Food Control 95 (2019) 106–114

Contents lists available at ScienceDirect

Food Control

journal homepage: www.elsevier.com/locate/foodcont

Quality assessment and multivariate calibration of 5-hydroxymethylfurfural during a concentration process for clarified apple juice

Andrés Córdova[a,*], Jorge Saavedra[a,b], Valentina Mondaca[a], Juan Vidal[a], Carolina Astudillo-Castro[a]

[a] Escuela de Alimentos, Facultad de Ciencias Agronómicas y de los Alimentos, Pontificia Universidad Católica de Valparaíso, Waddington 716 Playa Ancha, Valparaíso, 2360100, Chile
[b] DATAChem AgroFood Group, Escuela de Alimentos, Pontificia Universidad Católica de Valparaíso, Waddington 716 Playa Ancha, Valparaíso, 2360100, Chile

ARTICLE INFO

Keywords:
Hydroxymethylfurfural
Clarified apple juice
Concentration process
Multivariate calibration
Quality

ABSTRACT

Variations in the quality of clarified apple juices subjected to a lab-scale concentration process were assessed. The processing conditions were similar to those used in an industrial three-effects evaporator: 85°C for 25 minutes during the first effect (E1), 75°C for 13 minutes during the second effect (E2) and 58°C for 20 minutes for the third effect (E3). The following parameters were measured at different times from samples of the three effects: Brix content, absorbance spectrum (200 to 670 nm), processing temperature, viscosity, pH, activity of water (Aw) and 5-hydroxymethylfurfural (HMF) concentration (measured via HPLC). The highest increase in HMF occurred during E3, reaching a concentration of 22.26 ± 1.32 mg/kg, with a Brix content of 65.93 ± 0.95. Such HMF concentrations were just below the European Food Regulation Standards. An increase of HMF correlated well with a decrease of Aw and pH. Absorbance spectral values within the UV range increased with increasing processing time, reflecting the non-enzymatic browning effect. Additionally, at measurements above 50° Brix, the effect of temperature and the Brix content had a significant effect on the viscosity. Partial least squares (PLS) regression and pre-processing data under an Orthogonal signal correction OSC + Wavelets (DWT) scenario yielded a multivariate calibration model that accurately predicted the appearance of HMF during the concentration process (R2 0.947). The proposed methodology may serve as an early warning against a critical threshold of HMF by offering a simple and fast physic-chemical analysis conventionally measured by most of the juice processing industry.

1. Introduction

Thermal processes are frequently used in most of food manufacturing industries in order to obtain safe products. Currently, heating is the principal strategy in the destruction of enzymes and micro-organisms, since developments in food technology are a battle against thermodynamic instability (van Boekel, 2008). Thermal processing such as baking, frying or roasting results in desired effects to various chemical reactions, with the Maillard reaction (MR) being one of the most prominent; however, its occurrence during drying, Pasteurization and sterilization is unfavourable not only due to nutritional losses but also due to the formation of reaction products with unwanted effects (Rufián-Henares, Delgado-Andrade, & Morales, 2009; Van Boekel, 2006). Among the products obtained by the MR, acrylamide and 5-hydroxymethylfurfural (HMF) can be regarded as the most important heat-induced contaminants occurring in foods subjected to high temperatures. Acrylamide has been demonstrated to be carcinogenic in rodents, and some recent epidemiological studies have highlighted the association between dietary acrylamide and an increased risk of some types of cancer; HMF at high concentrations is cytotoxic, irritating the eyes, upper respiratory tract, skin and mucous membranes (Capuano & Fogliano, 2011). The major concern for HMF is related to its conversion to 5-sulfoxymethylfurfural (SMF), a highly reactive intermediate that can react with DNA and other macromolecules to produce mutagenic effects (Lee, Shlyankevich, Jeong, Douglas, & Surh, 1995; Bakhiya, Monien, Frank, Seidel, & Glatt, 2009).

Quantification of HMF may serve as quality indicator related to excessive temperatures during heat treatment and inappropriate or long-term storage (Burdurlu & Karadeniz, 2003; Rada-Mendoza, Olano, & Villamiel, 2002). The evidence in recent years suggests that HMF is a widespread heat-induced contaminant with a dietary intake that is several orders of magnitude higher than that reported for other food

---

[*] Corresponding author.
E-mail address: andres.cordova@pucv.cl (A. Córdova).

https://doi.org/10.1016/j.foodcont.2018.07.050
Received 21 June 2018; Received in revised form 30 July 2018; Accepted 31 July 2018

Abbreviations

MR	Maillard reaction
HMF	5-hydroxymethylfurfural
PLS	Partial least squares
OSC	Orthogonal signal correction
MSC	Multiplicative signal correction
DWT	Wavelet;
SNV	Standard normal variate
E1	First effect evaporator
E2	Second effect evaporator
E3	Third effect evaporator
R2Y(cum)	Cumulative explained fraction of the variation of Y
Q2Y(cum)	Cumulative predicted fraction, according to cross validation of the Y variable
SDY	Standard deviation of the Y residuals
RMSEP	Root Mean Square Error of the prediction for observations in the prediction set.

toxins such as acrylamide (Capuano & Fogliano, 2011). Daily dietary personal intake of HMF has been reported to range from 2.1 to 23 mg, which is far above the threshold of concern (540 µg/person/day) that was established based on a large database containing data on subchronic and chronic animal studies (JECFA, 1996).

