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Evaluation of the heat damage of whey and whey proteins using multivariate analysis

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ABSTRACT

Maillard reaction (MR) was assessed in 10 powdered whey samples. Initial stages of MR were evaluated using furosine, intermediate stages with hydroxymethylfurfural (HMF) and absorbance at 284 nm, advanced stages with color parameters (CIELab color) and final stages with browning index; additionally, insolubility, pH and water activity (Aw) were measured. Principal component analysis (PCA) and cluster analysis (CA) were used to establish the heat damage of samples based on relations between variables. Three principal components were found which explained 79.0% of the total variance and they were the basis for cluster analysis where 5 clusters were formed. PCA and CA can separate samples according to their heat damage and they help in a clearer interpretation of the information from indicators which shows that samples with high lactose content exhibited the higher heat damage.

1. Introduction

Whey is a byproduct of the dairy industry (Londoño, Sepulveda, Hernández, & Parra, 2008) used for multiple applications in food industry (Aider, de Halleux, & Melnikova, 2009; Foegeding, Davis, Doucet, & McGuffey, 2002). The most common uses are natural and sugary concentrates, whey powders, protein extraction, bakery, confectionery, whey butter, baby food, pharmaceutical pills, beer and feed (Castrillón, 2013). In the dairy chain, and in relation with the development of exterior trade, imports of whey in Colombia showed an increment of 107% over the last 11 years (Moya, 2012).

According to the Trade Map- International Trade Statistics, the main whey exporter countries in 2015 to Colombia were the United States (29.8%), Uruguay (16.8%), Chile (15.4%), France (14%) and Czech Republic (10%) (Trade Map, 2016). This study would reflect the reality of whey proceeding from the world, characterized in terms of thermal damage processing, storage and transport conditions.

Whey powder is obtained by using concentration and separation techniques through membranes that permit selective cleavage of whey components (Johnson & Law, 2010). Subsequently, a drying process is used to obtain a powder (Tunick, 2008), the commonest process used is the spray drying (Aider et al., 2009). During spray drying, the inlet air temperature is usually high (160–200 °C), which leads to the partial denaturation of proteins (Osorio et al., 2014) and promotes undesirable reactions that adversely affect the nutritional and technological properties of proteins (Rufián-Henares, García-Villanova, & Guerra-Hernández, 2004). In addition, imported dairy products can be stored for long periods of time under extreme conditions (Granda-Restrepo, Peralta, Troncoso-Rojas, & Soto-Valdez, 2009) causing further decline in the nutritional properties (García-Risco, Ramos, & López-Fandio, 2002).

One of the most significant changes induced by drying and long-term storage is Maillard reaction (MR) which involves reducing carbohydrates and amino acids. MR compromises the nutritional value of whey protein by blocking essential amino acids (Jelen, 2009). Usually, whey is valued for its net protein content, without being reflected the declining nutritional value of blocked amino acids during heat treatments, since this effect and the way to evaluate it are usually ignored or unknown.

Some chemical indicators have been used to evaluate the heat damage of the protein due to the MR. The initial stages of MR can be followed by determining furosine; some authors have reported it as a useful indicator of the heat damage in dairy products (Contreras-Calderón, Guerra-Hernández, & García-Villanova, 2009; Thao, Bhandari, Holland, & Deeth, 2011). Hydroxymethylfurfural (HMF) and furfural are indicators of intermediate stages of MR, these have been evaluated in different dairy- based products, such as proteins (Contreras-Calderón, Guerra-Hernández, & García-Villanova, 2008), baby foods (Mesías-García, Guerra-Hernández, & García-Villanova, 2010) and whey powders (Dattatreya & Rankin, 2006).

MR produces molecules that absorb between 250 nm and 300 nm; specifically, HMF absorbs at 284 nm (Singh, Dean, & Cantor, 1948).

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This absorbance has been used as an indicator of intermediate stages of MR (Contreras-Calderón, 2008; Ju-Woon et al., 2006). The color development is an indirect indicator of advanced and final stages in MR (Friedman & Kline, 1950). The color in final stages can be followed by using the absorbance at 420 nm, also known as browning index (BI); it has been used as a color pointer in powder milk (Seiquer, Delgado-Andrade, Haro, & Navarro, 2010; Thao et al., 2011). Alternatively, color measurements have been made using reflectance (Color parameters L*, a*, b* in the CIELab system) as an indicator of heat damage in intermediate (Dattatreya & Rankin, 2006) and advanced stages of MR (Rufián-Henares et al., 2004). Additionally, yellowness index (YI) which is calculated as 142.86b*/L* (Francis & Clydesdale, 1975) has shown to be a sensitive indicator to follow the formation of yellowish compounds during the MR (Delgado-Andrade, Seiquer, Haro, Castellano, & Navarro, 2010; Rufián-Henares et al., 2004; Rufián-Henares, Guerra-Hernandez, & García-Villanova, 2006).

The above-mentioned indicators are usually used separately in order to explain the advance in MR. However a single indicator does not determine the heat damage of a sample, so it requires at least one indicator for each stage of the MR (initial, intermediate, advanced and final) in order to know the progress of MR in the samples. Even if several indicators are analyzed, it is not easy to establish the heat damage without the use of robust statistical tools. Multivariate analysis can assist the interpretation of several variables in a meaningful manner since it is a set of statistical tools designed to obtain information from data composed of simultaneous measurements of many variables (Johnson & Wichern, 2007). Multivariate analysis has been widely used in food science (Correddu et al., 2017; Fernández Pierna et al., 2016; González-Martín, Palacios, Revilla, Vivar-Quintana, & Miguel Hernández-Hierro, 2017) and has shown good results.

