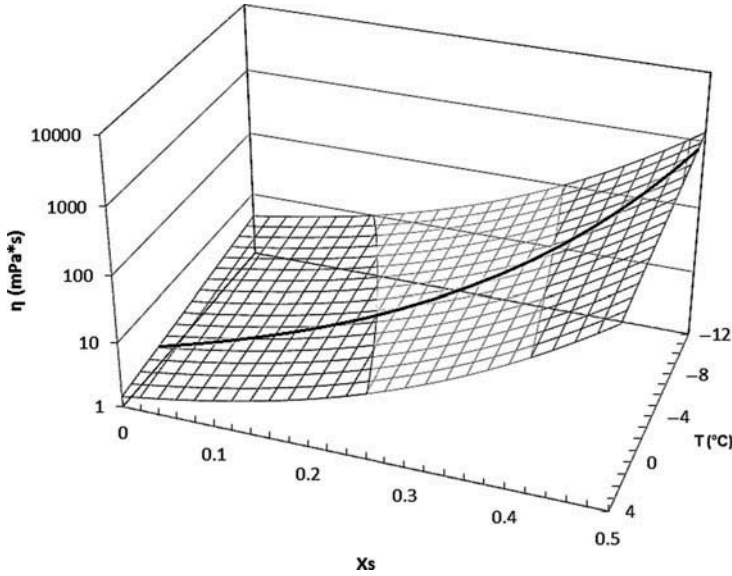
FIGURE 3 Coffee solution's viscosity as a function of temperature and coffee mass fraction. Predicted values using Eq. (11). The curve on surface represents freezing point curve for coffee solutions modeled by Eq. (10).

TABLE 7
Density of coffee extract (kg·m^{-3}) as a function of coffee mass fraction and temperature

Xs	T (°C)					
	0	5	10	15	20	25
0.1	1083.1 ± 11.7	1073.6 ± 12.2	1053.0 ± 14.3	1042.1 ± 11.4	1037.4 ± 8.2	1036.3 ± 8.9
0.2	1133.4 ± 11.3	1115.7 ± 13.0	1087.3 ± 14.9	1072.1 ± 15.0	1062.8 ± 8.4	1058.6 ± 16.4
0.3	1177.0 ± 9.6	1159.8 ± 19.9	1134.9 ± 22.6	1114.3 ± 17.2	1107.6 ± 20.7	1099.6 ± 7.5
0.4	1224.2 ± 8.4	1205.2 ± 5.8	1174.3 ± 16.3	1153.6 ± 13.2	1147.1 ± 13.7	1141.7 ± 26.6
0.5	1277.2 ± 3.5	1263.0 ± 11.9	1230.0 ± 4.4	1215.1 ± 6.9	1204.2 ± 10.9	1196.1 ± 16.5

$$\frac{1}{\rho} = \frac{Xs}{\rho_c} + \frac{(1 - Xs)}{\rho_w}, \qquad R^2 = 0.989; \tag{12}$$

where

$$\rho_c = 1878.1 - 40.76T + 1.035T^2, \tag{13}$$

$$\rho_w = 1000 + 2.30T - 0.11T^2. \tag{14}$$

CONCLUSIONS

The viscosity of coffee solutions at temperatures close to the freezing point can be predicted by three general models as a function of temperature and coffee mass fraction. The coffee solutions presented

a Newtonian behaviour. A slight pseudoplasticity was found at high concentrations and low temperatures, but this result was not significant. In turn, a linear relationship between coffee mass fraction and °Brix was found; this expression allows measuring coffee mass fraction by a simple technique, such as refractometry. Meanwhile, the freezing curve presented a quadratic behaviour within the zone for food fluids. Finally, the density of coffee solutions can be expressed as an average of coffee solids and water densities. The characterisation of physical properties, rheological behaviour, and freezing curve of coffee solutions is useful for designing operations, such as freeze-concentration and freeze drying. Mathematical models for °Brix, viscosity, freezing point depression, and density of coffee solutions were fitted. These models can contribute in designing technologies, such as freeze concentration and freeze drying in the coffee industry.

NOMENCLATURE

°Brix	Brix degrees
a, b, c, d	Parameters of Eq. (3) and Eq. (4)
a_1, a_2, b_1, b_2, c_1	Parameters of Eq. (5)
a_3, a_4, a_5, a_6, a_7	Parameters of Eq. (7)
E_a	Activation energy (kJ•mol^{-1})
FPD	Freezing point depression
Γ	Shear rate (s^{-1})
K	Consistency coefficient (Pa•s^n)
k_0	Frequency factor (mPa•s)
n	Flow behaviour index
Nd	Refractive index
R	Universal gas constant (8.314 kJ•mol^{-1}•K^{-1})
R^2	Coefficient of determination
T	Temperature (°C)
Xs	Coffee mass fraction (g coffee/g solution)
ρ	Density
ρ_c	Density of coffee solids
ρ_w	Density of water
σ	Shear stress (Pa)
Φ	Temperature correction
Ω	Rotational speed (rpm)
η	Viscosity (mPa·s)
η^*	Standard reference viscosity (1 mPa·s)

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