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ESTUDO SENSORIAL E FÍSICO-QUÍMICO EM DOCE DE LEITE PASTOSO

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Dissertação apresentada ao Programa de Pós Graduação em Medicina Veterinária da Universidade Federal Fluminense como requisito parcial para obtenção do Grau de Mestre. Área de concentração: Higiene Veterinária e Processamento Tecnológico de Produtos de Origem Animal.

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Dedico este trabalho à minha família e amigos, em especial aos meus pais Miriam S.V. Gaze e Reinaldo V. Gaze pelo apoio que nunca faltou.

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“Dizem que a vida é para quem sabe viver, mas ninguém nasce pronto. A vida é para quem é corajoso suficiente para se arriscar e humilde o bastante para aprender.

Clarice Lispector

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RESUMO

O Doce de Leite (DL) constitui-se de leite concentrado e sacarose, sendo produzido tipicamente na América do Sul. O objetivo deste trabalho foi conhecer as características sensoriais, físicas e químicas do Doce de Leite pastoso. A partir de sete marcas tradicionais do mercado, obtidas em suas embalagens originais, foram realizados testes sensoriais de aceitação empregando a escala hedônica, escala do ideal (JAR) e de intenção de compra. As amostras também foram submetidas à análise descritiva quantitativa (ADQ), e diferentes modelos estatísticos foram empregados para avaliar as semelhanças sensoriais entre grupos de amostras, as variáveis de importância preditiva e as variáveis afetivas importantes no momento da compra, o que resultou no Artigo I. O Artigo II teve como base o estudo do perfil físico-químico, que foi realizado através dos métodos de rotina, para quantificar umidade, cinzas, proteínas e lipídios, e os seguintes métodos instrumentais: HPLC – para quantificação de lactose, sacarose e glicose; ICP-OES – empregado na quantificação de sódio, cálcio, fósforo e potássio; CG-MS – utilizado na identificação de compostos voláteis; e, por fim, colorimetria – apta a quantificar os parâmetros de qualidade de cor *L**, *a**, *b**, *h**, *C** e diferença total de cor (*ΔE**).A discussão dos resultados desse segundo artigo empregou o teste de Correlação de Pearson e a Análise de Componentes Principais (ACP). Os DLs II, V e VI foram os que apresentaram maior aceitação e características mais semelhantes àquelas do produto ideal. As Redes Neurais Artificiais demonstraram melhor capacidade preditiva que o PLSR para identificar as variáveis de importância preditiva, que foram cor, viscosidade, adesividade oral e sabor caramelo. Foram identificados 32 compostos voláteis, *ΔE** demonstrou ser uma variável com boa capacidade de indicar diferenças do padrão de cor, a sacarose demonstrou ser o glicídio de maior predominância no produto e foi observado que as quantidades de lactose, cinzas, lipídios e proteínas estão diretamente relacionadas à presença da matriz láctea. Através do conhecimento da composição desse produto e da influência que os seus ingredientes tem sobre o perfil sensorial, o direcionamento das melhorias do processo produtivo se torna mais racionalizado. Como consequência, a satisfação do consumidor se torna mais acessível e os órgãos de fiscalização e as indústrias

passam a possuir maior base científica para aprimorar os padrões de identidade e qualidade do DL pastoso.

Palavras-chave: Doce de Leite, Aceitação, Escala do Ideal, ADQ, Redes Neurais Artificiais, HPLC, CG-MS, ICP-OES

ABSTRACT

The Dulce de Leche (DL) consists of concentrated milk with sucrose, typically produced in South America. The objective of this work was to investigate the sensory, physical and chemical characteristics of pasty Dulce de Leche (DL). From seven traditional brands in the market, obtained in their original packaging, sensory acceptance tests were performed using the hedonic scale, the Just-About-Right scale (JAR) and purchase intent. The samples were also subjected to quantitative descriptive analysis (QDA) and different statistical models were used to acess the sensory similarities between groups of samples, variables of importance in projection (VIP's) and major affective variables at the time of purchase, which resulted in Article I. Article II was based on the study of physicochemical profile, which was accomplished through the routine methods to quantify moisture, ash, protein and fat, and the following instrumental methods: HPLC - for quantification of lactose, sucrose and glucose; ICP- OES - used in the measurement of sodium, calcium, phosphorous and potassium; GC -MS - used to identify volatile compounds; and finally colorimetry - able to quantify the color quality parameters L^*, a^*, b^*, h^*, C^* and the total color difference (ΔE^*) The discussion of the results of this second test used Pearson Correlation and Principal Component Analysis (PCA). The DLs II, V and VI were those with greater acceptance. Artificial Neural Networks have shown best predictive power than PLSR in identifying variables of predictive importance, which were color, viscosity, adhesiveness and oral caramel flavor. 32 volatile compounds were identified. ΔE^* proved to be a variable with good capacity in indicating differences in the pattern of color, sucrose proved to be the most predominant carbohydrate in the product and it was observed that the amounts of lactose, ashes, lipids and proteins are directly related to the presence of milk matrix. Through knowledge of the composition of the product and its ingredients influence that has on the sensory profile, targeting the improvement of the production process becomes more streamlined. As a result, consumer's satisfaction becomes more accessible and oversight agencies and industries shall possess greater scientific basis to enhance the standards of identity and quality of the pasty DL .

Keywords: Dulce de Leche, Acceptability, Just-about-right scale, QDA, Artificial Neural Network, HPLC, CG-MS, ICP-OES.

1 INTRODUÇÃO

O estudo do perfil sensorial e físico-químico é de grande valia para a indústria laticínia, uma vez conhecendo as características de um produto ideal é possível se pensar em métodos menos onerosos de produção gerando um produto altamente competitivo (MACFIE, 2007). Os limites físico-químicos que são seguidos para a produção do DL são estabelecidos pela atual legislação, em consonância com a do Mercado Comum do Sul (MERCOSUL), através da Portaria nº354 (BRASIL, 1997), Regulamento Técnico de Identidade e Qualidade do Doce de Leite.

O equilíbrio entre elaborar um produto de alta aceitação, viável economicamente, e dentro dos padrões físico-químicos estabelecidos pelos órgãos oficiais é um desafio diário de toda indústria (MACFIE, 2007). Para se ter um maior controle da qualidade físico-químico, cada vez mais a indústria e os órgãos oficiais requerem metodologias rápidas e precisas. Junto a essa evolução e à necessidade que o consumidor vem tendo de saber a composição do produto que ele está adquirindo, é necessário o estabelecimento de novos parâmetros e limites.

A aceitação do consumidor é crucial para o desenvolvimento, reprodução e melhoramento de produtos. Tendo isso em vista, as escalas hedônica, do ideal e de atitude são as análises afetivas mais comumente utilizadas (MACFIE, 2007). Juntamente com a Análise Descritiva Quantitativa (ADQ), que promove a descrição qualitativa e quantitativa do produto através de uma equipe de julgadores treinados, os resultados desses testes afetivos fornecem uma base de dados para se determinar os atributos sensoriais mais importantes na aceitabilidade do produto pelo consumidor final (STONE; BLEIBAUM; THOMAS, 2012).

Além da análise de variância (ANOVA) procedida de testes de diferença de média, a estatística multivariada consta como uma importante ferramenta para se elaborar mapas descritivos e correlações entre diferentes metodologias. A Análise de Componentes Principais (ACP) vem sendo classicamente utilizada na representação gráfica da ADQ a fim de destacar as características mais marcantes respectivas de cada amostra testada (STONE; BLEIBAUM; THOMAS, 2012). Novas análises multivariadas vêm sendo adaptadas à análise sensorial com o objetivo de identificar os “drivers” que estão mais relacionados ao comportamento afetivo do consumidor, obtido através de testes como de aceitação e intenção de compra ou consumo. Uma ferramenta empregada com sucesso para esta finalidade são os testes de regressão, sendo de alta adequabilidade à ciência sensorial a Regressão de Quadrados Mínimos Parciais (PLSR – “Partial Least Squares Regression"), Logística (LR –"Logistic Regression"), por Componentes Principais (PCR – “Principal Componente Regression”) e Multilinear (MLR - "Multilinear Regression") (NAES; BROCKHOFF; TOMIC, 2010). Visando uma melhor adequação aos órgãos dos sentidos e à complexidade de informações que estes processam, métodos não lineares vem sendo desenvolvidos. As Redes Neurais Artificiais (ANN - "Artificial Neural Network") utilizam a tecnologia da informação para simular as diversas vias nervosas evocadas através das percepções sensoriais com o objetivo de, como nas regressões, identificar os “drivers” mais importantes para a percepção afetiva do consumidor. As ANN se moldam com destreza às matrizes alimentares mais complexas do ponto de vista sensorial, que são altamente heterogêneas entre si, trazendo resultados verossímeis (CRUZ, 2011; BAHRAMPARVAR; SALEHI; RAZAVI, 2013).

Em função de haver uma lacuna na literatura recente com relação ao perfil sensorial e físico-químico do DL, a presente dissertação visa: (i) estabelecer os “drivers” de aceitação e compra do DL pastoso; (ii) caracterizar sensorialmente o DL ideal; (iii) testar metodologias estatísticas multivariadas sobre os dados sensoriais dessa matriz; (iv) caracterizar esse produto físico-quimicamente; (v) testar metodologias instrumentais para a análise de carboidratos, voláteis e minerais (respectivamente, HPLC, CG-MS e ICP-OES); (vi) e discutir a influência desses parâmetros sobre os aspectos sensoriais.

2 **FUNDAMENTAÇÃO TEÓRICA**

2.1 DOCE DE LEITE PASTOSO

O Doce de Leite (DL) é um derivado lácteo produzido basicamente a partir da desidratação do leite fluido e/ou reconstituído, em condições de temperatura e pressão que variam de acordo com o fabricante, e adicionado de sacarose. A esse produto também pode ser adicionado o bicarbonato de sódio. Esse composto incrementa a coloração amarronzada, típica de compostos gerados a partir reação de Maillard - que é favorecida quando o pH do DL se encontra entre 6.0 e 7.0. Além disso, essa adição evita a formação de grumos resultantes da desestabilização da caseína, dada quando compostos ácidos são concentrados durante o processo de evaporação (PERRONE, 2011). A reação de caramelização também interfere na cor do DL devido ao seu alto teor de glicídos.

O DL é fabricado basicamente na América Latina, principalmente na Argentina e Uruguai e, em menor escala, no Chile, Paraguai, Brasil e Bolivia (ZALAZAR; PEROTTI, 2011). Além do consumo interno, o Brasil exporta para outros mercados, como para a União Européia (EU) e para a Cooperação Econômica da Ásia e do Pacífico (APEC). A sua importância nutricional está relacionada à concentração dos diversos componentes do leite, como proteínas, glicídios e sais minerais, além da sacarose que, juntamente à lactose, oferece ao DL a propriedade de ser um alimento altamente energético (OLIVEIRA, 2009).

2.2 ANÁLISES FÍSICO-QUÍMICAS

No Brasil alguns autores já avaliaram os aspectos físicos e químicos do DL, como DEMIATE, KONKEL e PEDROSO (2001) e SILVA *et al.*(2007), encontrando uma enorme variedade de padrões dessa matriz.

Os requisitos físico-químicos básicos estabelecidos pela Portaria Nº 354 (BRASIL, 1997) são: umidade (no máximo 30% - 30g/100g de doce de leite); matéria gorda (entre 6,0 e 9,0% - 6,0 a 9,0g/100g de doce de leite); cinzas (no máximo 2,0%

- 2,0g/100g de doce de leite); e proteínas (no mínimo 5,0% - 5,0g/100g de doce de leite).

A cor dos derivados lácteos é determinada por diversos fatores variando desde os relacionados à alimentação do rebanho (composição da matéria-prima) até a adição de corantes artificiais feita pelas indústrias (WADHWANI; McMAHON, 2012). Esse é um atributo sensorial de extrema importância, principalmente naquilo que tange à aparência, influenciando diretamente na aceitação por parte do consumidor (STONE; BLEIBAUM; THOMAS, 2012). Generalizando, a cor e a aparência do alimento criam uma expectativa no consumidor que afeta o modo como ele observa e se comporta diante do produto (WADHWANI; McMAHON, 2012), também exercendo influência direta nos padrões de identidade e qualidade dos derivados (DELWICHE, 2004).

Glicídios são compostos orgânicos de composição básica de carbono, hidrogênio e oxigênio, mas que também pode possuir outros elementos associados, e estão vinculados a dietas energéticas (FEENEMA, 1996). Os glicídios simples são chamados açúcares. Estes, como glicose, sacarose e lactose, possuem características que podem influenciar diretamente na qualidade sensorial do produto. Dentre estas características, se destacam as seguintes: poder edulcorante, solubilidade em água e fácil formação de xaropes, formação de cristais quando a água é evaporada a partir de suas soluções, capacidade de serem prontamente fermentados por microrganismos e de evitar o seu desenvolvimento em altas concentrações, escurecimento do produto através da caramelização ou Reação de Maillard ao aquecimento e formação de corpo e paladar diferenciado quando em solução (POTTER e HOTCHKISS, 1995).

Apesar de existirem alguns estudos acerca da composição centesimal do DL, existe uma lacuna de informação sobre o seu perfil químico, principalmente através do uso de técnicas instrumentais como a espectrofotometria de massas acoplada à Cromatografia Gasosa (CG-MS), a espectrometria de emissão óptica com plasma indutivamente acoplado (ICP-OES) e a cromatografia líquida de alta eficiência (HPLC) (OLIVEIRA, 2009). A CG-MS possui valor na identificação de componentes voláteis dos alimentos ao se obter o índice de retenção linear (LRI) dos compostos retidos na coluna (CONDURSO, 2008; PANSERI; 2011; PADILLA, 2014). A ICP-OES é uma técnica que que permite a identificação e quantificação de elementos presentes tanto em grandes, quanto pequenas quantidades e até mesmo traços em matrizes alimentares complexas (NAOZUKA, 2011). Dentre os componentes do DL, os carboidratos possuem maior importância devido à influência que o processamento tecnológico exerce sobre eles. Os dois carboidratos mais importantes do DL são a lactose e a sacarose (DEMIATE, 2001; OLIVEIRA, 2009). No entanto não são encontrados na literatura recente trabalhos com DL quantificando carboidratos por cromatografia líquida de alta performance (HPLC), que é comumente vista em outros derivados lácteos, como leite (GIMÉNEZ, 2008; ERICH, 2012) e iogurte (CRUZ, 2013; VÉNICA, 2013; CRUZ, 2012).

2.3 ANÁLISES SENSORIAIS

A análise sensorial é uma ciência que possui aplicabilidade em "marketing", uma vez que permite correlacionar padrões de tecnologia de fabricação com as impressões que o produto causa no consumidor (MACFIE, 2007; STONE; BLEIBAUM; THOMAS, 2012). Os testes sensoriais afetivos, com consumidores, buscam quantificar os impactos positivos e negativos que os produtos teste geram. Dessa forma, atuam como ferramentas importantes na obtenção do perfil sensorial de um produto adequado ao mercado consumidor. Para tal, podem ser feitas correlações entre a aceitação e a escala do ideal ("Just-about-right scale" - JAR), através da Análise de Penalidades (PA) (CADOT, 2010; LEE, 2011). O método estatístico de Regressão Logística (LR) pode ser utilizado para correlacionar os diversos testes afetivos à escala de intenção de compra (como uma variável resposta dicotômica), fornecendo informações sobre quais atributos são mais importantes no momento da compra (GARCIA, 2009; CRUZ, 2011). Os testes sensoriais descritivos podem ser utilizados para se obter as intensidades de percepção de descritores, que são classicamente levantados através da Análise Descritiva Quantitativa (ADQ), empregando um painel treinado (STONE; BLEIBAUM; THOMAS, 2012). Com a finalidade de rebuscar o perfil sensorial do produto, os testes afetivos e os descritivos podem ser correlacionados entre si através de estatística multivariada, como o Mapa de Preferência (MACFIE, 2007), Regressão por Mínimos Quadrados Parciais (PLSR) (KRISHNAMURTHY, 2007; BAYARRI, 2011; VILANOVA, 2012) e Redes Neurais Artificiais (ANN) (KRISHNAMURTHY, 2007; BAHRAMPARVAR, 2013). Dessa forma, se torna possível chegar a conclusões sobre quais atributos e suas respectivas intensidades têm maior influência na aceitação do produto.

3 DESENVOLVIMENTO

3.1 ARTIGO 1: OPTIMIZATION OF THE DULCE DE LECHE PROCESSING: CONTRIBUTIONS OF THE SENSOMETRIC TECHNIQUES

Optimization of the dulce de leche processing: contributions of the Sensometric techniques

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ABSTRACT

Sensometric techniques for the production of dulce de leche with optimal sensory profile and high acceptance by consumers were evaluated. Dulce de leche samples available in the Brazilian market were submitted to the development of sensory profile by quantitative descriptive analysis and acceptance test, as well sensory evaluation using the just about right scale (JAR) and purchase intent. Moreover, the ideal sensory characteristics of dulce de leche were determined. The results were evaluated by principal component analysis (PCA), hierarchical cluster analysis (HCA), partial least squares regression (PLS), artificial neural networks (ANN) and logistic regression (LR). Overall, a significant product acceptance is related to intermediate scores of the sensory attributes in descriptive test, and this trend was observed even after consumer's segmentation. However, there is need for standardization of certain attributes, since no product was characterized as ideal for the attributes evaluated in this study. The results obtained by sensometric techniques showed that optimizing an ideal dulce de leche from the sensory standpoint is a multidimensional process, with necessary adjustments on the appearance, aroma, taste and texture of the product for better consumer's acceptance and purchase. In industrial terms, this means changing the parameters used in the thermal treatment and quantitative change of the ingredients used in the formulations.

Key-words: sensometric technique, dulce de leche, optmization

INTRODUCTION

Multivariate statistical techniques are very useful for analyzing complex data obtained for consumer and trained panel, as they are able to provide a spatial representation of the experimental data (Ennis and Ennis, 2013, Zielinski et al., 2014). In addition, they proportionate the acquisition of the drivers of consumer liking and purchase intent, which is a popular concept frequently used in sensory and consumer research (Bi, 2013). Indeed, when it is noted differences among foods products that may drive consumer liking and purchase intent, it is helpful to visualize a space in which each possible product is placed (Cadena et al., 2012). Another outcome is consumer's food choices, which are complex interactions between the product and the consumer as well as the consumer’s personality and the previous familiarity and experience with the product (Cadena et al., 2013)

Dulce de leche (DL) is a dairy-based product, produced mainly from the dehydration of fluid milk under conditions of temperature and pressure varying according to the manufacturer, with added sucrose. Sodium bicarbonate can also be added to the milk, increasing the typical brown color caused by the Maillard reaction, which is favored at pH 6-7, and avoiding the formation of lumps resulting from the concentration of acidic compounds generated during evaporation (Perrone et al., 2011). DL is manufactured and consumed in Latin America, especially Argentina and Uruguay and to a lesser extent in Chile, Paraguay, Brazil and Bolivia (Zalazar and Perotti, 2011). In Brazil, the production is performed exclusively by small dairy producers, without control of the operational parameters, resulting in products with different physicochemical properties, with direct influence on the sensory characteristics. The consumer market is basically formed by two groups: the end consumers and the institutional consumers, formed by the food service and the food industry. The institutional segment is a large market, represented by fast food chains, ready prepared food, ice cream shops, confectionery, and wholesale centers. In addition, hotels, motels, convenience stores and board services have also acquired this product in the form of mini portions (Milkpoint, 2013).

The product quality depends on the continuous consumer satisfaction with respect to the sensory attributes, thus it is necessary to evaluate the relevant attributes for acceptance and purchase intent of a food product. In this context, this study aims to identify the possibilities of improvement of dulce de leche available in the Brazilian market, identifying relevant sensory attributes for acceptance and purchase intent. Given the multidimensional nature of the study, multivariate statistical techniques were used to analyze the results, such as Partial Least Squares Regression (PLS), artificial neural networks (ANN) and logistic regression (LR). The results of this study may be useful to provide information for dairy companies to make decisions, such as the development and marketing of new products and / or the reformulation of existing products, besides establishing quality control specifications.

MATERIAL AND METHODS

Samples

Seven commercial brands of dulce de leche were purchased from dairy companies inspected by the Brazilian Federal Inspection Service (SIF), which enables the marketing throughout the Brazilian territory. The samples were acquired right after processing so shelf life was not considered as a factor in this study. Then, samples were coded as I, II, III, IV, V, VI and VII to maintain the confidentiality of the trademarks. The ingredients used in manufacturing the product, as well as the nutritional composition displayed on the label, are shown in Table 1. The samples were presented in randomized and balanced manner for both the descriptive analysis as consumer tests, according to Mac Fie et al. (1989).

Sensory profiling (Quantitative Descriptive Analysis, QDA)

To quantify the descriptive attributes of the samples, Quantitative Descriptive Analysis (QDA) was performed. This technique is traditionally used in the evaluation of sensory profiling of processed foods, especially dairy products (Kaaki et al., 2012; Albenzio et al., 2013; Murtaza et al., 2013; Pimentel et al., 2013).

In the recruitment stage, 40 assessors were evaluated regarding their oral health status, interests, schedule availability, ability to verbal descriptions of sensory perceptions and use of scales. In the selection stage, a triangle test was used to check for differences (Stone et al., 2012), in which assessors evaluated the perception of sweetness in water solutions containing different concentrations of sucrose (0.45% and 0.65% w/v). Four replications were carried out, in which the assessors should present at least 75% accuracy. Fifteen assessors were selected for the training stage. During training, the sensory attributes were collected using the Kelly's repertory grid method (Morais et al., 2014a). Then, a meeting with the assessors was performed to define the final list of attributes as well as their references of weak and strong intensity. The training stage consisted of nine sessions lasting an hour each, totaling 9 hours. A descriptive vocabulary was drawn up and the intensity terms and reference materials were defined (Table 2) (Moskowitz, 1983). The performance was monitored at the end of the training sessions in triplicate using the samples with markedly different sensory characteristics and presenting the pre-established attributes. Data were obtained through a non-structured evaluation sheet containing the attributes in a 15 cm linear scale. From these data, 5 assessors were eliminated, forming a trained team of 10 assessors, 4 men and 6 women aged between 23 and 42 years, which meets the recommendations of Heymann et al (2012), who suggested at least 8 and preferably 10 assessors as a suitable number for implementation of QDA. The whole process was conducted in individual booths at 25 °C, with the samples presented in randomized and balanced way in disposable plastic cups coded with three-digit numbers, for trial of oral attributes (Mac Fie et al, 1989.); in watch-glasses for appearance attributes; and in beakers covered with watch-glasses for aroma attributes. Unsalted cracker biscuits (Piraquê, Rio de Janeiro, Brazil) and water for cleansing the palate were provided at all stages.

Consumer test

The consumer tests were carried out under laboratory conditions, at the Sensory Analysis Laboratory of the Universidade Federal Fluminense (UFF), with samples served in plastic cups in a randomized and balanced manner. Cracker biscuits and mineral water were provided for cleansing the palate between the samples. One hundred and twenty-five consumers participated in the trial, aged between 15 and 57 years, being 37 men and 88 women.

Before the sensory tests, the assessors completed and signed a written consent to participate the tests, stating that they were physically fit for that. Acceptance testing was conducted using a nine-point hedonic scale (9 - like extremely, 1 - dislike extremely) to assess the following attributes: appearance, aroma, taste, texture and overall acceptance, and the purchase intention was assessed by a five-point scale (1- definitely would not buy, 5 - I definitely would buy) (Cruz et al, 2012). The attributes color, sweet taste, caramel taste, and consistency were evaluated using just about right scale of 9 points, with 9 - extremely over than the ideal; 5 - Ideal, and 1 - extremely less than ideal (Morais et al., 2014b; Chollet et al., 2013).

Data analysis

Overview of sensometric techniques

Partial Least Squares Regression (PLS) is a method widely used in sensory analysis using both consumer and sensory descriptive analysis by a trained panel, enabling the identification of positive and negative attributes that contribute to product acceptance (Cadena et al., 2012). PLS components are created by the explanatory variable (X-data) and dependent variable (Y-data), being the original data decomposed into principal components called factors (Cruz et al., 2011). These factors are linear combinations of the original predictive variables and are calculated so that a maximum amount of variation in the x variables (sensory attributes) is explained (Meullenet et al., 2007). However, it presents linear character, and does not adequately address non-linearity, which is common in the analysis of QDA and consumer liking data (Cruz et al., 2011).

Artificial neural network (ANN) is a mathematical algorithm capable of relating input and output parameters through training, without requiring a prior knowledge on the relationships between the process variables (Cevoli et al., 2011). ANNs consist of a number of simple processing units (or neurons) interconnected by a modifiable weight, originally designed to mimic the function of the human brain and applied to quantitative and qualitative analysis during the last decades. ANN requires a training process in which the weights of those connections are adjusted, building a model that will allow performing the prediction of the desired parameters (either qualitative or quantitative). Its main advantages include a high modeling performance, being especially suited for nonlinear systems, besides being very much related to human pattern recognition (Cetó et al., 2013). Between the input and the output layers, there is at least one hidden layer with any number of neurons. The number of neurons in the hidden layer (s) depends on the application of the network. In the hidden and output layers, the net input (x_j) to node j is of the form:

$$X_j = \sum_{i=1}^{n} f\left(W_{ij} y_i\right) + b_j$$

Where y_i are the inputs, W_{ij} are the weights associated with each input/node connection, n is the number of nodes, and b_j is the bias associated with node j. Additionally, bias is an extra input added to neurons. The reason for adding the bias term is that it allows a representation of phenomena having thresholds. Each neuron consists of a transfer function expressing internal activation level. Output from a neuron is determined by transforming its input using a suitable transfer function. The transfer function can be linear or nonlinear (commonly sigmoid and hyperbolic tangent) functions, depending on the network topology (Bahramparvar et al., 2013).

Penalty (mean-drop) analysis is used by market researchers and product developers to understand the product attributes that most affect liking, purchase intent or any other product-related measure, being obtained from the Just about right data. Penalty analysis (PA) measures the changes in product liking (or any other measure) due to the product having “too much” or “too little” of a specific attribute (Market Research World, 2013). It has been used extensively by practitioners in the industry to identify the lower acceptance of a product associated with sensory attributes not at optimal levels (Sensory Society, 2013). There are few reports about using penalty analysis in dairy foods consumer study, being related twos studies covering dairy foods: cottage cheese (Drake et al., 2011) and vanilla yogurt added with stevia (Narayanan et al., 2014).

Logistic regression (LR) is a powerful tool for the statistical analysis of categorical data with the main purpose to discover exploratory variables that drive a choice outcome, without necessity of evaluating integrals (Ennis and Ennis, 2013). It can be used to correlate affective tests, in general, the purchase intention (which in this case is presented as a dichotomous response variable), providing information about the most important attributes at time of purchase (Prinyawiwatkul and Chompreeda, 2007). The sensory attributes can be used as limiting factors for obtaining optimal formulations.

Statistical analysis

The consumer test and the QDA means values were analyzed by one way analysis of variances (ANOVA) and Tukey's mean difference ($P < 0.05$) test, considering the sample as fixed effect (Granato et al., 2014). The QDA data were also subjected to principal components analysis (PCA) using the correlation matrix, while the hierarchical cluster analysis (HCA) was applied to the overall liking data to identify groups of consumers with similar preferences. In HCA, Euclidean distances (dissimilarity), Ward's method (agglomeration method) and automatic truncation were employed (Cruz et al., 2013).

To identify the attributes that were related positively with the product acceptance, two different methodologies were used: partial least squares regression (PLS) and artificial neural networks (ANN) considering that both methods have opposite behavior with respect to linearity of the data. In both models, the overall liking was coded on binomial scale (0/1), representing respectively the rejection, value 0, overall liking values among 1.00 to 5.99, and acceptance, value 1, overall liking values among 6.00 to 9.00, Vidigal et al., 2011). To identify natural variation among consumers in the product acceptance test, the variables were not subject to any pre-processing of data. The PLS model quality was evaluated by three parameters: coefficient of determination (R^2), related to the variation in the dependent variable explained by the regression model and the cumulative index (Q^2), which measures the global contribution of the ‘h’ first components as to predictive quality of the model (Donadini et al., 2012; Aquino et al., 2014).

ANN architectures and topologies were assayed employing Bayesian regularization algorithms, which used different number of neurons (5-55 neurons) and training algorithms (Scaled Conjugate Gradient and Levenberg - Marquardt) in the hidden layer, and different activation functions in the hidden and output layer (tangent, identity, logistic, softmax, sigmoid and exponential). The number of input neurons corresponds to the number of input variables into the neural network, and the number of output neurons is similar to the number of desired output variables. The input dataset was comprised by the sensory attributes obtained from QDA. The output layer included two neurons corresponding to two possible acceptance classes, which can be classified according to the overall liking (OL) as accepted (OLG > 6.0) or rejected (OLG ≤ 6.0). The target output was 1.0 in the correct class output, and 0.0 in the other. The outputs are probabilities of membership in every class, provided that the total across all output units is 1.0. The original datasets (280 samples) were randomly divided into training set (75%) and test set (25%) for all network topologies tested. The training set was used to calculate the transfer function parameters of the network, and the test set was used to estimate the correct classification in which the neural network is performing well. An ideal network would classify correctly all sets.

The number of neurons in the hidden layer was obtained by trial and error. The stopping criterion was 1000 epochs or maximum sum of square errors (SSE), Eq. (1), equal to 0.001 during training. Various performance measures are computed during the test. Each predicted value was compared with the experimental value to test the network performance. For this purpose, mean square error (MSE) was calculated using Eq. (2). On the lower values of MSE, the network predicts the values more truly and the correlation coefficient (r), Eq. (3), gives information about the performance. If the correlation coefficient is close to one, it shows how much the learning and prediction is successful.

$$SSE = \sum_{i=1}^{N} (O_i - T_i)^2$$

(1)

$$MSE = \frac{\sum_{i=1}^{N} (O_i - T_i)^2}{N}$$

(2)

$$r = \sqrt{1 - \frac{\sum_{i=1}^{N} (O_i - T_i)^2}{\sum_{i=1}^{N} (O_i - T_m)^2}}$$

(3)

Where O_i is the i^{th} actual value, T_i is the i^{th} predicted value, N is the number of data, and T_m is given by:

$$T_m = \frac{\sum_{i=1}^{N} O_i}{N}$$

(3)

A confusion matrix was performed to determine sensitivity (true positive rate), specificity (true negative rate) and accuracy values in order to evaluate the classification performance of the binary classifier system (Xu et al., 2012). The sensitivity (Sens), specificity (Spec) and accuracy (Accu) were determined as follow:

Sensitivity, specificity and accuracy analysis were used to evaluate the performance of the pattern classification techniques for each class (Xu et al., 2012). Sensitivity (Sens), specificity (Spec) and accuracy (Accu) were determined as follows:

$$\mathrm{Sens} = \frac{\mathrm{TP}}{\mathrm{TP} + \mathrm{FN}}$$

…...(4)

$$\mathrm{Spec} = \frac{\mathrm{TN}}{\mathrm{TN} + \mathrm{FP}}$$

(5)

$$\mathrm{Accu} = \frac{\mathrm{TN} + \mathrm{TP}}{\mathrm{TN} + \mathrm{TP} + \mathrm{FN} + \mathrm{FP}}$$

(6)

Where *TP*, *FN*, *TN*, and *FP* denote the numbers of true positives, false negatives, true negatives, and false positives, respectively. For calculations purpose, samples classified as accepted were considered as “positive”, and the rejected samples were considered as “negative”. Furthermore, a sensitivity analysis was performed to provide a measure of the relative importance among the inputs of the neural network model and to illustrate the model output variability as a function of the change in the input variable.

JAR scores were evaluated through the penalty analysis, being considered significant when more than 20% consumers evaluated the sample above or below the Just Right (Drake et al., 2011; Narayanan et al., 2014). The purchase intent data, computed in binomial form (1 representing buy, > 3 and 0, representing not buy, ≤ 3), were correlated with data from the JAR scale and acceptance test by Logistic Regression (LR), in order to find the affective characteristics that most influenced the purchase intent of the product (Cruz et al., 2011).

Except for neural networks, all analyses were performed using the software XLSTAT version 2013 (Addinsoft, Paris, France). The artificial neural networks were modeled by the software Statistica v. 8.0 (StatSoft Inc., Tulsa, OK, USA) using a supervised multilayer perceptron (MLP) network to predict the sensory acceptability of DL samples obtained using QDA (Cruz et al., 2011; Cruz et al., 2009).

RESULTS AND DISCUSSION

Sensory profile

Table 3 shows the average attributes obtained in the quantitative descriptive analysis of dulce de leche. The sensory profile was composed of fifteen descriptors, namely apparent adhesiveness, apparent viscosity, color, brightness, heated milk aroma, caramel aroma, sweet taste, heated milk taste, caramel taste, butter, pungent aftertaste, oil layer, adhesiveness, viscosity and sandiness. Significant differences were observed between all attributes for all samples ($P < 0.05$). In particular, significant difference was also observed for some sensory descriptors such as brightness (ranging from 2.26 to 13.07), viscosity (ranging from 0.865 to 13.32), and sandiness (ranging from 0.705 to 13.82) among others. With respect to the samples, the DL samples I, IV, and VII showed extreme scores on the attributes brightness, color, adhesiveness and viscosity (apparent and oral) and caramel and heated milk (aroma and taste) while DL II presented significant scores for the attribute sandiness. Finally, the samples V and VI showed a higher number of attributes with intermediate scores. Overall, the results suggest that there is a wide variety of products offered to the consumer resulting from different formulations and parameters used in the manufacturing process, such as intensity of heat treatment and amount of sodium bicarbonate, sucrose and glucose, in which the latter is a facultative ingredient.

The two dimensional principal component analysis (PCA) accounted for 87.22% (68.34% and 18.88 % for dimensions I and II, respectively, as shown in Figure 1), and sample II was characterized by the attribute sandiness, and to a lesser extent by the attributes apparent adhesiveness, viscosity, and adhesiveness. The sample IV was characterized by pungent aftertaste, color, caramel taste and aroma, while samples V and VI presented sweet taste, caramel taste and aroma, and color. With respect to the samples I and III, they were characterized by buttery taste and oil layer, while the sample VII was characterized by heated milk aroma and heated milk taste. As can be seen in Figure 1, the first principal component is characterized by the attributes brightness, pungent aftertaste, butter taste, and viscosity, while the second principal component is characterized by sandiness, heated milk aroma and color.

Consumer test

The results of the consumer's test are shown in Table 4. Corroborating the data from the sensory profile obtained by QDA, significant differences were observed for all attributes ($P < 0.05$), suggesting again heterogeneous products from the sensory point of view. The sample VI followed by the samples V and II showed the highest values for the overall acceptance (7.5, 6.8, and 6.5, respectively, $P < 0.05$), whose behavior was also observed for appearance (7.5, 6.6, and 7.2, $P < 0.05$, respectively), aroma (6.8, 6.6, and 6.4, $P < .05$, respectively), taste (7.4, 7.0 and 6.3, respectively, $P < 0.05$) and texture (7.6, 6.9, and 6.2, $P < 0.05$, respectively). In contrast, the samples I and VII presented lower scores for overall appearance (4.6 and 4.1, respectively, $P < 0.05$), ranging from 4 (extremely disliked) to 6 (liked slightly) for the other attributes, with no attribute scored above 6, which represents the lower limit of acceptance zone on a 9-point scale (Milagres et al., 2011).

Interestingly, the samples II and VI showed higher scores for appearance, as opposed to the sample VII, which had the lightest color according to the trained panel, thus evidencing the importance of color in the product appearance. The higher scores found for the sample VI in overall impression may be related to their descriptive characteristics that, in general, did not present discrepant mean values, given the expectation of a greater number of consumers. It is important to emphasize that the composition of sample VI declared on the label is quite simple, once besides milk and sucrose, the formulation contained only sodium bicarbonate and potassium sorbate. This fact indicates the possibility of manufacturing a dulce de leche with better acceptance and simplified composition, facilitating the widespreading of the product and reducing manufacturing costs by using a less complex and more economical technology. It may also be noted that despite it is not within the values recommended for dulce de leche, the attribute sandiness did not have relevant influence on the overall impression, since the DL II was accepted and showed significant scores for this attribute.

Cluster analysis

Cluster analysis was performed with the aim of targeting based on their global acceptability consumers. Three clusters CL1, 2 and 3 were identified with 74, 24 and 47 consumers, corresponding to 59.2, 19.2 and 37.6% respectively (Table 5).

Since 88 of the 125 consumers were women (70.4%) in all clusters was observed predominance of womem. With respect to age, due to the fact the study was developed in a university center, was also observed in general predominance of a younger audience, aged 18-24 (68.5 and 59.6% of consumers present in clusters CL1 and 3 respectively while for cluster II predominance was observed for an audience between 25-34 years (corresponding to 58.3% of consumers in this cluster members). Regardless of the segment formed, samples II, V and VI showed the highest scores for overall acceptability (values between 7.1 and 8.1, respectively). Analyzing the differences between clusters for each food (P <0.05), one can observe that the cluster I have a greater tendency to accept the DLs regardless of how they are heterogeneous among themselves. The cluster I gave the highest scores of acceptance for all seven DLs, with statistical difference (P <0.05), compared the other two clusters, except CL2 in the sample V and CL 3 in sample II. The relevance of CL 1 is its high concentration of consumers. Additionally, the high score of the sample "II" in the cluster III, suggests that sandiness is not a relevant parameter for rejection of that product. This reinforces the findings of previous studies where it was observed that sandiness is tolerated in different ways with respect to consumers of fresh milk (Giménez et al., 2008).

JAR scale and penalty analysis

Table 4 shows the penalty analysis performed using data from the just-about right-test for the attributes color, sweet taste, caramel taste, and consistency. The DL VI showed smaller mean drops for all the attributes evaluated (0.4, 0.5, 0.7, and 0.8, respectively), confirming its high acceptability demonstrated by the overall impression, and suggesting an optimized formulation from the sensory point of view of the consumers. The DL VII showed the highest response percentages in color below JAR (94.40%), and greater mean drop value used to estimate the penalty due to its below JAR (3.1), which were the highest among all the samples. This corroborates their negative acceptance in the overall impression and shows that the attribute color is of utmost importance as a criterion for sensory quality in the eyes of the consumer. Opposite behavior produced the same effect, as the excessive browning of DL IV showed high frequency (89.6%) and mean drop (2.3), considering it much too brown, above JAR. Probably, since it is a traditional product containing high carbohydrate levels with sweetening power, all DLs were considered sweet taste above JAR, with a frequency response above 20% of the population. Although lower frequencies were reported, the characteristic sweet taste below JAR had larger mean drops when compared to too much sweet taste, indicating that the loss of expectation with respect to this attribute had a greater influence on the product acceptance. The higher frequency of caramel taste below JAR was found for the sample VII (82.4%) that, as occurred earlier in JAR color attribute, presented a high mean drop (2.3), indicating the strong influence of this attribute on its low acceptance, and a direct relationship with the color due to excessive Mailard reaction. The DL VI showed higher response percentages of caramel taste JAR (61.6%) while the attribute consistency most influenced the DL IV overall liking, with greater frequency (81.6%) and greater mean drop (2.4) for consistency above JAR when compared to the previous attributes. The DL I was considered less consistent, obtaining greater mean drop for such attribute (1.7).

In general, DLs I, IV, and VII presented the lowest mean values for overall liking. The mean drops indicate that this may be due to the answers sweet taste below JAR and caramel taste below JAR for the DL I, brownish above JAR and consistency above JAR for the DL IV, and brownish below JAR and caramel taste below JAR for DL VII.

According to Meullenet et al. (2007), a specific attribute is present in optimal levels in a product when a minimum of 70% of the answers are in the "JAR" group. Based on this, the response frequencies show that the DL VI can be considered in JAR category with respect to its consistency, since it reached 74.40% of the responses, although a significant number of responses was also observed for the attribute caramel taste, with 61.60%. Corroborating the above, the results indicate the need for improvements in the attributes for all samples, indicating the imminent need for standardization of the manufacturing stages of product.

Drivers of liking using Partial Least Squares Regression (PLS) and Artificial Neural Networks (ANN)

The use of PLS generated three components, with Q^2 acum, R^2 Xacum, and R^2 Yacum values of 0.564, 0.719 and 0.411, respectively. Thus, it indicates low predictive ability of the model and a little explanation of the variability of the data, which may be related to the formulation heterogeneity, which contributed to the nonlinear behavior data, once samples with high scores in certain descriptors presented opposite behavior for other descriptors. In this context, the PLS does not seem adequate to estimate the drivers of liking of dulce de leche, therefore a non-linear method was needed, such as artificial neural networks.

The ANN performance was evaluated using prediction accuracy and mean square error (MSE) of training and testing sets. The proximity of the accuracy values to 100% and closeness of the mean square error values to 0 shows the efficiency of the prediction of ANN model. The best ANN architecture was composed by 15 input neurons, 5 hidden neurons and two output neurons using logistic and hyperbolic tangent function in hidden and output layer, respectively. The receiver operating characteristic (ROC) curve is a graphical plot, which illustrates the performance of a binary classifier system as its discrimination threshold is varied. The ROC curve analysis achieved sensitivity (true positive rate), specificity (true negative rate) and accuracy values of 98.0, 100.0, and 98.6% for all dataset. The high accuracy of the ANN model can be corroborated by the low MSE value of 1.73%, with 100% of recognition and prediction ability for the accepted class, while the rejected class presented 95% and 93% of recognition and prediction ability for training and testing dataset, respectively. The sensitivity analysis showed color, apparent viscosity, adhesiveness, and caramel taste as the sensory attributes with the most discriminative power, presenting variable of importance in projection (VIP) coefficients of 7.009, 3.915, 3.501, and 2.321 for all dataset, respectively. In this context, improving the acceptance of Dulce de leche requires a reformulation of the ingredients and process parameters that influence these attributes, such as control of temperature and time of heat treatment and addition of ingredients such as sucrose, glucose and sodium bicarbonate.

External preference mapping

Figure 2 shows the external preference mapping obtained from the regression of the acceptance data of each cluster on the 2-dimensional principal component analysis. For cluster 1, a circular model was obtained by the existence of an ideal point (-0.723, 0.542), while quadratic and elliptical models were obtained for CL2 and CL3, with the existence of saddle points that are shown on the map. For a specific individual, the ideal point shows the location of his/her most preferred sample (a global maximum in terms of preference), while the saddle point represents a threshold where the variability of the preference is low, before increasing or decreasing in the opposite direction (Resano et al., 2010).

As shown in the two-dimensional map, samples V and VI are located in the region that comprises acceptance values above the overall value for 80-100% of consumers. In this region, there is the presence of the ideal point, and these samples are associated with the attributes color, sweet taste, caramel taste, and caramel aroma. The saddle point region precedes the region in which the acceptance values were 60-80 % above the overall acceptance, where the samples II and III are placed. The sample II associated with sandiness to a greater extent, followed by the attributes apparent and oral adhesiveness, apparent and oral viscosity while the sample III is related to oil layer and butter taste.

Sensory profiling of the ideal products

Besides establishing the sensory profile and the characteristics that drive the products acceptance by consumers, there is a need to determine the sensory characteristics that should be exhibited by the ideal products. This procedure is performed by reverse regression, which in our case it was a PLS regression of the sensory scores on either the preference space coordinates (obtained from circular model - CL1) of the ideal product in their respective spaces.

It was observed that the optimum Dulce de leche is character

ized by high scores for the attributes sweet taste, caramel taste, brightness, color, and caramel aroma (10.3, 9.1, 9.0, 8.5, and 8.4, respectively), intermediate scores for apparent adhesiveness, heated milk taste, apparent viscosity, heated milk aroma, and adhesiveness (7.1, 6.8, 6.7, 6.6, and 6.0, respectively), and low scores for viscosity, pungent aftertaste, butter taste, oil layer, and sandiness (6.0, 5.8, 4.8, 4.6 and 2.2 respectively), considering a 15 cm scale.

From an industrial perspective, intermediate heat-treatments may be used, since attributes such as caramel color, aroma and taste are also influenced by this operational parameter, together with the formulation ingredients, such as sucrose, glucose (which contributes to the brightness and browning) and sodium bicarbonate (acidity regulator, which positively influences the Mailard reaction).

Purchase intent using Logistic Regression (LR)

The Table 6 shows the attributes that influenced the purchase intent of Dulce de leche using logistic regression. One predictive value of 87.54%, equivalent to a good ability to fit the experimental data was observed. The results suggest that buying products is a multidimensional parameter, influenced by mainly two attributes including overall liking and taste, with odds-ratio values of 3.23 and 1.81, respectively. The higher scores for the attributes overall liking and taste suggest that these attributes are more critical for the purchase of the product, with a purchase probability of 3.23 and 1.81 times higher (than not being purchased, $P < 0.0001$), with every one-unit increase of the overall liking score (based on a nine-point hedonic scale). However, the texture is also relevant, once the probability of the product being purchased increases 1.21 times (than not being purchased, $P < 0.034$), resulting in one-unit increase of the overall liking score.

Overall, overall liking is not easy to understanding when it is related the purchase intent. So, the logistic regression become easy to understand because they show the importance of taste and texture that are commonly observed in processed food products. Additionally, in agreement with the results obtained in the penalty analysis, there is a need to reformulate the taste (caramel and sweet) and consistency of the dulce de leche samples, which were not considered ideal for these attributes.

CONCLUSIONS

The expansion and conquest of new consumer markets requires the standardization of sensory characteristics of processed products, resulting in greater consumer's acceptance.

In the case of dulce de leche of the present study, a large heterogeneity was observed from the sensory point of view, and the products most appreciated by consumers showed intermediate scores for the sensory attributes established in the descriptive test, and this trend was observed even after consumer's segmentation. However, there is still a need for an effective optimization, since no product was considered as ideal for the attributes under study.

In general, the sensometric methodologies proved to be useful, and indicated that the sensory optimization of the dulce de leche is a multidimensional process, requiring simultaneous adjustments in the attributes appearance, aroma, taste, and texture. From a practical standpoint, the parameters of heat treatment and quantity of ingredients used in the formulation should be standardized.

The present results may be useful to include dulce de leche on the production line of dairies, with optimized sensory quality and high probability of acceptance by consumers, thus resulting in increased revenues for the producing unit.

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TABLES AND FIGURES

Table 1. Ingredients and nutritional composition of Dulce de Leche samples

Sample	Main ingredients	Energetic Value (Kcal/100g)	Glycids (g/100g)	Protein (g/100g)	Total Fat (g/100g)	Saturated Fat (g/100g)	Sodium (g/100g)	Calcium (g/100g)
I	Milk, sugar, sodium bicarbonate,	305	55	7	6.5	4	0.210	X[a]
II	Milk, sugar, sodium bicarbonate, sodium chloride, lactose	325	55	8	8	5	0.165	0.280
III	Milk, sugar, sodium bicarbonate, potassium sorbate	315	60	7	6	0	0.275	X
IV	Milk, sugar, modified starch, sodium citrate, lactase, potassium sorbate	315	55	10	5	40	0.165	0.025
V	Milk, sugar, glucose syrup, sodium bicarbonate	305	60	5	5	5	0.110	X
VI	Milk, sugar, sodium bicarbonate, potassium sorbate	400	65	10	5	2.5	0.125	0.175
VII	Milk, sugar, glucose syrup, modified starch, sodium bicarbonate, potassium sorbate	395	80	5	6	3	0.105	X

[a]No information labeled.

Table 2. Sensory profiling of the *dulce de leche* samples

Term	Definition	Reference
Apperance		
Color	Print feature of sweet milk generated from the reflectance of light on the product and generating color ranging from yellow to brown	BEIGE = Dulce de leche - Ylagam
		BROWN = Dulce de leche – Macuco
Brightness	Intensity of light reflection.	LOW = Dulce de leche – Macuco HIGH = Dulce de leche - Além
Adhesiveness	Ability of the product to adhere the spoon or spatula when lying on the surface of the product, using only its own weight, and raised manually up to 90 °.	LOW = Dulce de leche - Além
		HIGH = Dulce de leche - Macuco (SIF 614)
Viscosity	Force required to mix the sample with circular motion with a spoon or spatula	LOW = Dulce de leche - Além (SIF 202)
		HIGH = Dulce de leche - Macuco (SIF 614)
Aroma		
Heated milk	Flavor of cow milk associated with the heated milk until its scalding point	NONE = Pasteurized milk - Sabor da Serra
		STRONG= 300 mL Pasteurized milk - Sabor da Serra (SIE/RJ 682) heated in 1 L of water in a warm bath for 10 min.
Caramel	Aroma of heated carbohydrates in solutions of concentrated milk	NONE = Pasteurized milk - Sabor da Serra STRONG = One portion of Toffee Arcólor essence diluted in distilled water at a concentration of 0.12% and the other part of Pasteurized milk - Sabor da Serra (SIE/RJ 682)
Taste		
Sweet	Perceived taste on the tongue stimulated by sugars	WEAK = Condensed milk – Moça and pasteurized milk - Sabor da Serraat a proportion of 1:3 (w/w) STRONG = Condensed milk – Moça and pasteurized milk -

		Sabor da Serra at a proportion of 3:1 (w/w)
Heated milk	Flavor of cow milk heated up to its scalding point.	NONE = Pasteurized milk - Sabor da Serra STRONG - 300 mL Pasteurized milk - Sabor da Serra heated in 1 L of water in a warm bath for 10 min.
Caramel	Taste of carbohydrates heated in solutions of concentrated milk	NONE = Pasteurized milk - Sabor da Serra STRONG = One portion of Toffee Arcólor essence diluted in distilled water at a concentration of 0.12% and the other part of Pasteurized milk - Sabor da Serra
Butter	Flavor associated with the unsalted butter	NONE = Creamy Dulce de leche - Macuco STRONG = Creamy Dulce de leche - Itaocara
Pungent aftertaste	Slightly spicy sensation after swallowing	NONE = Glucose corn syrup - Karo and Pasteurized milk - Sabor da Serra at a proportion of 3:5 (w/w) HIGH = Glucose corn syrup - Karo (Unilever).
Oil layer	Feeling oily film on the oral mucosa and lips	LOW = Dulce de leche - Souvenir HIGH = Unsalted butter - Aviação and dulce de leche - Ylagam at a proportion of 1:5 (w/w)
Texture		
Adhesiveness	Adhesion of the product on the palate when pressed against the roof of the mouth by the tongue.	LOW = Dulce de leche - Além HIGH = Dulce de leche - Macuco (SIF 614)
Viscosity	Speed in which the sample crumbles in the mouth. The faster, less viscous the product is	LOW = Dulce de leche - Além HIGH = Dulce de leche - Macuco
Sandiness	Presence of small granules dispersed uniformly throughout the sample	NONE = Dulce de leche – Além HIGH = Dulce de leche - Itambé

Table 3. Average sensory scores for seven Dulce de Leche samples

Attribute	Sample						
	I	II	III	IV	V	VI	VII
Color	4.4^{d}	5.7^{d}	9.5^{c}	14.5^{a}	11.6^{b}	12.4^{b}	0.2^{e}
Brightness	13.1^{a}	9.6^{bc}	11.1^{ab}	2.3^{e}	7.1^{d}	8.0^{cd}	12.4^{a}
Apparent Adhesiveness	1.9^{d}	12.1^{a}	4.5^{c}	13.6^{a}	6.7^{b}	6.1^{bc}	4.3^{c}
Apparent Viscosity	1.3^{f}	11.8^{b}	3.1^{e}	13.6^{a}	7.9^{c}	5.7^{d}	3.0^{e}
Heated Milk Aroma	9.0^{b}	8.8^{b}	6.7^{b}	2.9^{c}	3.5^{c}	4.0^{c}	12.0^{a}
Caramel Aroma	5.6^{e}	7.0^{de}	8.5^{cd}	13.0^{a}	10.9^{ab}	10.5^{bc}	2.4^{f}
Sweet Taste	11.1^{a}	10.9^{a}	10.5^{ab}	10.0^{ab}	10.2^{ab}	10.5^{ab}	8.8^{b}
Heated Milk Taste	9.0^{b}	8.1^{b}	7.3^{b}	3.0^{c}	4.6^{c}	4.2^{c}	12.1^{a}
Caramel Taste	6.8^{d}	8.0^{cd}	9.5^{bc}	13.2^{a}	11.1^{ab}	11.4^{ab}	2.8^{e}
Butter taste	7.2^{ab}	2.4^{cd}	7.9^{a}	1.4^{d}	3.3^{cd}	4.7^{bc}	7.0^{ab}
Pungent Aftertaste	5.3^{bc}	6.8^{ab}	5.2^{bc}	8.4^{a}	6.3^{ab}	5.4^{bc}	2.9^{c}
Oil Layer	6.2^{ab}	2.8^{de}	7.6^{a}	2.0^{e}	3.4^{cde}	4.7^{bcd}	5.4^{abc}
Adhesiveness	0.7^{e}	10.5^{b}	2.4^{de}	13.3^{a}	6.5^{c}	5.4^{c}	2.9^{d}
Viscosity	0.9^{e}	10.4^{b}	2.2^{e}	13.5^{a}	6.8^{c}	5.0^{d}	2.6^{e}
Sandiness	0.7^{b}	13.8^{a}	0.8^{b}	0.2^{b}	0.2^{b}	0.2^{b}	0.2^{b}

$^{a-f}$Means with the different letters in the same rows are significantly different ($P <$ 0.05) using Tukey's test.

Table 4. Overall liking attribute means from consumer acceptance testing of Dulce de Leche[1]

Item	Dulce de Leche Brands						
	I	II	III	IV	V	VI	VII
Appearance liking	4.7^{c}	7.2^{a}	5.1^{c}	4.8^{c}	6.6^{b}	7.5^{a}	3.7^{d}
Aroma liking	5.2^{d}	6.4^{ab}	6.0^{bc}	5.8^{c}	6.6^{a}	6.8^{a}	4.6^{c}
Taste Liking	4.6^{cd}	6.3^{b}	6.1^{b}	5.0^{c}	7.0^{a}	7.4^{a}	4.0^{d}
Texture Liking	4.6^{f}	6.2^{bc}	5.5^{de}	4.9^{ef}	6.9^{ab}	7.6^{a}	5.6^{cd}
Overall liking	4.6^{de}	6.5^{b}	5.8^{c}	5.0^{d}	6.8^{b}	7.5^{a}	4.1^{e}
Purchase Intent	2.2^{de}	3.3^{bc}	2.9^{c}	2.4^{d}	3.7^{b}	4.1^{a}	1.9^{e}
Color (%)							
Below JAR	67.2	43.2	36.0	0.8	3.2	5.6	94.4
	(1.3)	(1.7)	(0.8)	-	-	-	(3.1)
JAR	27.2	51.2	44.0	9.6	37.6	57.6	4.0
Above JAR	5.6	5.6	20.0	89.6	59.2	36.8	1.6
	-	-	(0.5)	(2.3)	(1.1)	(0.4)	-
Sweet Taste (%)							
Below JAR	20.8	10.4	17.0	30.4	16.0	15.2	49.6
	(2.3)	-	-	(2.2)	-	-	(1.3)
JAR	20.8	33.6	38.4	21.6	49.6	59.2	19.2
Above JAR	58.4	56.0	44.0	48.0	34.4	25.6	31.2
	(1.6)	(1.2)	(0.8)	(1.9)	(1.2)	(0.5)	(0.8)
Caramel taste (%)							
Below JAR	44.8	39.2	38.4	31.2	18.4	18.4	82.4
	(2.3)	(1.8)	(1.3)	(2.2)	-	-	(2.3)
JAR	16.8	35.2	37.6	18.4	41.6	61.6	8.8
Above JAR	38.4	25.6	24.0	50.4	40. 0	20.0	8.8
	(1.3)	(1.0)	(1.3)	(2.1)	(1.2)	(0.7)	-
Consistency (%)							

Below JAR	87.2	15.2	68.0	5.6	16.8	15.2	42.4
	(1.7)	-	(1.2)	-	-	-	(0.8)
JAR	12.0	56.0	26.4	12.8	49.6	74.4	38.4
Above JAR	0.8	28.8	5.6	81.6	33.6	10.4	19.2
	-	(1.5)	-	(2.4)	(0.9)	-	-

[a-d] Means with the different letters in the same rows are significantly different ($P < 0.05$) using Tukey's test. [1]Data represent 125 consumers. Liking attributes were scored on a 9-poin hedonic scale, where dislike extremely = 1 and like extremely = 9, and purchase intent were scored on a 5-point hedonic scale, where "I definitely would not buy" = 1 and "I definitely would buy" = 5, JAR scale were scored on a 9-point scale where below JAR = 1 to 5, JAR = 5 and above JAR = 6 to 9. Resuts indicate the percentage of assessor that selected these options. The number in the parenthesis is the mean drop calculated when the percentage of citations exceed 20%.

Table 5. Cluster analysis results of Dulce de Leche consumers[1]

Items	Clusters		
	CL1	CL2	CL3
Category			
Gender			
Male	16 (29.6)	7 (29.2)	14 (29.8)
Female	58 (70.4)	17 (70.8)	33 (70.2)
Age (%)			
Up to 17	1 (1.9)	-	-
18 – 24	37 (68.5)	10 (41.7)	28 (59.6)
25 – 34	13 (24.1)	14 (58.3)	16 (34.0)
35 – 44	2 (3.7)	-	3 (6.4)
45 – 54	-	-	-
55 – 64	1 (1.9)	-	-
From 65	-	-	-
Total assessors (%)	74 (59.2)	24 (19.2)	47 (37.6)
Overall liking			
I	5.9[a]	3.0[c]	3.9[b]
II	6.9[a]	3.9[b]	7.2[a]
III	6.4[a]	4.6[c]	5.5[b]
IV	5.7[a]	4.0[b]	4.7[b]
V	7.2[a]	7.1[a]	6.0[b]
VI	8.1[a]	7.1[b]	7.0[b]
VII	5.3[a]	3.0[b]	3.1[b]

[a–c] Means with the different letters in the same rows are significantly different ($P < 0.05$) using Tukey's test. [1]Data represent 125 consumers reflecting their gender, age and liking. Liking attributes in CL1, CL2 and CL3 were scored on a 9-poin hedonic scale, where dislike extremely = 1 and like extremely = 9.

