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Analytical Methods

Prediction of sensory score of Italian traditional balsamic vinegars of Reggio-Emilia by mid-infrared spectroscopy

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ABSTRACT

In this study the potential of Fourier Transform Mid-Infrared (FT-MIR) spectroscopy to predict the sensory score of traditional balsamic vinegar (TBV) of Reggio-Emilia was investigated. The composition of two hundred commercial TBV samples was analysed and the sensory scores, ranging from 133 to 306 points, were evaluated by a certified panel of master experts (reference method). Partial least squares (PLS) regression, obtained from selected pre-processing signal techniques, was used for multivariate calibration to relate the sensory score to the MIR spectra. Performance of different models was compared in terms of coefficient of correlation (r) and root mean square error of cross-validation (RMSECV). The overall best prediction results were obtained using second order derivative with autoscaling and mean-centering of spectral data with the correlation coefficient of 0.889 and 0.885, respectively. It was concluded that the MIR spectroscopy is suitable for rapid instrumental screening of TBV sensory quality.

1. Introduction

Traditional balsamic vinegar (TBV) of Reggio-Emilia is a dark, creamy and tasty syrup obtained from alcoholic fermentation and acetic bio-oxidation of cooked grape must aged in small wood barrels for at least 12 years (up to 25–40 years). TBV is a product with ancient tradition that has been recently recognised as a "Protected Designation of Origin" product (PDO) by the European Union (Commission Regulation (EC) No. 813/2000) due to the typical production process and the defined geographical areas of production, Emilia-Romagna region, North of Italy (GURI, 1987).

TBV is a complex mixture of water and many classes of compounds including carbohydrates (Cocchi et al., 2006a; Consonni & Cagliani, 2007), organic acids (Cocchi, Lambertini, Manzini, Marchetti, & Ulrici, 2002; Giudici, 1993), phenolics (Meglioli, Parisini, Tedeschi, & Pesenti, 1997; Plessi, Bertelli, & Miglietta, 2006), furans (Antonelli, Chinnici, & Masino, 2004; Masino, Chinnici, Franchini, Ulrici, & Antonelli, 2005), volatiles (Cocchi, Durante, Grandi, Manzini, & Marchetti, 2008; Del Signore, 2001; Zeppa, Giordano, Gerbi, & Meglioli, 2002), amino acids (Blasi et al., 2002; Del Signore, Stancher, & Calabrese, 2000), and mineral elements (Cocchi et al., 2004; Del Signore, Campisi, & Di Giacomo, 1998). These compounds are formed during the production and ageing process and all of which can contribute to the sensory properties of TBV (Cocchi et al., 2006b; Masino, Chinnici, Bendini, Montevecchi, & Antonelli, 2008). Consumer preference for a food product is mainly driven by its sensory characteristics. In this view, the quality certification of TBV of Reggio-Emilia is obtained on the basis of sensory evaluation together with few chemical and physical analyses, such as total acidity, density and dry extract (GURI, 1987). Sensory evaluation of TBV is carried out using a trained panel which is time consuming and expensive.

Considerable interest arises in the application of instrumental techniques, such as near- (NIR) and mid-infrared spectroscopy (MIR), to enable more objective, rapid, and less expensive assessments of food quality to be made (Versari, Parpinello, Mattioli, & Galassi, 2008). MIR spectra have been used to discriminate between TBV and other vinegars (Del Signore, 2000), whereas NIR allowed to monitoring the vinegar ageing process (Casale, Sáiz Abajo, González Sáiz, Pizarro, & Forina, 2006) and has been also used for detection of adulteration and to predict the sensory characteristics of a variety of foodstuffs, including peas (Martens & Martens, 1986), meat (Næs & Hildrum, 1997), coffee (Esteban-Díez, González-Sáiz, & Pizarro, 2004), wine (Cozzolino et al., 2005) and cheese (Woodcock, Fagan, O'Donnell, & Downey, 2008). There appear to be only one attempt to investigate the application of MIR for the prediction of sensory quality of food. The study on sensory evaluation of cheese has shown that mid-infrared spectroscopy produced results similar to or better than the models developed using NIR (Fagan et al., 2007).

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The aim of this preliminary study is to examine the feasibility of using MIR spectra in conjunction with chemometric analysis to predict the sensory scores given to two-hundreds TBV of Reggio-Emilia by a certified panel of tasters.

2. Materials and methods

2.1. Vinegar samples

Two hundred samples of TBV of Reggio-Emilia were collected from the local producers' that supervised the complete process of production to ensure the authenticity. Dataset included 127 not commercial, 58 orange, 12 silver and 2 gold TBV samples. The quality of TBV samples was evaluated by means of sensory analysis using a certified panel of master experts (Confraternita dell'Aceto Balsamico Tradizionale Reggiano, Reggio-Emilia, Italy) that classified the TBV into four commercial categories, gold (min 300 points), silver (min 270 points), orange (min 240 points), and not commercial (<240 points) using a score card up to 400 total points. Each sample was tasted by at least 5 expert panelists and the mean sensory score for the panelists was computed. The score card used for sensory evaluation is based on a total of 400 points distributed as follow: visual attributes (56 points), aroma attributes (104 points), taste and texture attributes (200 points), and 40 points for the final overall sensation. Obviously, the final score is the aggregate number of different attributes, thus samples with the same total score not necessarily would have the same chemical composition. The sensory analysis of TBV was performed by means of a certified panel of master experts (Confraternita dell'Aceto Balsamico Tradizionale Reggiano, Reggio-Emilia, Italy) trained according to the official methodology (ISO 8586-1, 1993; ISO 8586-2, 1994). The judges attended a several steps training based on the identification and memorisation of TBV descriptors by means of standards and actual samples (TBVs). Moreover, judges learn to score TBV for the descriptors of interest. The tasting session, carried out according to the conditions and general methodology in accordance with ISO 6658 (1985) and ISO 8589 (1988), was based on the evaluation of the olfactory-gustatory descriptors of TBV. The sensory performance of panel' members was evaluated in terms of discriminatory capacity and consistency among judges (Parpinello, Versari, & Galassi, 2008).

