Food Research International 44 (2011) 1427–1433

Contents lists available at ScienceDirect

Food Research International

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

Near infrared (NIR) spectroscopy as a tool for monitoring blueberry osmo–air dehydration process

Nicoletta Sinelli [a,*], Ernestina Casiraghi [a], Stefania Barzaghi [b], Ada Brambilla [c], Gabriella Giovanelli [a,**]

[a] Dipartimento di Scienze e Tecnologie Alimentari e Microbiologiche, Università degli Studi di Milano via Celoria 2, 20133 Milano, Italy
[b] CRA-Centro di ricerca per le produzioni foraggere e lattiero-casearie, via Piacenza 29, 26900 Lodi, Italy
[c] CRA-IAA, Unità di ricerca per i processi dell'industria agroalimentare, via Venezian 26, 20133 Milano, Italy

ARTICLE INFO

Article history:
Received 20 December 2010
Accepted 27 February 2011

Keywords:
NIR spectroscopy
Osmo–air dehydration processes
Blueberries
Two-dimension correlation analysis

ABSTRACT

Osmo–air dehydration treatments are widely applied to fruits in order to prolong shelf-life, reduce packaging and logistic costs, and improve both sensory and nutritional quality of the end products. In this work osmo–air dehydration was applied to blueberries (*Vaccinium corymbosum*), a fruit that is gaining increasing attention due to its high content of dietary antioxidants. In particular, the aim of this study was to investigate the performance of near infrared (NIR) spectroscopy as a tool for monitoring blueberry osmo and air dehydration processes.
Blanched blueberries were dipped in sucrose + glucose osmotic solutions for 24 h, and the osmotic exchanges were determined by mass balances (water loss, solid gain, sugar intake, changes in total phenolics and anthocyanins); NIR spectra were collected in order to study modifications due to the osmotic treatments. Untreated and infused berries were subsequently air-dried at 70 °C to final moisture content of 10–14%. During drying chemical, nutritional and structural changes were monitored and NIR spectra were acquired on whole berries, using an optic probe working in diffuse reflectance. Spectral data were standardized, transformed into first derivative and processed by Principal Component Analysis. Results show that NIR spectroscopy was able to follow the osmotic and the air-drying processes and to discriminate untreated and osmo-dehydrated berries. Spectral differences reflect the main molecular modifications associated with water absorption bands due to OH stretch + OH bending and sugar absorption bands due to CH stretch + CH bending and OH stretch + OH bending. In order to investigate the variation of main constituents (sugars and water) involved in the osmo-dehydration process, two-dimensional correlation analysis of spectral data was also carried out.

1. Introduction

In recent years blueberries, such as other small red fruits, are emerging as a functional fruit for improving health: these berries contain high quantities of anthocyanins, mainly in the glycosidic form, flavonols (such as quercetin, kaempferol and myricetin), catechins (such as (+) catechin, (−) epicatechin and their oligomeric forms), and benzoic and cinnamic acids (Prior, Lazarus, Cao, Muccitelli, & Hammerstone 2001; Sellapan, Akoh, & Krewer 2002; Kalt et al. 2001). Due to their high phenolic content, blueberries show a strong antioxidant activity (Wang, Cao, & Prior 1996), and the consumption of these fruits has been associated with a diet-induced increase in *ex vivo* serum antioxidant status (Kay & Holub 2002). Blueberries are available as fresh products during the growing season (mid-end summer) and as derived products such as jams, juices, fruit under syrup, etc.

Drying is traditionally applied to fruits and vegetables to increase the stability and shelf-life, and to obtain ingredients for complex food preparations. Besides its wide application, traditional air drying produces detrimental effects on the quality of fruits, mainly oxidative damage, browning, loss of flavour and extensive shrinkage, which reduce both sensory and nutritional quality of the products (Aguilera & Karel 1997). Infusion of fruits in concentrated sugar or juice solution can be applied prior to air drying, in order to increase the initial sugar content and simultaneously decrease the moisture content by an osmotic process. Infused fruits are then air-dried to obtain the final moisture content.