Due to their technological properties, as well as because they are a good source of compounds with antioxidant activity, apple products such as apple juice concentrates are widely used in different food formulations, including infant foods, jams, jellies, marmalades and confectionery and stabilizing acidified dairy drinks (Henriquez, Córdova, Lutz, & Saavedra, 2013; Nikolic & Mojovic, 2007; Santini, Romano, Meca, Raiola, & Ritieni, 2014). Nevertheless, the browning of fruit is believed to be one of the main causes of quality loss during processing (Quevedo, Jaramillo, Díaz, Pedreschi, & Aguilera, 2009). Enzymatic browning is the oxidation of phenols to quinones catalysed by the enzyme polyphenol oxidase (PPO) in presence of oxygen, but it can be partially controlled by lowering the pH through acidification, while non-enzymatic browning is due to MR or caramelization reactions produced by thermal preservation treatments, (Echavarría, Torras, Pagán, & Ibarz, 2011). The latter is the main source of non-enzymatic browning in apple juice concentrate manufacturing, due to the degradation of reducing sugars that are naturally present in the product. Hence, their quality is affected by the appearance of HMF during thermal processing.

Several methods have been reported for HMF quantification, principally through the use of HPLC (Jalil et al., 2015; Lee, Sakai, Abdul Manaf, Mohd Rodhi, & Saad, 2014; Vorlová, Borkovcová, Kalábová, & Vecerek, 2006). Typically, these methods are time-consuming, and the results are not immediately available by the time of need, when a fast decision must be made during processing. In this sense, the use of chemometric tools has proven to be an effective way to detect food adulteration (Elzey, Pollard, & Fakayode, 2016; Garrido-Delgado, Muñoz-Pérez, & Arce, 2018), as well as for modelling and describing the quality changes occurring in fruit processing (Ayvaz et al., 2016; Orlandi, Calvini, Foca, & Ulrici, 2018). This methodology exploits the correlation structure of the original variables by revealing latent relations underlying the process that can drive the phenomenon, revealing information that under a classical univariate approach is not evident (Brereton, 2009; Erikson et al., 2006). Thus, chemometric tools can be helpful, not only in giving a better description of the HMF formation under certain conditions but also for being a tool for the prediction of its concentration using simple physicochemical analyses (Wlodarska, Khmelinskii, & Sikorska, 2018), providing a faster alarm when the product is overheated compared to the usual method wherein the HMF detection is available only after the product has been already processed.

Despite its wide industrial use, scarce information on the quality changes occurring *in situ* during the manufacturing of apple juice concentrates is available. The aim of this work was to propose a multivariate methodology to assess the quality changes and to predict the appearance of HMF during the concentration process of clarified apple juice using chemometric tools. Within the framework of these objectives, this research was carried out at laboratory scale simulating a concentration process of a triple effect evaporator as preliminary validation of this methodology.

2. Theory

2.1. Multivariable calibration

A fundamental task in science and technology is modelling a property “y” by one or several variables “x”, such as data matrix, arrays, spectra, UV-vis, NIR, etc. (Varmuza & Filzmoser, 2008). According to Naes and Martens (1984), multivariate calibration can be defined by a tool to reduce the dilemma of precision and speed vs. relevance to predict some relevant information from some easily measured data. The choice of mathematical formula type and determination of the parameter may together be termed calibration. Multivariate calibration model parameters can be estimated where responses depend on the target analyte, in addition to other chemical or physical variables and, hence, multivariate calibration corrects for these interfering effects (Gemperline, 2006).

Partial least squares (PLS) regression is a well-known and widely used method to carry out multivariate calibration. Essentially, PLS regression used x-data transformed into a set of a few intermediate linear latent variables, and these new variables (with maximum covariance) are used in the ordinary least squares (OLS) regression (Varmuza & Filzmoser, 2008). For a detailed analysis of multivariate calibration by PLS, the reader can consult the work of Wold and Josefson (2000).

2.2. Pre-processing data analysis

Commonly, the signal of spectra must be “corrected” prior to calibration in order to enhance the predictive power of multivariate calibration models. This is because variation in X that is unrelated to Y may degrade the predictive ability of these models. Preprocessing of spectra data has the objective of removing undesired systematic variation in the data, such as: baseline drift, multiplicative scatter effects, and wavelength region of low information content (Eriksson, Byrne, Johansson, Trygg, & Vikström, 2013).

2.2.1. Savitzky-Golay

Savitzky and Golay is indeed a derivate method for smoothing data from spectra. The method fits a low degree polynomial function (generally quadratic or cubic) piece-wise to the data, followed by calculating the first, second and third derivate from the resulting polynomial at points of interest. It provides a simplified method for calculating smoothing and differentiation of data using a least-squares technique (Gorry, 1990).

2.2.2. Orthogonal signal correction (OSC)

OSC is a “correction vector” algorithm using the NIPALS (Nonlinear estimation by Iterative Partial Least Square) algorithm. This algorithm computes a first factor with useful information jointly with a second orthogonal factor containing uncorrelated and unhelpful information related with Y (Eriksson et al., 2013).

2.2.3. Multiplicative signal correction (MSC)

MSCregresses each spectrum (rows) against an average spectrum with a lineal model. The result of MSC is that each “corrected” spectrum has the same offset and amplitude (Eriksson et al., 2013).