Numerous studies have evaluated dairy products in relation to heat damage indicators as a useful tool to assess the MR during processing and storage (Contreras-Calderón et al., 2009; Ferrer, Alegria, Farre, Abellan, & Romero, 1999; Ferrer, Alegría, Farré, Clemente, & Calvo, 2005; Rufián-Henares et al., 2004). However, there are few studies using multivariate analysis to interpret MR indicators in food (Contreras-Calderón et al., 2016; Contreras-Calderón, Guerra-Hernández, García-Villanova, Gómez-Narváez, & Zapata-Betancur, 2017). Additionally, there are no studies relating all the variables employed in the present study which utilize multivariate analyses to explain heat damage in whey. For this reason, this study aimed at using multivariate analysis to help in the evaluation of heat damage in commercial samples of whey, whey protein concentrate (WPC) and whey permeate (WP) powders, in order to determine what extent chemical indicators are related, and this way, to group samples according to their heat damage.

2. Materials and methods

2.1. Chemicals

All reagents were of analytical grade. Acetonitrile (HPLC grade), methanol, hydrochloric acid, glacial acetic acid and chloramine T were obtained from Panreac (Barcelona, Spain). The Sep-Pack (C_{18}) cartridges were obtained from Millipore Waters (Milford, MA, USA). Furosine standard was purchased from PolyPeptide Laboratories (San Diego, USA). Hydroxymethylfurfural and furfural Standards were obtained from Merck (Darmstadt, Germany).

2.2. Samples

Five commercial samples of whey, three WPC and two WP powder of the local market (Medellin-Colombia) were analyzed (Table 1).

Table 1
Protein, lactose, water activity and age of samples used in the study.

Sample	Protein analysis[a] (g (100 g)$^{-1}$)	Lactose analysis[a] (g (100 g)$^{-1}$)	LPR[c] (g/g)	Aw[d]	Age[b] (months)
Whey permeate					
Sample 1	1.83 ± 0.18	86.8 ± 1.8	47.43	0.288	20
Sample 2	3.99 ± 0.75	80.6 ± 1.3	20.20	0.455	21
Average	2.91 ± 1.25	83.7 ± 3.6	33.82	–	–
Whey					
Sample 3	9.24 ± 0.23	79.4 ± 0.3	8.593	0.418	7
Sample 4	9.52 ± 0.06	80.6 ± 1.4	8.466	0.400	15
Sample 5	9.99 ± 0.07	83.3 ± 0.7	8.338	0.289	6
Sample 6	11.73 ± 0.08	76.8 ± 1.1	6.547	0.318	3
Sample 7	12.04 ± 0.27	70.5 ± 0.9	5.855	0.259	12
Average	10.50 ± 1.22	78.1 ± 4.6	7.56	–	–
Whey protein					
Sample 8	28.49 ± 0.18	51.2 ± 1.4	1.797	0.357	24
Sample 9	68.50 ± 0.61	19.7 ± 0.7	0.287	0.288	9
Sample 10	81.92 ± 0.85	16.5 ± 1.2	0.201	0.421	23
Average	59.64 ± 24.86	29.1 ± 17.1	0.761	–	–

[a] Mean value ± standard deviation (n = 3).
[b] Time elapsed between sample manufacture and analysis.
[c] Lactose-protein ratio.
[d] Water activity.

2.3. Methods

2.3.1. Furosine determination

Furosine content was determined by the method described by Rufián-Henares et al. (2004) with some modifications. 50 µL of sample were analyzed in an HPLC Shimadzu equipment, which had a quaternary gradient pump (LC-20AD), a diode array detector (SPD-M20A), an autosampler (SIL-20A HT), and a LiChospher column 100 RP-8 (5 µm) in LiChroCART 250-4. The mobile phase was 100% 0.06 M sodium acetate adjusted to pH 4.3 with acetic acid, the elution was isocratic and the flow rate was 1 mL min^{-1}. The UV detector was set at 280 nm and the data was processed using LC software. Furosine (0.00638–0.486 mg kg^{-1}) was quantified by using the external standard method. Duplicate analyses of duplicate samples were carried out (n = 4).

2.3.2. HMF and furfural determination

Furanic compounds were determined by HPLC technique using the method described by Guerra-Hernández, García-Villanova, and Montilla-Gómez (1992) with some modifications. Around 1.5 g of sample were clarified with Carrez-I and Carrez-II solutions, the supernatant was filtered through a 0.45 µm filter, and the samples were analyzed by HPLC. 50 µL of sample were analyzed in the HPLC Shimadzu equipment as previously described. HMF (0.01–1.5 mg kg^{-1}) and furfural (0.002–0,232 mg kg^{-1}) were quantified by using the external standard method. Duplicate analyses of duplicate samples were carried out (n = 4).

2.3.3. Absorbance at 284 nm

Absorbance of the filtered extracts obtained for determination of HMF and furfural were measured according to the method proposed by Guerra-Hernandez, Leon, Corzo, Garcia-Villanova, and Romera (2002). Duplicate analyses of duplicate samples were carried out (n = 4).

2.3.4. Browning index (BI)

The BI was determined by using absorbance at 420 nm in the extracts obtained for determination of HMF and furfural (Meydav, Saguy, & Kopelman, 1977). Duplicate analyses of duplicate samples were carried out (n = 4).