Table 6. Parameter estimates, probability and odds ratio estimates for purchase intent of dulce de leche

Variable	Parameter	Pr > Qui²	Odds ratio
Appearance	0.18	0.052	1.19
Aroma	-0.01	0.907	0.99
Taste	0.59	**<0.0001**	1.81
Texture	0.19	0.034	1.21
Overall Liking	1.17	**<0.0001**	3.23
Color (JAR)	0.11	0.257	1.12
Sweet Taste (JAR)	0.12	0.267	1.13
Caramel taste (JAR)	-0.02	0.846	0.98
Consistency (JAR)	-0.05	0.611	0.95

Based on the logistic regression analysis, using a full model with nine sensory attributes. The analysis of maximum likelihood estimates was used to obtain parameter estimates. Significance of parameter estimates was based on the Wald *Qui²* value at $P < 0.05$.

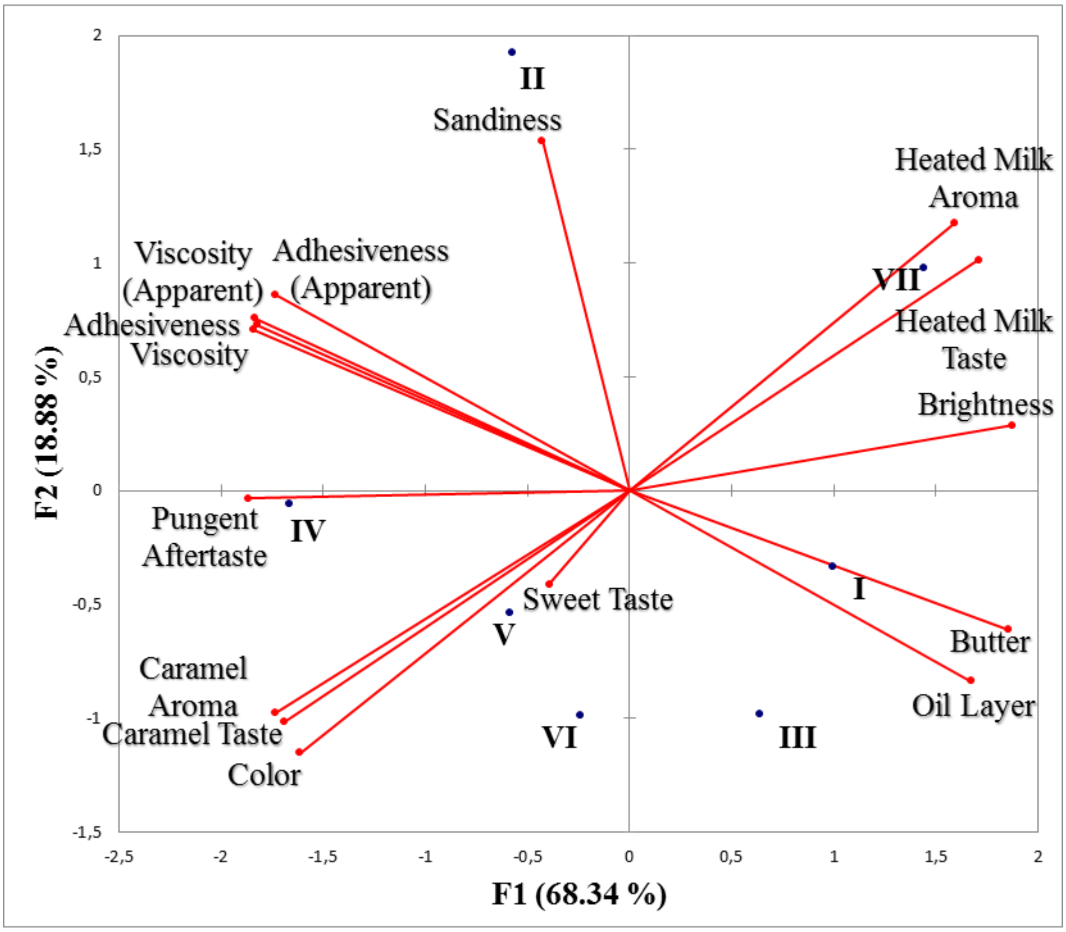

Figure 1. Principal component Analysis (PCA) of Dulce de Leche samples, F1 x F2, of attributes and samples (I, II, III, IV, V, VI ,VII), as given in Table 3.

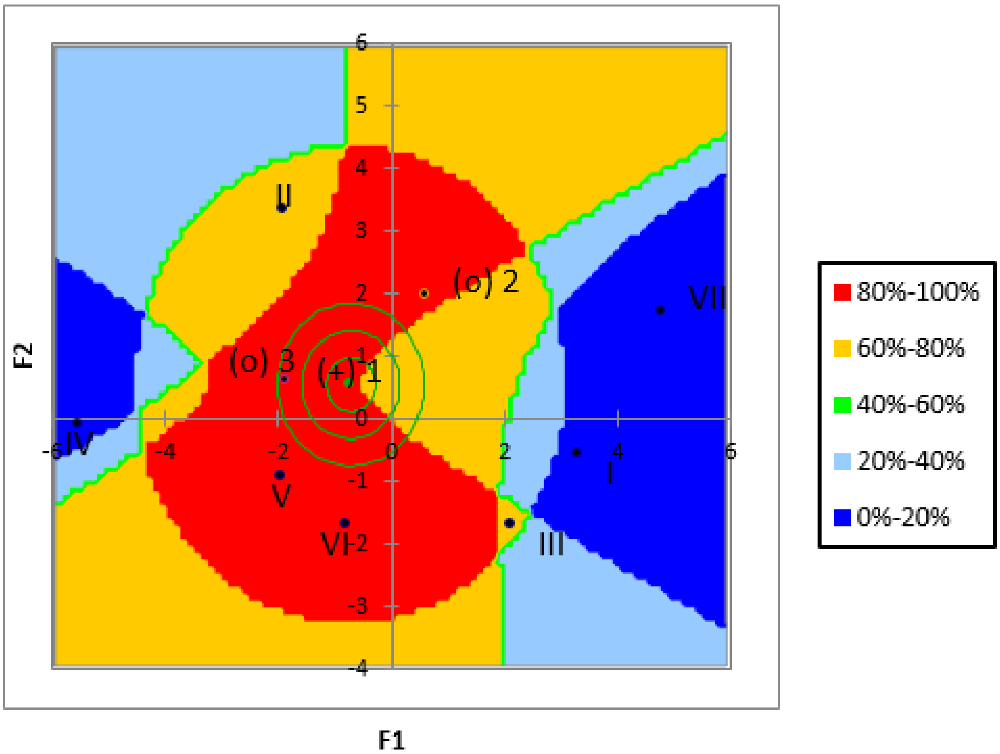

Figure 2. External preference mapping illustrating: three clusters, 1 (circular, “(+)“), 2 and 3 (saddle, “(o)”); samples (I, II, III, IV, V, VI and VII); and the five regions of the global average value of acceptance.

3.2 ARTIGO 2: DULCE DE LECHE, A TYPICAL PRODUCT OF LATIN AMERICA: CHARACTERIZATION BY PHYSICOCHEMICAL, OPTICAL AND INSTRUMENTAL METHODS

Dulce de Leche, a typical product of Latin America: characterization by physicochemical, optical and instrumental methods

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Abstract

The physicochemical profile of Dulce de Leche (DL) was determined by both routine analysis and others techniques (HPLC, GC-MS and ICP-OES). Seven Brazilian commercial brands were characterized for moisture content, protein, fat, ash, pH and titratable acidity, mineral content (sodium, potassium, calcium, and phosphorus), optical parameters and instrumental analysis (carboidrates content and volatile compounds). Overall, extensive variability among all the parameters evaluated were observed, suggesting different operational procedures in the dairy factories along the DL processing. In this sense, an increase of intrinsic quality of DL is related closely the standardization of operacional parameters using during the manufacture.

Key-words: dulce de leche, quality, physico-chemical analysis.

1. Introduction

Dulce de Leche is a concentrated milk product obtained by heat treatment with or without negative pressure, with ingredients added, especially sucrose conferring differential sensory and physicochemical characteristics as compared to other dairy products (Velasco, Quezada, Parra, Campos, Villalobos & Wells, 2010; Perrone, Stephani & Neves, 2011; Ranalli, Andrés & Califano, 2012). It is a highly consumed product (Giménez, Arés & Gambáro, 2008; Oliveira, Penna & Nevarez, 2009) in Latin America where it is traditionally made, mainly in Argentina and Uruguay, followed by Brazil, Chile, Paraguay and Bolivia (Zalazar; Perotti, 2011). Additionally, some countries as Brazil have exported DL to other economic blocs such as European Union (EU) and Asia Pacific Economic Cooperation (APEC), evidencing the expansion process of the export market of Dulce de Leche (MDIC, 2014).

Although DL is composed of milk, sucrose, sodium bicarbonate and other additives, it may exhibit distinct characteristics that vary greatly among industries and production areas. Some factors such as management of cows, genetics, good agricultural practices, and formulation and final processing can affect DL characteristics (Smit, 2000). Different processing parameters including heating time and temperature, intensity of negative pressure, and mass balance have direct influence on the physicochemical and sensory attributes of the final product (Smit, 2001; Perrone, 2011). These characteristics are strongly related to nutritional, technological and sensory quality of DL, consequently affecting the consumers purchase intention, opening new markets, reducing production costs, and improving quality control (Giménez, 2008). Thus, the physicochemical characteristics of the DL should be compulsorily monitored.

However, currently there are few studies on the chemical composition of the DL, and there is a lack of information on its chemical profile using instrumental techniques such as Gas Chromatography Mass - Spectrometry (GC-MS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and High Performance Liquid Chromatography (HPLC). (Oliveira, 2009). In this context, further studies on the physicochemical characteristics using these techniques are needed.

Under this view, the aim of this study was to characterize different commercial DL brands by conventional methods and other instrumental techniques such as HPLC, GC-MS and ICP-OES, contributing to relevant information about a product with increasing demand and great relevance in terms of Latin American economy.

2. Materiais and methods

2.1 Sampling

Seven DL samples were purchased in Brazilian markets. All brands were produced in processing plants under inspection by the Federal Inspection Service (SIF), being marketed throughout the Brazilian territory. The transport to the laboratory was done at room temperature in original containers. For the analyses, the mean values were calculated by using three analytical replicates, except for the optical characterization, performed with 10 replicates.

2.2 Proximate composition, acidity and pH

The proximate composition (moisture, lipid, protein and ash) was determined according to the recommendations of the Association of Official Analytical Chemists (AOAC, 2005). The pH and the percentage of lactic acid were determined according to Adolfo Lutz Institute methodology (IAL, 2008). Moisture was determined gravimetrically by oven drying (Micronal, São Paulo, Brazil) until constant weight. The ash content was determined gravimetrically after incineration of 3 g sample at 550 °C in a muffle furnace. Protein content was calculated using the total nitrogen determined by Kjeldahl method with subsequent multiplication by the factor 6.38. The fat was determined using soxhlet extraction method after denaturation of proteins and carbohydrates with hydrochloric acid. The pH was measured in digital potentiometer (MICRONAL B-375) by direct insertion of the electrode in 10g of the samples. The lactic acid was mensured by titration with sodium hydroxide using phenolphthalein as indicator.

2.3 Sodium, Calcium, Potassium and Phosphorus by ICP-OES

Sodium, calcium, potassium, and phosphorus were determined by mineralization in a microwave oven, followed by quantification in ICP-OES Spectrometry (Spectro Analytical Instrument – Spectroflame P) (AOAC, 2005). Sample digestion (1-2 g) was carried out by acid hydrolysis, using 2 ml nitric perchloric acid solution (2:1) for approximately 16h at room temperature. After oxidation, the samples were heated in a digestion block (Tecnal, São Paulo, Brazil) in a fume hood at low boil to 100 °C (± 2 °C) for 1h, and maintained for additional 2h at 170 °C (±2 °C). The mineral content of the Dulce de Leche samples was determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The micronutrient concentrations were calculated based on calibration curves with sodium, calcium, potassium and phosphorus standard solutions.

2.4 Carbohydrates by HPLC

The analysis of carbohydrates (lactose, sucrose, and glucose) was performed by high performance liquid chromatography (HPLC) according to the extraction methodology described by Llano, Rodriguez & Cuesta (1996) with some modifications. Firstly, 1g DL was weighted in a 25 mL Becker and dissolved with 5 mL sulfuric acid (45 $mmol.L^{-1}$). Then, the sample was transferred to a conical tube, homogenized in a shaker (Certomat® MV, B. Braun Biotech International, Melsungen, Germany) for 1 min at 2500 rpm, and stirred for an hour on a shaker table set at 250 rpm. Subsequently, it was centrifuged at 1.000*g* for 30 min at 4°C and the supernatant was filtered on filter paper Whatman # 1. The filtered samples were injected (20μL) into the liquid chromatograph (Shimadzu®, Japan) Model LC/20 AT, equipped with integrator CBM-20A, and with detector RID-10A kept at 40ºC using a cation-exchange Aminex HPX-87H column 300 x 7.8 mm (Bio-Rad, Hercules, CA, USA) maintained at 60°C.

The mobile phase was water (Millipore Corp., Billerica, MA) at a flow rate of 0.5 mL min^{-1} (Isocratic). HPLC chromatograms were obtained using LC Solution software (Shimadzu Corp.). Quantitation was performed by external standard method using lactose, glucose and sucrose (Sigma-Aldrich, St. Louis, Missouri, USA) as standards at the following dilutions: 6.25, 10, 12.5, 15, 20, 25, 30, 35, 50, and 75 $mg.mL^{-1}$. Under these conditions, sucrose showed a double peak that coeluted with the glucose in the first peak. Thus, the glucose peak was measured by difference using the ratio between the major and minor sucrose peaks

2.5 Volatile compounds by GC-MS

The extraction and identification of volatiles were made by solid phase microextraction (SPME) and by gas chromatography coupled to mass spectrometry (GC-MS), respectively, according to methodology described by Condurso, Verzera, Romeo Ziino & Conte (2008). The volatile compounds were extracted by the static headspace method. SPME was performed with a commercially available fibre housed in its manual holder (Supelco, Bellefonte, PA, USA). All extractions were carried out using a DVB/CAR/PDMS (divinylbenzene / carboxen / polydimethylsiloxane) fiber, 50/30 μm film thickness (Supelco, Bellefonte, PA, USA).

