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Prediction of Zamorano cheese quality by near-infrared spectroscopy assessing false non-compliance and false compliance at minimum permitted limits stated by designation of origin regulations

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ABSTRACT

Near-infrared transmittance (NIT) spectroscopy was used to predict the percentage in weight of the fat, dry matter, protein and fat/dry matter contents in Zamorano cheeses, protected with a Designation of Origin by the European Union. A total of 42 cheeses submitted to official control were analysed by reference methods. Samples were scanned (850–1050 nm) and predictive equations were developed using Partial Least Squares regression with a cross-validation step. Eight pretreatments independent from the remaining calibration samples were first considered. The most adequate one was that performing the second derivative (using a Savitzky–Golay method with a nine-point window and a second-order polynomial) followed by the standard normal variate transformation. Percentages of the root mean square error in cross-validation, the coefficient of determination and the mean of the absolute value of relative errors found were, respectively, for fat (0.62; 96.16; 1.05), dry matter (0.76; 96.03; 0.83), protein (0.41; 97.82; 0.81) and the fat/dry matter ratio (0.61; 92.51; 0.66). At a 99% confidence level, the trueness of the NIT+PLS methods for fat, dry matter and protein was verified. The official regulation for Zamorano cheese demands minimum permitted limits on the percentages in weight for protein (25%), dry matter (55%) and the ratio of fat to dry matter (45%). The adaptation of both the decision limit and the detection capability to the case of a minimum permitted limit ($CD\alpha$ and $CD\beta$, respectively) when a Partial Least Squares calibration is used has been applied for the first time for a food product protected by a Designation of Origin. The values of $CD\alpha$ with a probability of false non-compliance equal to 0.05 and of $CD\beta$ when, in addition, the probability of false compliance was equal to or less than 0.05, both provided by the corresponding NIT+PLS-based method, were, respectively, for protein (24.78%; 24.57%), dry matter (54.14%; 53.28%) and the fat/dry matter ratio (44.39%; 43.78%).

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1. Introduction

Infrared (IR) spectroscopy has currently become one of the most common techniques for a wide range of analyses in various industries due to the achievement of a fast and non-destructive method of analysis and the rapid development of multivariate calibration techniques.

Abbreviations: IR, infrared; NIR, near-infrared; MIR, mid-infrared; NIT, near-infrared transmittance; FFFS, front-face fluorescence spectroscopy; PLS, Partial Least Squares; PDO, Protected Designation of Origin; PGI, Protected Geographical Indication; DO, designation of origin; SNV, standard normal variate; SG, Savitzky–Golay; RMSEC, root mean square error in calibration; RMSECV, root mean square error in cross-validation; LMS, least median of squares; SR, standardized residual; DR, diagnostic resistance; RLS, reweighted least squares; $CD\alpha$, decision limit; $CD\beta$, detection capability

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Regarding dairy industry, both near-infrared (NIR) and mid-infrared (MIR) spectroscopy have been tested to determine their potential in acquiring information on process monitoring, determination of quality, geographical origin and adulteration of dairy products in processes such as milk, milk powder, butter and cheese production.

Despite the low sensitivity of the NIR region [1], it is possible to use these signals to determine the concentration of nearly all major constituents of dairy products such as water, protein, fat and carbohydrate using absorption spectroscopy with sufficient accuracy. In particular, NIR spectroscopy [2–5] has been more widely used than MIR spectroscopy for cheese composition determination [6–8], since the radiation light of MIR, in spite of its better specificity, has a very short penetration depth (usually a few micrometres) and cannot pass through glass, plastics and other materials. On the contrary, most packaging stuff is transparent to NIR light [9].

Since dairy products contain a lot of important intrinsic fluorophores such as vitamin A and the aromatic amino acids tryptophan, tyrosine and phenylalanine in proteins, the potential of front-face fluorescence spectroscopy (FFFS) to succeed in cheese evaluation has also been investigated [10–12], in some cases coupled with an IR spectroscopic technique [13,14]. Ref. [15] is a review of recent developments in this field.

On the other hand, nuclear magnetic resonance (NMR) has proved to be a versatile spectroscopic technique in dairy research [16], since some processes such as pressure, heating or changes in pH, which alter the milk protein conformation and/or the aggregation state, can be studied by NMR [17].

However, for most food samples, all this chemical information is obscured by changes in the spectra caused by physical properties such as the particle size of powders. This means that NIR spectroscopy becomes a comparative technique requiring calibration against a reference method for the constituent of interest [18]. Nowadays, most NIR spectroscopic applications are carried out by using Partial Least Squares (PLS) regression [19,20]. This technique was devised to find a few linear combinations (latent variables) of the spectral intensities, \mathbf{X} , in order to explain the values of the reference method, \mathbf{y} . The m -th latent variable, \mathbf{lv}_m , is the result of maximising the product of $\text{corr}^2(\mathbf{y}, \mathbf{X}\boldsymbol{\alpha})$ by $\text{Var}(\mathbf{X}\boldsymbol{\alpha})$ with the restrictions $\|\boldsymbol{\alpha}\|=1$ and $\mathbf{lv}_i^T \boldsymbol{\alpha} = 0 (i=1, \dots, m-1)$ to ensure that $\mathbf{X}\boldsymbol{\alpha}$ is uncorrelated with all the previous linear combinations $\mathbf{X}\mathbf{lv}_i$. PLS is a biased regression method to achieve the highest prediction capacity. Regarding dairy products, the International Standard ISO 21543:2006 “Milk products—Guidelines for the application of near infrared spectrometry” governs the performance criteria of this type of analyses with multivariate calibration techniques [21].