It is well known that TBV is aged in a battery of 5–7 small casks called '*vaselli*' and each battery need a long time to produce high quality TBV with consistent physico-chemical and sensorial properties. Besides, TBV have to be aged for at least 12 years (up to 25–40 years) in barrels of different sizes and wood (e.g., oak, chestnut, mulberry or juniper) during which time the volume decreases due to evaporation and the barrels are refilled using the '*Solera*' method. The ageing of TBV in wood is a key process during which the sensorial properties and chemical composition of TBV change.

2.2. Analytical methods

For each TBV sample the following physico-chemical parameters were measured: total acidity (TIM 900 titration manager, Radiometer, Copenhagen, NL), total soluble solids (refractometer mod. 79585, Carl Zeiss, Milan, Italy), turbidity (turbidimeter mod. 18900, Hach, Milano, Italy) (GURI 1986), and optical density at 625, 550, 495 and 445 nm (Lambda 45 UV/Vis spectrophotometer, Perkin-Elmer, Milano, Italy). Data from spectral analysis were expressed as absorbance unit (AU) with 1 cm path length and corrected by dilutions (OIV 2007). The tristimulus values X, Y, Z (CIE 1986) were calculated according to the literature (Blouin, 1992).

Fourier-Transform Mid-Infrared analyses were carried out using a Spectrum BX spectrometer (Perkin-Elmer) equipped with a horizontal ATR device with zinc selenide (ZnSe) crystal. Measurements were carried out at 20 °C and the spectra were recorded for each sample from 4400 to 600 cm^{-1} by averageing 6 scan for each sample with a spectral resolution of 1 cm^{-1}. Although the whole spectral range (4400–600 cm^{-1}) was stored for each sample, only selected intervals were used for calculation (1500–950, 1750–1685, and 3000–2800 cm^{-1}) to prevent noise being included in the calculation (Fig. 1) (Versari, Boulton, & Parpinello, 2006). The full IR spectra of liquid sample shows the presence of some regions that introduce noise to the calibration due to the presence of interferences compounds, especially water that absorbs at 1717–1543 and 3627–2971 cm^{-1}. Moreover, it is well known that the spectra interval from 5012–3627 cm^{-1} contains very little useful information. Prior to data analysis, each spectrum was corrected for the variation in effective path-length using the ATR correction option available on the Spectrum One 5.3.1 software (Perkin–Elmer). The spectra were transferred via a JCAMP.DX format into the statistical software for chemometric analysis.

2.3. Chemometric analysis

The experimental approach included preliminary checking for grouping by principal component analysis (PCA), setting up a calibration model for TBV sensory quality by FT-MIR, and cross-validation of the models using partial-least squares (PLS) regression (Martens & Martens, 2001). Each raw spectrum was mean-centered prior to the statistical analyses. The method of full cross-validation, following the leave-one-out procedure, was used to determine the maximum number of latent variables (LV), to ensure the predictive ability and to avoid over-fitting of the data (Martens & Næs, 1989). In spectroscopy applications it is often appropriate to refine the model by selecting wavelengths and the *b*-coefficients (regression coefficients) give the accumulated picture of the most important wavelengths. The optimum number of wave-numbers for inclusion in the calibration equations was determined by comparing the regression results in terms of correlation coefficient (r) and the root mean squared error of cross-validation (RMSECV), which should be minimised (Esbensen, Schönkopf, Midtgaard, & Guyot, 1998). Statistical analyses were performed using commercially available chemometric software (Unscrambler 7.6, CAMO ASA, Oslo, Norway; Opus 5.5, Bruker Optics, Milano, Italy). Several data pretreatment techniques were compared, including smoothing, autoscaling, first and second derivatives with Savitzky–Golay algorithm.

Soft independent modeling of class analogies (SIMCA) was used to classify TBV samples by modeling the scores previously obtained using PCA. The reliability of the model was tested in terms of recognition ability given by the percentage of the samples correctly classified (Wold et al., 1984).

3. Results and discussion

3.1. TBV composition

Table 1 summarizes the mean, SD, and range of TBV data set for sensory score, total soluble solids, titratable acidity and colour parameters of TBV. The TSS in the TBV samples ranged from 18° to 79°Brix and the titratable acidity varied from 1.13 to 8.86 g/l showing values in agreement with previous study (Meglioli et al., 1997). The compositional parameters and sensory scores of TBVs showed a wide range of values which is important for PLS calibration of spectra data.