For that, 10 g sample was dissolved in 12 mL saturated NaCl solution, keeping the vial at 40ºC, with equilibrium time of 20 min and extraction time of 30 min. After sampling, the SPME fibre was introduced onto the GC-MS injector, kept in the splitless injector, and maintained at 260 ºC for 3 min for thermal desorption of the analytes. To identify the components, the linear retention index (LRI) of the experimental spectra was calculated and compared to LRI of NIST'98 (NIST/EPA/NIH Mass Spectra Library, version 1.7, USA) (Van den Dool and Kratz, 1963).

2.6 Optical Characterization

The color parameters were determined using Chroma meter (CR-410, Konica Minolta Sensing, Inc., Tokyo, Japan) using iluminant D65, previously calibrated. All measurements were performed at 8 °C. The results were expressed in *L** (lightness; 0 = black, 100 = white), *a** (+ *a** = redness, - *a** = greenness) and *b** (+ *b** = yellowness, - *b** = blueness) values. Chroma (*C**) was calculated using the color coordinates *a** and *b**. These attributes indicate the color intensity of the samples by the degree of perceived hue as compared with the gray tone with the same lightness. To identify a certain colour dfference with reference to grey colour with the same lightness, the hue angle (*h**) was calculated. The total color difference (*ΔE**) was used to compare one sample to the other. To better guide the discussion, total color difference, $(\Delta a^{*2} + \Delta b^{*2} + \Delta L^{*2})^{1/2}$ was classified as very distinct (>3), distinct (1.5< *ΔE*<3) and small difference (<1.5) (Pathare, Opara, Al-Said, 2013).

2.7 Statistical Analysis

The results of the physicochemical analyses were subjected to one-way ANOVA, considering the sample as fixed effects. The differences between means were submitted to Tukey's test at 95% confidence level. In addition, Pearson's correlation was performed to appreciate and interpret interactions between the variables through the linear correlation coefficient (Granato, Calado & Jarvis, 2014).

Principal Component Analysis (PCA) was performed using with the means values of the physicochemical and optical parameters (Aquino, Silva, Freitas, Felicio, Cruz, & Conte-Junior, 2014). The matrix data set was composed of 7 lines and 19 columns, being the former the samples and the latter the values of the different analyses. The data were auto scaled before the analysis. The statistical package was XLSTAT software version 2013.2.03 (Addinsoft, Paris, France).

3.Results and Discussion

3.1 Chemical composition, acidity and pH

Results of proximate composition, pH and titratable acidity of the DL samples are in Table 1 . Protein, lipid, ash, moisture, lactic acid content and pH ranged respectively from 3.51 to 7.12; 3.56 to 6.99; 1.31 to 2.05; 17.49 to 29.67; 0.23 to 0.50; and 6.14 to 6.37 w/w (p < 0.05), with a significant variability in all parameters. These results are in agreement with other studies on DL (Demiate, Konkel & Pedroso, 2001; Ranalli, 2012). A strong correlation between lipid and ash contents ($r = 0.89$, $p < 0.008$) was observed. Once the lipids of DL comes only from milk (BSR 1997), probably the ash comes from milk despite a small portion may be added to the formulation by the addition of sodium bicarbonate (Perrone, 2011). Therefore, a high percentage of these compunds may indicate high representativeness of milk in the Dulce de Leche formulations.

Faced with the need to establish standards for DL, the Mercosur countries have created an identity and quality regulation (BSR, 1997), establishing the following limits for the pasty DL: moisture (max 30 g / 100 g), fat (6 – 9 g / 100 g), ash (max 2 g / 100 g) and protein (up 5 g /100 g). Therefore, low protein and lipids contents were found in the present study (samples II, IV, V and VII). The deficit of proteins and lipids compromises the nutritional value of the product, suggesting the replacement of milk by water or carbohydrates such as sucrose and starch. Indeed, food fraud often has been considered to be foremost an economic issue and less a concern of the traditional food safety or food protection intervention and response infrastructure (Moore, Spink, & Lipp, 2012). However, any adulteration may result in changes of identity and/or purity of the original and purported ingredient by replacing, diluting, or modifying it by physical or chemical means.

Regarding the acidity, only samples II and V were statistically ($P<0.05$) equal, with values of 0.37 and 0.36, respectively. This is important for sensory characteristics, since the acid taste has a negative influence on the product acceptance for masking the sweet taste (Giménez, 2008).

3.2 Sodium, Calcium, Potassium and Phosphorus content

Minerals are important compounds in dairy products (Cashman, 2006). Sodium, for example, is present in milk (Oliveira, 2009) and has been gaining importance due to the need for reducing sodium in human diet to prevent hypertension (Felicio et al., 2013; Tanase, Griffin, Koski, Cooper & Cockell, 2011; Cruz et al., 2011). In addition, the effect of other minerals including calcium, potassium and phosphorus in consumer health has been widely investigated (Tanase, 2011; Childers, Corman, Edwards & Elser, 2011). Since an information gap remains in the recent literature, instrumental analytical methods can be used to identify and quantify these minerals, including the mineralization technique by microwave cavity and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

Table 1 shows the concentrations of sodium, calcium, potassium and phosphorus in Dulce de Leche samples. A significant difference between these parameters was observed for all samples, ranging from 0.12 to 0.16 g / 100 g; 0.28 to 0.40 g / 100 g; 0.19 to 0.36 g / 100 g; 0.14 to 0.24 g / 100 g for sodium, calcium, potassium and phosphorus, respectively (p <0.05), with the highest differences observed for sodium and calcium (p <0.05).

Sodium bicarbonate acts as a processing adjuvant or as a sodium based preservative, such as citrate allowed by BSR (1997). Another possibility for the high sodium levels could be salt imbalance in cattle feed, or a loss of homeostasis of their mammary glands, probably due to health issues, producing milk with low mineral content (Ferreira, Bislevc, Bendixenc & Almeida, 2013). To discuss better, the correlation of sodium and ash content must be investigated, since ash represents a set of all minerals found in milk.

A moderate correlation was observed between ash content and sodium (r = 0.53, p <0.219) as compared to the correlations with potassium (r = 0.98, p <0:00), calcium (r = 0.99, p <0.0001), and phosphorus (r = 0.97, p <0.000), with coefficients close to 1.00, indicating strong positive dependence between these variables. The same strong correlation is obtained when potassium, phosphorus and calcium are compared with each other - sodium x phosphorus (r = 0.97, p <0.000), potassium x calcium (r = 0.99, p <0.0001), and calcium x phosphorus (r = 0.98, p <0.000). Therefore, it can be deduced that the presence of sodium in the different DL samples may be related to its addition during the manufacturing process as a technological adjuvant, rather than the physiology of dairy cattle influencing the raw material. It should be taken into account that the World Health Organization (WHO, 2006) recommends the consumption of less than 2.0 g sodium chloride per day to prevent the incidence of hypertension. Once the DL contains low sodium levels (about 0.14 g/100 g), its consumption does not significantly contribute to the occurrence of hypertension even in moderate amounts, since consumer should eat unreal amounts of DL (at least 1.42 kg / day) to meet WHO requirements. In the sensory point of view, the changes in sodium levels do not alter flavor and / or aftertaste (Hough, Bratchell & Macdougall, 1992b), but can influence color, which in turn may affect consumers acceptance (Hough, Bratchell & Wakeling, 1992a).

From a nutritional standpoint, calcium is the most important element of milk, being fundamental for healthy bones and osteoporosis prevention. Calcium levels in milk do not vary greatly (Smit, 2000; Cashman, 2006). Moreover, since the dry extract is concentrated during the manufacturing process, calcium, potassium, and phosphorus are interesting attributes to indicate the representativeness of the raw material in DL formulations.

3.3. Carbohydrates by HPLC

Among the DL components, carbohydrates have greater importance due to its influence on technological processing. The two most important carbohydrates in DL are lactose and sucrose (Demiate, 2001; Oliveira, 2009). Lactose is present in milk products without added β-galactosidase or acid-lactic cultures (Giménez, 2008; Oliveira, 2009; Vénica, 2013), and is responsible for about 50% of the osmotic pressure due to its concentration (4.8%) in the fluid phase (Smit, 2000). A large amount of sucrose is added to DL formulations during manufacturing (Perrone, 2011), which is responsible, on a larger scale than lactose by the non-enzymatic browning during heat treatment, and by providing the characteristic sweet taste of DL

(Velasco, 2010; Perrone, 2011; Golon & Kuhnert, 2012; Jiang, Wang, Wu & Wang, 2013). Moreover, it is a common practice adding glucose to aid the browning process, to promote greater brightness, and let the product pleasing to the palate (Oliveira 2009). Therefore, it can be concluded that the DL is a typically brownish product (Pathare, 2013).

Rapid methods for quantification of carbohydrates in processed foods have been developed (Parc, Lee, Chen & Barile, 2014). Quantification and characterization methods for DL have been reported and adapted by enzymatic and photometric methods (Demiate, 2001; Guimarães, Leão, Pimenta, Ferreira & Ferreira, 2012). However, recent literature studies have focused on quantifying carbohydrates in dairy foods by high performance liquid chromatography (HPLC), which is commonly used for other dairy products such as milk (Giménez, 2008; Erich, Anzmann & Fischer,, cheese (Gomes et al ., 2011) and yogurt (Cruz et al., 2012a,b; Cruz et al., 2013),

Table 2 shows lactose, sucrose and glucose contents of Dulce de Leche samples. Again, differences were observed for all sugars and for total carbohydrates between samples (p <0.05). The samples I and III showed the highest lactose content (11.75 and 13:51/ 100 g, respectively) while samples II, III and IV presented the highest sucrose values (49.59, 47.40, and 47.36 g/ 100 g, respectively). With respect to glucose, the samples II, V and VII presented the three highest values (0.40, 0.25 and 0.75 g/ 100 g, respectively). The total carbohydrates ranged from 61.08 to 43.67 g/100 for samples III and V, respectively. A great variation was observed for glucose content, which ranged from 0.09 to 0.75 g /100 g for the sample I and VII, respectively, suggesting heterogeneity of the technological processing of DLs.

Lactose has a strong correlation with most milk components, such as protein (r = 0.82, p <0.023), fat (r = 0.93, p <0.003), ash (r = 0.89, p <0.008), potassium (r = 0.93, p <0.003), calcium (r = 0.90, p <0.006) and phosphorus (r = 0.87, p <0.010). A strong correlation between the three carbohydrates (total) and sucrose was observed (r = 0.95, p <0.001), thus demonstrating the importance of sucrose in glycide profile of DL and hence the characterization of this product. The large amount of sucrose and lactose found in sample III increased its susceptibility to non-enzymatic browning reactions and especially lactose crystallization. Sample III was the only sample that exhibited perceptible crystals while still within the shelf life. This can be explained by the fact that the addition of sucrose is inversely proportional to the solubility of lactose. To avoid this, the industry can add glucose syrup for its influence on the plasticity, which allows obtaining higher solids content without reaching the saturation point of lactose (Oliveira, 2009). Another strategy to avoid crystallization by decreasing solubility in traditional DL is to reduce the non-hydrolyzed lactose content in relation to other saccharides, as observed in the sample II.

Regarding the sweet taste, only samples V and VII did not present this parameter with high intensity, due to the high sweetening effect of sucrose when compared to other carbohydrates. To harmonize this situation, glucose as a reducing sugar, has the ability to optimize browning at high temperatures and generate caramel and bitter compounds, masking the too sweet taste. Besides the high temperatures, increasing cooking time is directly proportional to the generation of complex compounds that influence flavor and residual sensation (Hough, 1992b). Nevertheless, Hough (1992a) reported that the flavor has a low impact on the overall impression.

The correlation between sucrose and moisture content ($r = -0.59$, $p < 0.158$) highlights the importance of balance between both concentrations. The high levels of sucrose have beneficial technological effects, such as reducing water activity, reducing microbial growth and increasing shelf life (Oliveira, 2009). Sample II was manufactured in a food exporting industry, therefore it is interesting to extend their validity due to the long distances to reach overseas markets and the shelf life period. Among all samples, the sample II exhibited greater shelf life shown on the label, corroborating the low moisture and high sucrose content found in this sample.

The analytical techniques used in this study were not intended to quantify the starch.Nevertheless, it is possible that starch had been added to the DL formulations containing low sucrose, glucose and lactose contents (samples II, V and VII) in order to supplement their glycidic matrix, since the addition of this component was informed on labels of these brands. Demiate (2001) also suggested that whey protein could be added. Despite the addition of sucrose and starch is permitted, it decreases protein, lipid and ash contents, affecting negatively the nutritional composition (Demiate, 2001; Konkel, Oliveira, Simões, Demiate, 2004). Therefore, starch addition should be evaluated carefully by the surveillance authorities.

Glucose added at the end of the manufacturing process is capable of forming a strongly hydrated complex with protein, which increases the DL viscosity and directly interfering with the formation of lactose crystals perceptible in the mouth (Giménez, 2008; Perrone, 2011). The replacement of sucrose by glucose also results in higher brightness, thin, soft and smooth texture, thus increasing consumer’s acceptance. Opposite attributes are observed when high levels of glucose syrup are added to the formulations (Hough, 1992a; Hough, 1992b). Therefore, the addition of this important sugar should be done at the end of the process, when the temperature tends to decrease, in order to prevent drastic changes in DL characteristics (Perrone, 2011). As a reducing sugar, glucose is more reactive than sucrose. Then, at pH 5-6, there is an active participation of this monosaccharide in the Maillard reaction, increasing the tendency to browning (Oliveira, 2009). This is an important factor, since the acceptance of DL is related to its appearance and texture (Hough, 1992a). Additionally, texture attributes such as hardness, viscosity, and tooth packing are related to the formation of caramel (Steiner, Foegeding & Drake, 2002). Although no abrupt changes in color attributes were observed, higher brightness was observed in the three samples containing higher contents of glucose (samples II, V and VII). Their addition was probably for this purpose.

The presence of glucose in the other samples can be explained by two different ways: first, it may have been added without informing the consumer and the regulatory agencies that approve the labels; second, and more likely, it is related to the formation of this monosaccharide from the sucrose inversion, releasing glucose and fructose. This could easily occur in the DL due to the technological processing at high temperatures. To a lesser extent, it could be related to the presence of minerals or deficient alkalization during manufacturing process (Oliveira, 2009). Similar situation was observed by Demiate (2001), who identified glucose in 37 Brazilian trends, of which only 26 have this carbohydrate reported on the label.

