Chemometrics and Intelligent Laboratory Systems 246 (2024) 105092

Contents lists available at ScienceDirect

Chemometrics and Intelligent Laboratory Systems

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

PLS class modelling using error correction output code matrices, entropy and NIR spectroscopy to detect deficiencies in pastry doughs

D. Castro-Reigía [a,b], M.C. Ortiz [a,*], S. Sanllorente [a], I. García [b], L.A. Sarabia [c]

[a] Departamento de Química, