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Analytical Methods

A validated fast difference spectrophotometric method for 5-hydroxymethyl-2-furfural (HMF) determination in corn syrups

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ABSTRACT

Corn syrups, important ingredients used in food and beverage industries, often contain high levels of 5-hydroxymethyl-2-furfural (HMF), a toxic contaminant. In this work, an *in house* validation of a difference spectrophotometric method for HMF analysis in corn syrups was developed using sophisticated statistical tools by the first time. The methodology showed excellent analytical performance with good selectivity, linearity ($R^2 = 99.9\%$, $r > 0.99$), accuracy and low limits ($LOD = 0.10\ mg\ L^{-1}$ and $LOQ = 0.34\ mg\ L^{-1}$). An excellent precision was confirmed by repeatability (RSD (%) = 0.30) and intermediate precision (RSD (%) = 0.36) estimates and by Horrat value (0.07). A detailed study of method precision using a nested design demonstrated that variation sources such as instruments, operators and time did not interfere in the variability of results within laboratory and consequently in its intermediate precision. The developed method is environmentally friendly, fast, cheap and easy to implement resulting in an attractive alternative for corn syrups quality control in industries and official laboratories.

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1. Introduction

Corn syrup, also known as glucose syrup, is defined as the purified, concentrated, aqueous solution of nutritive saccharides obtained from edible starch with a dextrose equivalent of 20 or more (Caballero, Trugo, & Finglas, 2003). Due to its physicochemical properties, they are widely used in the food and beverage industries (Belitz, Grosch, & Schieberle, 2009; Caballero et al., 2003).

Corn syrups can be obtained by corn starch hydrolysis in acidic medium under high temperature and pressure, by enzymatic process or still by a combination of both processes (Almandoz, Pagliero, Ochoa, & Marchese, 2010; Caballero et al., 2003; Newton, 2007). Factors such as thermal processing, long periods of storage and the chemical composition of corn syrups favour the formation of high levels of toxic contaminants such as 5-hydroxy-2-methylfurfural (HMF) (Belitz et al., 2009; De Andrade et al., 2016; Kavousi, Mirhosseini, Ghazali, & Ariffin, 2015; Spano et al., 2009).

Recently, a great interest in HMF quantification and distribution in different foods and beverages has been observed due to its possible toxicological effects (carcinogenicity, mutagenicity, cytotoxicity and genotoxicity) (Capuano & Fogliano, 2011; Kowalski, Lukasiewicz, Duda-Chodak, & Zieć, 2013; Truzzi et al., 2012). Taking this into account it is important to monitor HMF concentration in foodstuffs, especially in corn syrups, which can have high levels of this contaminant.

Different analytical methods have been developed for HMF analysis in foods and beverages. Liquid chromatography with UV detection (HPLC-UV) remains the most widely used method (Chávez-Servín, de la Carbot, García-Gasca, Castellote, & López-Sabater, 2015; De Andrade et al., 2016; Er Demirhan et al., 2015; Lee, Sakai, Manaf, Rodhi, & Saad, 2014; Spano et al., 2009; Teixidó, Núñez, Santos, & Galceran, 2011). In addition, UV–Vis spectrophotometric methods are considered also official methods for HMF determination in different matrices (Gürkan & Altunay, 2015; Truzzi et al., 2012; Zappalà, Fallico, Arena, & Verzera, 2005; Zhang, Wei, Liu, Lin, & Yuan, 2014).

On the other hand, a growing interest in green methodologies that minimize or eliminate the production of by-products, the use of organic solvents and toxic reagents, which are hazardous to human health or to the environment (Armenta, Garrigues, & De La Guardia, 2008), has made that simple techniques such as UV–VIS Spectrophotometry has called the attention of researchers. UV–VIS Spectrophotometry can be considered a green methodology,

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because it is fast, makes use of inexpensive instrumentation, does not require specialized training and does not use a large amount of toxic solvents as chromatographic methods do (Armenta et al., 2008; Gürkan & Altunay, 2015; Truzzi et al., 2012; Zhang et al., 2014). For this reason, spectrophotometric methods are still widely used in research, regulatory bodies and industry laboratories for HMF determination.

White (1979) developed a difference spectrophotometric method for HMF determination in honey. This method is based on reacting HMF with sulphite ion (HSO_3^-) (Teixidó et al., 2011; Truzzi et al., 2012; White, 1979). It uses low cost reagents and does not generate wastes, thus the difference spectrophotometric method is a green alternative to other analytical methods, a fact that is very important for laboratories that aim to get ISO standards (Armenta et al., 2008).

Nevertheless, in order to apply White's spectrophotometric method to other foods, such as corn syrups, the analytical methodology must be appraised for accuracy, and precision in HMF determination. It is known that factors such as operator, instrument, time and random errors might affect the analytical precision, and contribute to the variability of measurements carried out within a laboratory (ISO 5725-6, 1994; Kuttatharmmakul, Massart, & Smeyers-Verbeke, 1999). Additionally, the selectivity and sensitivity of the spectrophotometric method should be assessed when the analysis is performed directly in the presence of complex matrixes (Spano et al., 2009). Thus to guarantee the suitability of spectrophotometric methods to accomplish the desired purpose, rigorous validation studies must be undertaken.