Together with texture improvements, the penetration of solutes, combined with dehydration effect, could modify the fruit composition and improve pigment, colour, vitamin and aroma retention both during subsequent air dehydration and frozen storage (Torreggiani & Bertolo 2001). In many cases, osmo–air dehydrated fruits have better texture, colour and flavour than conventionally air-dried fruits (Torreggiani & Bertolo 2004). The kinetics of mass transfer during processing and the final characteristics of processed fruits are greatly influenced by several variables, among which the fruit itself (initial Brix, size, variety, and possible pre-treatments), the infusion process conditions (sugar

* Corresponding author. Tel.: +390250319179; fax: +390250319190.
** Corresponding author. Tel.: +390250319182; fax: +390250319190.
E-mail addresses: nicoletta.sinelli@unimi.it (N. Sinelli), gabriella.giovanelli@unimi.it (G. Giovanelli).

0963-9969/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodres.2011.02.046

concentration, temperature, syrup to product ratio, infusion time, agitation, etc.) and the air-drying conditions (mainly air temperature and air flow rate). Due to this high variability, processes need to be monitored and controlled to obtain the desired results.

Methods conventionally applied to determine the final quality of the products and to monitor the osmo and air dehydration process kinetics are time-consuming, require laborious preparation of the sample and are not suited for automation. It is therefore important to develop rapid methods to evaluate the major changes occurring during these processes. Near infrared spectroscopy (NIR) represents a powerful, convenient and rapid analytical tool which could be used to monitor the dehydration process, given that absorption in this spectral range (750–2500 nm) can be related, to a greater or lesser extent, to the main chemical modifications involved in the process. The near infrared (NIR) region is part of the electromagnetic spectrum related to vibration and combination overtones of the fundamental O–H, C–H and N–H bounds, which are the primary structural components of organic molecules (Williams & Norris 2001). Due to its non-invasive nature, NIR has the potential to be used in on-line monitoring systems.

Barzaghi, Gobbi, Torreggiani, Tornelli, and Giangiacomo (2008) applied NIR spectroscopy to the control of osmo–air dehydrated apple rings. The method appeared to be suitable to study the behaviour of the dehydrated apple rings during shelf-life in different environmental conditions and to interpret modifications during storage in connection with water–sugar binding.

In this paper, near infrared spectroscopy was used to follow osmo–air dehydration of blueberries and to investigate changes in the main constituents (water and sugars) involved in the dehydration process with the aim of obtaining information about the kinetics of mass transfer during processing from spectral data.

2. Materials and methods

2.1. Fruits and treatments

All trials were carried out on highbush blueberries (*V. corymbosum*) cv. Berkley, supplied by Fondazione Minoprio (Como, Italy). Fruits were individually quick frozen at −40 °C and stored at −20 °C until processed.

Prior to each treatment, aliquots of frozen berries (approximately 2 kg) were blanched in a continuous blancher using 85 °C steam for 3 min, and immediately cooled by cold water spray. Blanched berries were then submitted to the infusion process by dipping aliquots of 1 kg fruits in 60°Bx sucrose or 48.6°Bx glucose/fructose (1:1 w/w) solutions (aw = 0.90). The osmotic treatment was carried out in 5 L vessels, recirculating the osmotic solution by a peristaltic pump operating at 1.5 L/min. Fruit to osmotic solution ratio was 1:5 (w/w) and all treatments were replicated twice, in different days. To study the kinetics of the osmotic process, pre-weighted aliquots of berries were placed in individual numbered baskets which were taken out of the solution after 0.5, 1, 2, 4, 5, 6 and 24 h. The berries were drained, rinsed gently with tap water, placed a few minutes over adsorbent paper to remove excess water, and weighted.

Air drying was carried out at 70 °C, using alternate upward–downward air-circulated drier (Thermolab, Codogno, Italy), operating at an air velocity of 1.5 m/s. Untreated and infused blueberries were placed in one layer and dehydrated to constant weight (less than 2% weight loss in two subsequent samplings). Pre-weighted fruit aliquots (corresponding to at least 80 g fresh weight) were periodically taken from the dryer to follow the drying process kinetics in terms of weight loss and physico-chemical and structural changes. Each trial was repeated twice.