Corroborating BSR (1997), Perrone (2011) suggested a mass balance of a hypothetical DL manufactured from milk with proximate characteristics found in Brazil. The DL formulation should have 70 g/ 100 g total solids (30 g/ 100 g moisture), and processed from 1000L of milk containing 12.21 g/ 100 g total solids (87.79% water, 4.8% lactose, 3.3% lipids, 3.3% protein, and 0.81% ash), and with addition of 200 kg sucrose. Thus, 460.14 kg of DL would be produced, presenting all the physicochemical parameters (30 g /100 g water, 7.17 g /100 g fat, 7.17 g / 100 g protein, and 1.76 g / 100 g ash) established by Brazilian regulation. Furthermore, the final lactose (10.43 g / 100 g) and sucrose content (43.47 g /100 g) was calculated. Comparing these two glycidic levels, as seen in Table 2, there is an overestimation of the use of sucrose in the samples of this study.

The feasibility of measuring lactose, sucrose and glucose separately suggests that the current legislation (BSR, 1997) should be reviewed. Currently, the sucrose addition is still measured in fluid milk, which complicates the measurement of the amount added, since it would be necessary to know the yield to calculate the mass of sucrose added per liter of milk. Thus, it is suggested that the quantification and establishment of sucrose limits may be directly in the final product.

Similarly, other mono- and disaccharides should be investigated and studies on its characterization in DL should be performed. Due to the strong correlation between lactose and milk components (protein, fat, and ash), based on the results of the samples III and VI, which fully met the current legislation parameters (BSR, 1997), and on the calculation performed by Perrone (2011) (DL containing 10.43 g/ 100 g lactose), it can be stated that the most true lactose values were found in these samples (13.51 and 11.76 g / 100 g respectively), and on the calculation of Perrone.

3.4 Volatile compounds by GC-MS

The gas chromatography - mass spectrometry (GC-MS) is valuable in identifying volatile components in food systems, since it provides the linear retention index (LRI) of the compounds retained on the column (Condurso, 2008). These volatile compounds of the food matrix may be derived from chemical reactions involving various factors such as bacterial enzymes, heat treatment, or oxidation reactions in the presence of atmospheric oxygen. Therefore, their identification is important to verify desirable or undesirable changes that may occur in the product during processing or storage, which can result in loss of physicochemical and sensory characteristics, affecting the shelf life of the product. (Smit, 2000).

The volatile compounds and their respective retention indices identified in the Dulce de Leche samples are shown in Table 3. Overall, 32 volatile compounds were identified belonging to 10 different chemical families of which only two were not present in all samples. The compound 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol) was identified only in the sample VII, while the sorbic acid was detected in sample II. The former is known to be product of the degradation of milk poly-unsaturated fatty acids (PUFA) and it can be related with specific temperature used by this producer along the heat treatment (Bendall, 2011), while the latter is a known preservative used to prolong the shelf life of processed foods, with effective action against molds and yeasts. It is relevant to mention that potassium sorbate, which precedes sorbic acid, was not declared only in I and II labels. So, DL I is nonconforming under this point of view.

The flavor and aroma of cooked milk is related to dimethyldisulfides. These sulfur-containing compounds tend to be powerful odorants. Furans and lactones were also identified in the samples of the present study. These substances, which are associated with the Maillard reaction, confer flavor and aroma related to the sterilization process at high temperatures (Zabbia, Buys, & Koch, 2012) In general, the presence and the level of ketones is directly proportional to the "age "of the product, compromising its sensory quality, since it may lead to rancid flavor and aroma (Smit, 2000). Furfural is a known compound, generated from the non-enzymatic browning, mainly by the caramelization reactions (Paravisini et al., 2012).

3.5. Optical analyses

As shown in Table 4, significant differences ($p < 0.05$) were observed for all samples with respect to the optical parameters. The parameters *L** and *h** varied similarly between samples, which can be supported by the strong correlation between them (r = 0.93, p <0.003). In the present study, the sample I showed the highest lihtness (62.11) and Hue angle (62.17), while the sample VI had the lowest values for these parameters (48.59 and 51.97 respectively), tending to be darker. The positive values found for the color coordinates *a** and *b** indicate that the DL is a product with a tendency to red and yellow, with a predominance of the second, due to higher *b** values found in all samples. Therefore, the combination of these two colors can explain the color of the DL after the induced browning by the Maillard and caramelization reactions (Golon, 2012; Pathare, 2013). The parameter *a** ranged from 13.60 to 16.90 in the samples III and V, respectively. The samples VI and V had the lowest (17.89) and the highest (27.70) *b** values, respectively. The differences among the samples with respect to the color parameter are probably due to the differences in protein and sugar composition, as well as the changes in time, temperature and pressure, according to the protocol of each industry (Oliveira, 2009). This argument can be supported by the *h** values, in which the variation of 51.97 (sample VI) to 62.17 (sample I) represents the change, in degrees, from red to yellow. Therefore, this values (larger then 45º) illustrate the tendency of DL to be yellowish. Chroma was more intense (32.45) in the sample V and less intense (22.71) in the sample VI. Although a strong correlation between *C** and *b** (r = 0.99, p <0.0001) was observed, it may be because *b** values were higher than *a** values, thus increasing *C** with more efficiency.

The samples VI and IV, and I and II had the lowest and the highest *L** values, respectively. With respect to *b**, only the sample I did not present the highest value.

The other three samples presented the same behavior as observed for *L**. These dissimilarities are reflected in the total color difference observed between these samples: I x IV (11.90), I x VI (16.33), II x IV (10.20) and II x VI (14.73). In addition, V x VI had high *ΔE** (13.07), once V presented the highest *a** (16.90) and *b** (27.70) values, while the sample V exhibited the lowest *L** (48.59) and *b** (17.89). Only the samples I x II (2.32) and III x VII (1.70) were not considered "very different" to each other to the human eyes, according to Pathare (2013).

3.6. Principal component analysis

Figures 1 and 2 (a and b) shows the principal component analysis performed with the data of physicochemical and optical analyses of the DL samples. Three main components (F1, F2, F3) were used, which accounted for 84.05% of data with a range of 51.45 and 17.89% for the first and second component, respectively, while the third main component contributed to 14.73 % of the data. The results suggest that there is a wide variability in the operating parameters of the DL processing, which are intrinsic of formulations in the processing units. In a broader analysis, this study indicates the need to establish a quality standard for the Dulce de Leche in order to standardize the products available in the market.

F1 is associated positively with the DL physicochemical parameters comprising the dry extract, except for glucose, which stood on the negative quadrant. F2 highlighted the pH and the visual attributes, except a*. Through these two components, it is possible to separate the samples into three groups. Samples III, IV and VI are allocated on the positive quadrant of F1, identified by most of the DL physicochemical characteristics related to the composition of the raw material, with the exception of sucrose and sodium. The negative quadrant of F1 generated a second group consisting of samples V and VII, highly influenced by the high glucose content of the samples. Based on the optical characteristics, F2 cooperated with the formation of a third group consisting of samples I and II. The visual aspects are important to the product acceptance, and can vary in brightness, color and visual texture according to the process adopted (Giménez, 2008; Velasco, 2010; Perrone, 2011).

The F3 component is negatively associated with moisture content and optical parameters, including *a**. Glucose, positioned on the positive quadrant of F3, was important in the characterization of sample VII, since this sample contained higher levels of this monosaccharide in relation to the others. Visually, the sample VII had higher brightness, confirming the influence of the vector "glucose" on this sample (Perrone, 2011). The negative quadrant of F3 was responsible for completely separating the sample V from VII, due to both its differential color characteristic and high moisture (V), despite not having extrapolated the standard allowed by law (BSR, 1997).

4. Conclusion

This study successfully evaluated the physicochemical characterization of the pasty DL by conventional methods and instrumental techniques (HPLC, GC-MS, ICP-OES), providing results that are not yet available for this product.

Thirty-two volatile compounds were identified by GC-MS. With respect to the sugars, sucrose proved to be the most predominant in this food matrix as compared to lactose, glucose and other components. Regarding the physicochemical analyses, four commercial brands showed physicochemical parameters in disagreement to the Brazilian regulations, due to the low proportion of milk components, primarily lipids, proteins and ash.

There is a need of periodic studies covering the DL intrinsic parameters of quality which should receive special attention, as it can be directly related to the consumer acceptance. The malicious or accidental replacement of the dairy substrate by carbohydrates evidenced by the low-protein, lipid and ash, concurrently with the moisture within the recommended by law, is a topic that should be addressed by the industry in the quality control of the final product. Studies should be performed in this food typical of Latin America, with a view to establish strong identity and quality standards with the ultimate goal of reaching consumer markets in different countries.

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TABLES AND FIGURES

Table 1. Chemical composition and mineral mean values for dulces de leche brands*

Product	Protein (g/100g)	Fat (g/100g)	Ash (g/100g)	Moisture (g/100g)	Latic acid (g/100g)	pH	Na (g/100g)	K (g/100g)	Ca (g/100g)	P (g/100g)
I	6.61^{a} ± 0.18	5.93^{abc} ± 0.01	1.86^{c} ± 0.00	29.51^{a} ± 0.66	0.29^{e} ± 0.00	6.37^{a} ± 0.03	0.15^{bc} ± 0.01	0.37^{b} ± 0.01	0.31^{c} ± 0.01	0.21^{b} ± 0.01
II	4.16^{b} ± 0.69	4.93^{c} ± 0.57	1.83^{d} ± 0.00	17.49^{c} ± 0.49	0.37^{d} ± 0.01	6.33^{ab} ± 0.02	0.15^{ab} ± 0.00	0.37^{b} ± 0.01	0.32^{b} ± 0.00	0.24^{a} ± 0.00
III	6.45^{a} ± 0.00	6.99^{a} ± 0.19	1.87^{c} ± 0.02	26.74^{ab} ± 2.06	0.40^{c} ± 0.00	6.14^{d} ± 0.02	0.12^{e} ± 0.00	0.40^{a} ± 0.00	0.33^{b} ± 0.00	0.23^{a} ± 0.00
IV	4.60^{b} ± 0.35	6.93^{a} ± 1.02	2.05^{a} ± 0.01	25.30^{b} ± 1.05	0.50^{a} ± 0.00	6.20^{c} ± 0.01	0.16^{a} ± 0.00	0.40^{a} ± 0.00	0.36^{a} ± 0.00	0.24^{a} ± 0.00
V	2.10^{c} ± 1.05	5.04^{bc} ± 0.11	1.57^{e} ± 0.01	29.67^{a} ± 0.21	0.36^{d} ± 0.00	6.16^{cd} ± 0.02	0.14^{c} ± 0.00	0.33^{c} ± 0.00	0.24^{d} ± 0.00	0.18^{c} ± 0.00
VI	7.12^{a} ± 0.44	6.29^{ab} ± 0.26	1.97^{b} ± 0.00	24.67^{b} ± 0.30	0.45^{b} ± 0.00	6.21^{c} ± 0.02	0.16^{a} ± 0.00	0.40^{a} ± 0.00	0.33^{b} ± 0.00	0.24^{a} ± 0.00
VII	3.51^{bc} ± 0.35	3.56^{d} ± 0.37	1.31^{f} ± 0.00	24.30^{b} ± 1.73	0.23^{f} ± 0.01	6.31^{b} ± 0.02	0.13^{d} ± 0.00	0.28^{d} ± 0.00	0.19^{e} ± 0.00	0.14^{d} ± 0.00

- Values are means ± Standard deviation[1] Analyses were performed in triplicate. $^{a-f}$ Means with the different letters in the same column are significantly different ($P < 0.05$) using Tukey's test

Table 2. Carbohydrates (lactose, sucrose and glucose) in DLs obtained by HPLC*

Product	Lactose (g/100g)	Sucrose (g/100g)	Glucose (g/100g)	Total (g/100g)
I	$11.75^{b} \pm 1.45$	$46.94^{ab} \pm 1.85$	$0.16^{c} \pm 0.08$	58.85
II	$9.81^{c} \pm 1.22$	$49.59^{a} \pm 0.50$	$0.40^{b} \pm 0.13$	59.80
III	$13.51^{a} \pm 0.41$	$47.40^{ab} \pm 0.89$	$0.17^{c} \pm 0.08$	61.08
IV	$11.61^{b} \pm 0.89$	$46.63^{ab} \pm 1.93$	$0.09^{c} \pm 0.05$	58.33
V	$7.37^{d} \pm 0.59$	$36.04^{c} \pm 0.69$	$0.25^{bc} \pm 0.04$	43.67
VI	$11.76^{b} \pm 1.29$	$47.36^{ab} \pm 0.36$	$0.16^{c} \pm 0.27$	59.28
VII	$5.79^{e} \pm 1.15$	$44.03^{b} \pm 0.41$	$0.75^{a} \pm 0.23$	50.57

* Values are means ± Standard Deviation. [1] Analyses were performed in triplicate. [a-e]Means with the different letters in the same column are significantly different ($P < 0.05$) using Tukey's test,

Table 3. Volatile compounds in samples of Dulces de Leches identified by CG-MS

Compounds[a]	LRI[b]	I	II	III	IV	V	VI	VII
Acids								
Acetic acid	1256	X	X	X	X	X	X	X
Propanoic acid, 2-methyl	1676	X	X	X	X	X	X	X
Butanoic acid	1677	X	X	X	X	X	X	X
Hexanoic acid	1951	X	X	X	X	X	X	X
Sorbic Acid	2369	X	-[c]	X	X	X	X	X
Heptanoic acid	1197	X	X	X	X	X	X	X
Ketones								
2-Propanone, 1-hydroxy	1108	X	X	X	X	X	X	X
2-Pentanon	797	X	X	X	X	X	X	X
2-Pentanone, 4-hydroxy-4-methyl	1217	-[c]	-	-	-	-	-	X
2-Nonanon	1204	X	X	X	X	X	X	X
2-Undecanon	1601	X	X	X	X	X	X	X
Aldehydes								
Furfural	1269	X	X	X	X	X	X	X
Nonanal	1211	X	X	X	X	X	X	X
Undecanal	1538	X	X	X	X	X	X	X
Amines								
Benzeneethanamine, 2-fluoro-β,5-dihydroxy-N-methyl	764	X	X	X	X	X	X	X
Benzeneethanamine, 3-fluoro-β,5-dihydroxy-N-methyl	754	X	X	X	X	X	X	X
Amides								
Butanimidamide	770	X	X	X	X	X	X	X
Alcohols								
2-Furanmethanol	1861	X	X	X	X	X	X	X
(3-Methyl-oxiran-2-yl)-methanol	1094	X	X	X	X	X	X	X
1-Propanol, 2-methyl	898	X	X	X	X	X	X	X
1-Pentanol, 4-amino	760	X	X	X	X	X	X	X
2-Heptanol, 6-amino-2-methyl	763	X	X	X	X	X	X	X

Hidrocarbons								
Cyclobutene, 2-propenylidene	849	X	X	X	X	X	X	X
4-Cyclopentene-1,3-dione	1465	X	X	X	X	X	X	X
Trichloromethane	865	X	X	X	X	X	X	X
Methylene chloride	777	X	X	X	X	X	X	X
n-Hexane	757	X	X	X	X	X	X	X
Furan								
Furan, 2-methyl-	778	X	X	X	X	X	X	X
Lactones								
Butyrolactone	1730	X	X	X	X	X	X	X
Others								
Disulfide, dimethy	881	X	X	X	X	X	X	X
Oxime-, methoxy-phenyl	2028	X	X	X	X	X	X	X
Pyrimidine-4,6-diol, 5-methyl	2118	X	X	X	X	X	X	X

[a] Organized by families. [b] Linear Retention Index on CP-Wax 52 CB according to the Van der Dool and Kratz equation. [c] Non detected

Table 4. Average values of optical paraameters of Dulce de Leche*

Samples	Color quality attributes[1,2]				
	*L**	*a**	*b**	*C**	*h**
I	$62.11^{a} \pm 0.06$	$14.28^{c} \pm 0.06$	$27.05^{c} \pm 0.05$	$30.58^{c} \pm 0.05$	$62.17^{a} \pm 0.12$
II	$59.98^{b} \pm 0.04$	$15.17^{b} \pm 0.02$	$27.16^{b} \pm 0.07$	$31.11^{b} \pm 0.06$	$60.82^{b} \pm 0.06$
III	$59.09^{c} \pm 0.01$	$13.60^{f} \pm 0.02$	$23.39^{d} \pm 0.02$	$27.05^{e} \pm 0.01$	$59.83^{c} \pm 0.05$
IV	$51.51^{f} \pm 0.01$	$13.64^{e} \pm 0.02$	$21.69^{f} \pm 0.03$	$25.62^{f} \pm 0.02$	$57.83^{f} \pm 0.06$
V	$56.73^{e} \pm 0.00$	$16.90^{a} \pm 0.02$	$27.70^{a} \pm 0.02$	$32.45^{a} \pm 0.01$	$58.62^{d} \pm 0.08$
VI	$48.59^{g} \pm 0.09$	$13.99^{d} \pm 0.04$	$17.89^{g} \pm 0.10$	$22.71^{g} \pm 0.10$	$51.97^{g} \pm 0.09$
VII	$57.53^{d} \pm 0.09$	$14.25^{c} \pm 0.03$	$23.20^{e} \pm 0.07$	$27.23^{d} \pm 0.06$	$58.45^{e} \pm 0.08$

* Values are means ± Standard deviation. [1]Attributes measured through CIE *L*a*b** Color Spaces: *L** = lightness coordinate, 0 to 100; *a** = red(+)/green(−) colour attribute, ±60; *b** = yellow(+)/blue(−) colour attribute, ±60; *C** = Chroma, $(a^{*2} + b^{*2})^{1/2}$, 0 to 60; *h** = hue angle, arctan (b^*/a^*), 0º (red-purple), 90º (yellow), 180º (bluish-green), 270º(blue) [2] Analyses were performed in ten replicates.
[a-g] Means with the different letters in the same column are significantly different ($P < 0.05$) using Tukey's test

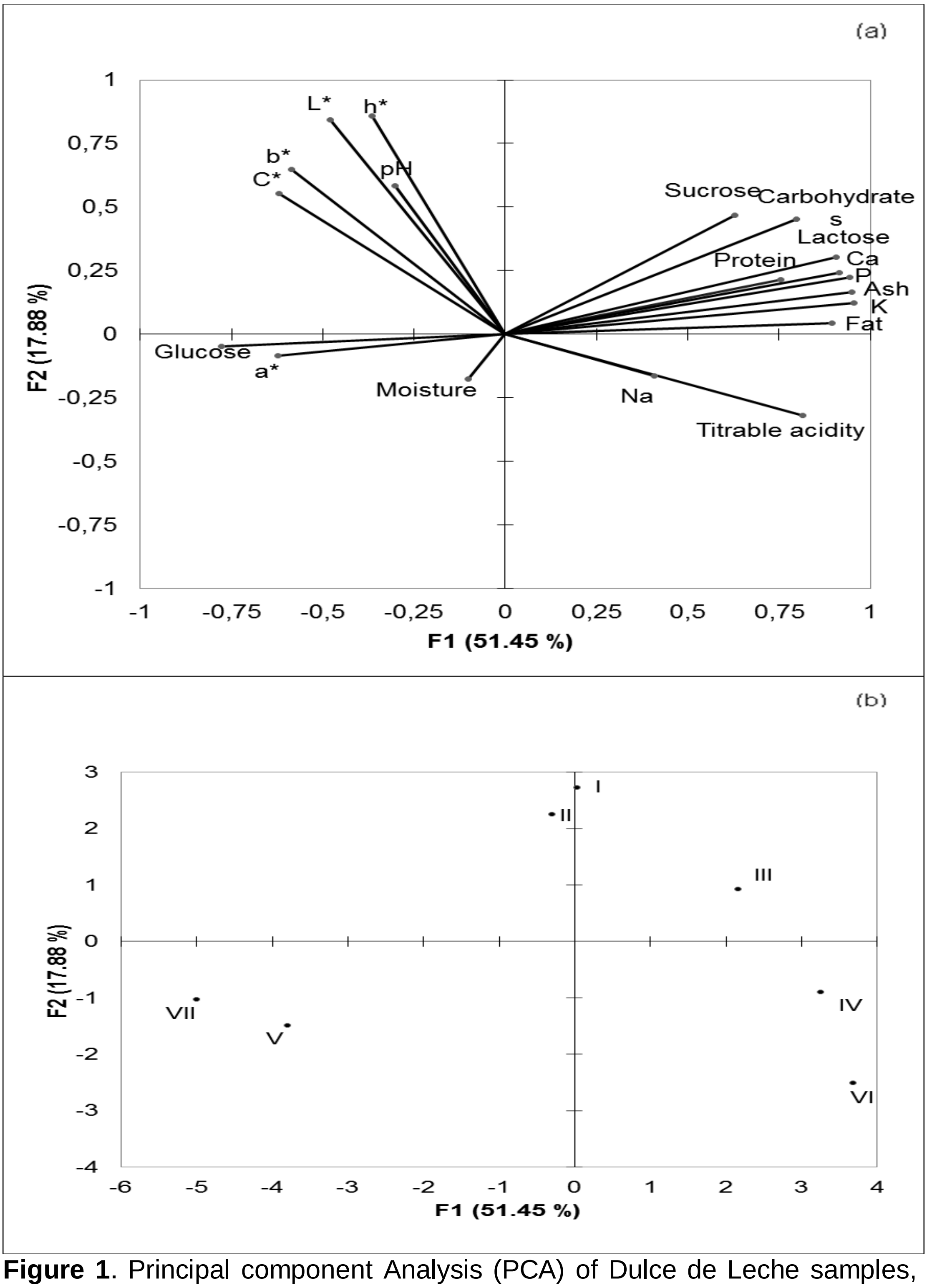

Figure 1. Principal component Analysis (PCA) of Dulce de Leche samples, F1 x F2, of parameters (a) and samples (I, II, III, IV, V, VI ,VII) (b) as given in Tables 1, 2, 3 and 5.

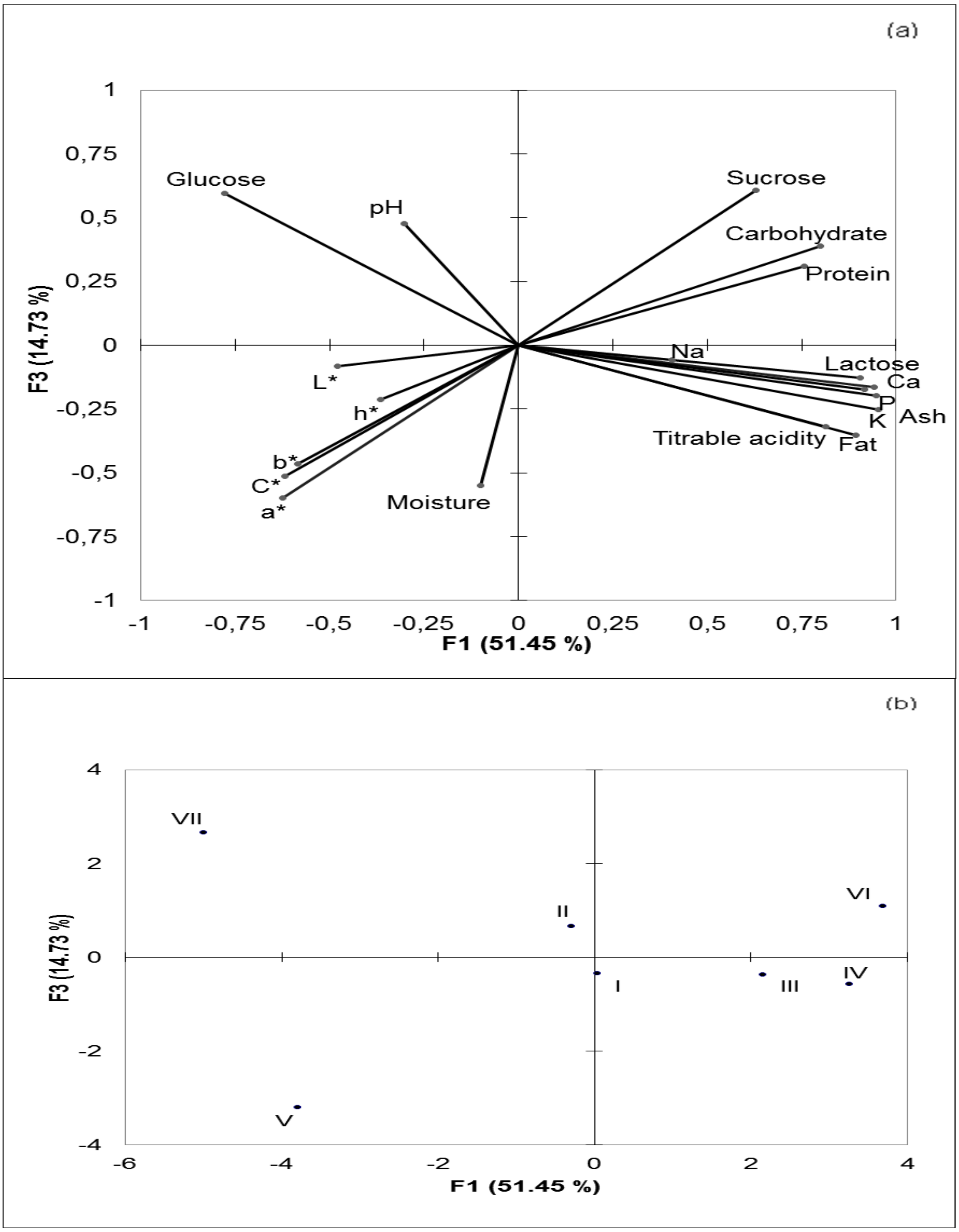

Figure 2. Principal component Analysis (PCA) of Dulce de Leche samples, F1 x F3, of parameters (a) and samples (I, II, III, IV, V, VI ,VII) (b) as given in Tables 1, 2, 3 and 5.

4 CONSIDERAÇÕES FINAIS

A aceitação e a escala do ideal tiveram resultados bastantes similares. Sendo assim, os DLs menos aceitos foram os que tiveram menos citações como ideais na escala do ideal. A escala do ideal indicou valores mais fora do ideal (acima ou abaixo) nos doces que apresentaram valores mais extremos na ADQ. Isso demonstra uma habilidade dessa metodologia em “semi-quantificar” atributos utilizando consumidores. A LR e a ANN se mostraram, através da alta acurácia, sensibilidade e especificidade, modelos adequado para predizer os atributos mais importantes para o consumidor. O método de PLSR demonstrou baixa aplicabilidade ao DL sugerindo um comportamento mais complexo, não linear, das características do DL.

Houve êxito na caracterização físico-química do DL pastoso através de métodos convencionais e técnicas instrumentais (HPLC, GC-MS, ICP-OES), o que trouxe à comunidade dados que anteriormente não haviam sido reportados. 32 compostos voláteis foram identificados pelo CG-MS. A sacarose demonstrou ser o açúcar de maior predomínio nessa matriz alimentar em comparação com a lactose, glicose e os outros componentes. Quatro marcas comerciais se apresentaram com parâmetros físico-químicos em desacordo com a regulamentação preconizada havendo baixa proporção dos componentes do leite – basicamente lipídios, proteínas e cinzas.

Mais estudos devem ser conduzidos nessa matriz alimentícia típica da América Latina com vistas a se estabelecer padrões mais nítidos da aceitação e das características físico-químicas com o objetivo final de se atingir mercados consumidores em diferentes países favorecendo o crescimento regional da economia.

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6 APÊNDICES

6.1 CONFIRMAÇÃO DE SUBMISSÃO DO ARTIGO INTITULADO: OPTIMIZATION OF THE DULCE DE LECHE PROCESSING: CONTRIBUTIONS OF THE SENSOMETRIC TECHNIQUES

Submission Confirmation

Thank you for submitting your manuscript to *Journal of Dairy Science*.

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6.2 CONFIRMAÇÃO DE SUBMISSÃO DO ARTIGO INTITULADO: DULCE DE LECHE, A TYPICAL PRODUCT OF LATIN AMERICA: CHARACTERIZATION BY PHYSICOCHEMICAL, OPTICAL AND INSTRUMENTAL METHODS

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Article Type: Research Article (max 7,500 words)

Keywords: dulce de leche; quality; physico-chemical analysis.

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Abstract: The physicochemical profile of Dulce de Leche (DL) was determined by both routine analysis and others techniques (HPLC, GC-MS and ICP-OES). Seven Brazilian commercial brands were characterized for moisture content, protein, fat, ash, pH and titratable acidity, mineral content (sodium, potassium, calcium, and phosphorus), optical parameters and instrumental analysis (carboidrates content and volatile compounds). Overall, extensive variability among all the parameters evaluated were observed, suggesting different operational procedures in the dairy factories along the DL processing. In this sense, an increase of intrinsic quality of DL is related closely the standardization of operacional parameters using during the manufacture.