In the last few years, numerous analytical methods have been developed for HMF analysis in food and beverages (Chávez-Servín et al., 2015; Er Demirhan et al., 2015; Lee et al., 2014). However, reports of rigorous validation studies about the appropriateness of these methodologies and using sophisticated statistical tools, as those recommended by ISO, IUPAC and AOAC guidelines are still scarce (AOAC, 2012; Araujo, 2009; De Andrade et al., 2016; Kuttatharmmakul et al., 1999). Considering the aforementioned facts, this work aimed to develop a fast, cheap, simple, green and direct methodology for HMF determination in corn syrup samples by difference spectrophotometry. To verify the analytical performance of the developed method a rigorous and sophisticated validation process based on AOAC, ISO and IUPAC guidelines was carried out. Additionally, a detailed precision study using nested design was carried out to evaluate the effect of factors such as different operators, instruments and time on intermediate precision. To our knowledge, no previous efforts have been made to optimize and validate the White's method adapted for HMF analysis in corn syrup samples.

2. Materials and methods

2.1. Reagents and samples

HMF (99%) and formic acid (95%) were purchased from Sigma-Aldrich (Brazil). Sodium hydrogen sulphite (97%) was purchased from Biotec (Brazil) and acetonitrile (HPLC grade) from EMD (Canada). Ultrapure water ($0.055\ \mu S\ cm^{-1}$) was obtained by a TKA-GenPure system from Thermo Scientific (Brazil) and a Simplicity UV Milli-Q system from Millipore (Canada). Commercial corn syrup samples were acquired in 2013 in supermarkets from Guarapuava (Brazil) (CS1–CS5) and from Winnipeg (Canada) (CS6) cities.

2.2. Standard and sample solutions

Stock standard solutions of HMF ($1000\ mg\ L^{-1}$) and sodium hydrogen sulphite (0.40% (w/v)) were daily prepared in ultrapure water. In order to apply the developed difference spectrophotometric method to HMF quantitation in corn syrup samples, aqueous solutions at $5.0\ mg\ mL^{-1}$ and at $160.0\ mg\ mL^{-1}$ were made for Brazilian and Canada corn syrup samples, respectively. For chromatographic analysis by HPLC-UV, aqueous solutions of corn syrup samples were prepared as described by De Andrade et al. (2016).

2.3. High-performance liquid chromatography (HPLC)

HPLC analysis of corn syrups samples was carried out following the methodology described by De Andrade et al. (2016).

2.4. Difference spectrophotometry UV

Spectrophotometric determinations were carried out in 1 cm quartz cells in a single beam spectrophotometer Cary 50 Bio from Varian. For the precision study and to record spectra, a double beam spectrophotometer SP-2000 UV from Spectrum Meter was utilized. Spectra were obtained with a bandwidth of 2 nm and a scan rate of $1\ nm\ s^{-1}$. Absorbance values were read at 285 nm.

2.5. Development of the difference spectrophotometric method

Firstly, to adapt White's difference spectrophotometric method (1979) to HMF analysis in corn syrups the optimal concentration of sodium hydrogen sulphite reagent was determined. This concentration was defined as the concentration that produces the maximum reduction in HMF ($4.0\ mg\ L^{-1}$) absorption band at 285 nm with minimal interference. Concentrations of sodium hydrogen sulphite were varied from 0.05 to 0.40% (m/v). Two solutions were prepared for each concentration of sulphite reagent evaluated. The first solution (S1) was prepared by mixing 5.0 mL of HMF standard solution ($4.0\ mg\ L^{-1}$) and 5.0 mL of water. The second solution (S2) was obtained by adding 5.0 mL of HMF standard solution ($4.0\ mg\ L^{-1}$) and 5.0 mL of the sodium hydrogen sulphite solution under evaluation (varied concentration from 0.05 to 0.40% (m/v)). Afterwards, the absorbance was read at 285 nm. Ultrapure water was used as blank.

When sulphite is added to HMF solution a reaction occurred and a reduction of HMF absorption band at 285 nm is observed. The percentage of reduction was determined by Eq. (1).

$$\%Reduction = ((A_{S1} - A_{S2}) * 100)/A_{S1} \quad (1)$$

A_{S1}: absorbance of solution 1 (S1) at 285 nm (sample solution);

A_{S2}: absorbance of solution 2 (S2) at 285 nm (sample solution with addition of sulphite reagent).

The optimal concentration of sodium hydrogen sulphite reagent was used in all HMF determinations in corn syrup samples by the difference spectrophotometric method described in 2.6.

2.6. HMF determination by difference spectrophotometry

For HMF analysis in corn syrup samples two solutions were prepared. The first solution (S1) was prepared by addition of 5.0 mL of corn syrup sample solution (obtained as described in 2.2) and 5.0 mL of ultrapure water. The second solution (S2) was obtained by addition of 5.0 mL of corn syrup sample solution (prepared as described in 2.2) and 5.0 mL of sodium hydrogen sulphite solution at 0.1% (w/v). Both solutions were analyzed at 285 nm. The concentration of HMF was expressed as mg of HMF per kg of corn syrup and it was calculated using Eq. (2).

$$HMF\,(mg\,kg^{-1}) = ([HMF\,(mg\,L^{-1})] * V_{sample})/w_{sample} \quad (2)$$

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