2.2. Analytical determinations

All analytical determinations were carried out on a fruit homogenate, obtained by a food blender (Black Decker, Hunt Valley, MD, USA). The following parameters were determined: dry matter (DM), according to AOAC, 1985 and soluble solids, by digital refractometer (ATAGO DBX-55). Polyphenolic components were extracted using acidic methanol (methanol:concentrated HCl (37%) 99:1, vol/vol) as described by Giovanelli and Buratti (2009); total phenolics were determined on the extract by the Folin–Ciocalteau method (Singleton & Rossi 1965); total monomeric anthocyanins were determined by the differential pH method (Giusti & Wrolstad 2001). Glucose and fructose concentrations were evaluated by HPLC on the aqueous extract of the fruit homogenate, using a Polysphere OA HY column (300 × 6.6 mm, Merck, Darmstadt, Germany), using 0.002 N H_2SO_4 as eluent at 0.45 mL/min flow rate. The analysis was carried out at 45 °C and glucose, fructose and sucrose were recognised and quantified by refractive index detector (RI 930, Jasco, Japan), by comparison with pure standards. All analyses were carried out at least in triplicate.

2.3. FT-NIR spectroscopy

Spectral data were collected over the range 12,500 to 3600 cm^{-1} using an FT-NIR spectrometer (MPA, Bruker Optics, Ettlingen, Germany). Blueberries infused in sucrose and fructose + glucose solutions for different times were homogenized before spectroscopic analysis. About 50 g of the sample were scanned in a Petri glass capsule (diameter 9 cm) and analysed in reflectance mode using an integrative sphere. The spectrum of each sample was collected at 25 °C with a resolution of 8 cm^{-1}.

During the air-drying process, the spectra of untreated and infused blueberries were collected directly on the surface of the berries during air drying (approximately every 30 min), using an optic probe working in reflectance mode (12,500–3600 cm^{-1}). At each drying time, 10–15 berries were scanned at room temperature with a resolution of 8 cm^{-1} and the average spectra was used for the data processing.

2.4. NIR data processing

Chemometric analysis was performed using The Unscrambler software package (v. 9.7, CAMO ASA, Norway). In order to minimize the effect of baseline shifts, the spectral data were pre-processed by several mathematical treatments. FT-NIR spectral data, collected both during the osmotic treatments and the air-drying process, were standardized by Standard Normal Variate (SNV) and pre-treated using derivative transform calculation (Savitzky–Golay method, gap size = 15) (Alciaturi, Escobar, & De La Cruz 1998). Principal component analysis (PCA) (Naes, Isaksson, Fearn, & Davies 2000) was applied as an exploratory tool to NIR spectral data, over the range 10,800–3800 cm^{-1} and 10,600–4020 cm^{-1} for the spectra collected during the osmotic treatments and air-drying process, respectively. All spectral data sets were mean-centered before performing PCA calculations.

Two-dimensional correlation spectroscopy (2D-CORR), performed using the Hilbert transformation according to Noda (2000), because of the small dynamic data set, was carried out using Matlab software (v. 7.0, the MatWorks Inc.). For this analysis, the average pre-treated spectra sorted in the course of the process were used. The intensity of two-dimensional correlation spectrum $X(\nu_1, \nu_2)$ represents the quantitative measure of a comparative similarity or dissimilarity of spectral intensity variations measured at two different spectral variables, ν_1 and ν_2, during a fixed interval. The correlation function is calculated between the spectral intensity variations measured at two independently chosen spectral variables, ν_1 and ν_2, which gives the basic two-dimensional nature of this particular correlation analysis (Noda & Ozaki 2004). In order to simplify the mathematical manipulation, $X(\nu 1, \nu 2)$ is treated as a complex number function $X(\nu_1, \nu_1) = \Phi(\nu_1, \nu_1) + i\Psi(\nu_1, \nu_1)$ comprising two orthogonal (i.e., real and imaginary) components, known respectively as the synchronous and asynchronous two-dimensional correlation intensities. The 2D cross-correlation function of the spectra is decomposed into in-phase and out-of-phase