In Spain, both Protected Designation of Origin (PDO) and Protected Geographical Indication (PGI) represent the system of recognition of a distinctive quality. This is the consequence of some typical and distinguishing characteristics caused by (i) a defined geographical area where raw materials are produced and products are made, and (ii) the human factor, i.e. the influence of people that take some part in all these procedures.

Council Regulation (EC) No. 510/2006 of 20 March 2006 [22] lays down the definitions for PDO and PGI, the two regulatory figures in a framework of protection applied on agricultural products and foodstuffs. For the purpose of this Regulation, “designation of origin” (DO) means the name of a region, a specific place or, in exceptional cases, a country, used to describe an agricultural product or a foodstuff: (i) originating in that region, specific place or country, (ii) the quality or characteristics of which are essentially or exclusively due to a particular geographical environment with its inherent natural and human factors, and (iii) the production, processing and preparation of which take place in the defined geographical area.

Zamorano cheese is protected with a DO since 1993 and registered as PDO in Commission Regulation (EC) No. 1107/96 [23]. According to the Order of 6 May 1993 (BOE No. 120 of 20 May 1993) [24], that name refers to a compressed-paste fatty cheese made from milk of ewes of the Spanish Churra and Castellana breeds and with a ripening step of at least 100 days duration.

This work was aimed to develop a simple and rapid analytical tool for monitoring simultaneously the fat, dry matter and protein contents in Zamorano cheese samples by near-infrared transmittance (NIT) spectroscopy. Calibration models based on a cross-validated PLS regression of the corresponding constituent, expressed as percentage in weight, on the spectra recorded were estimated. By comparing the models arisen, several pretreatments of the spectra were evaluated in order to achieve the best correlations with the values obtained by reference methods. Finally, considering for each constituent the best PLS model, the trueness of the method was estimated, and the minimum contents of protein, dry matter and the fat-to-dry matter

ratio were calculated in terms of detection capability of the corresponding procedure evaluating the probabilities of false non-compliance and false compliance according to specific regulations. Currently, these calibration models are being applied systematically in the Milk Technological Station to accredit the NIT+PLS procedure for the control of the quality of Zamorano cheese.

2. Materials and methodology

2.1. Cheese samples

Forty-two Zamorano cheese samples dated back to either 2010 or 2011 were supplied by the Regulatory Council from all the producers included in the POD “Zamorano cheese”. Cheese samples were vacuum-packaged and stored at frozen conditions (-20 ± 5 °C) until analysis. Sampling and subsequent analyses were performed in accordance with the general recommendations included in the International Standard ISO 21543:2006 [23].

2.2. Reference analyses

All reference analyses were carried out in the Milk Technological Station (Agro Technological Institute) in Palencia, which is an accredited laboratory for the performance of such determinations according to the criteria established in the regulation UNE-EN ISO/IEC 17025 [25].

The determination of the fat, dry matter and protein contents was achieved following the official methods [26–28]. As a step in their official accreditation, the uncertainty of these analytical methods had been previously evaluated as standard deviation and resulted in (i) 0.36% when the fat percentage in weight ranged from 0.90% to 45.0%; (ii) 0.64% when the dry matter percentage in weight ranged from 20.0% to 80.0%; and (iii) 0.41% when the protein percentage in weight ranged from 6.0% to 30.0%.

All the reference analyses were performed in duplicate. For each sample, the mean was used as the value of the fat, dry matter or protein content as appropriate.

2.3. Near-infrared spectroscopy

All samples were allowed to reach room temperature (25 ± 2 °C) before analysis. Then each sample was grated after being removed from its plastic package and once all outer portions had been cut off. Approximately 40 g of each homogeneous grated cheese was packed into a 100 mm-diameter Petri dish in order to achieve an air hole-free optical path length of about 10 mm. To minimise sampling error, all samples were analysed in triplicate, except for two of them, which were in duplicate.

The samples were measured using NIT mode on a FOSS FoodScan Lab (Hilleroed, Denmark). Because of its effect on spectral response [29], the temperature of the spectroscopic measurements was controlled within the range 26–30 °C. NIT spectra were collected from 850 to 1050 nm at 2 nm intervals in a $\log 1/T$ format, where T is the sample transmittance. Each spectrum was an average of 16 sub-spectra recorded at sixteen different points by rotating the Petri dish automatically in the analyser. Therefore, 124 NIT spectra (shown in Fig. 1a) were finally obtained, which made up the calibration set.

2.4. Chemometrics: multivariate analysis

2.4.1. Data preprocessing

Both a slightly curved baseline and a baseline offset can be seen in Fig. 1(a), which made preprocessing necessary to transform data in such a way that the multivariate signals would

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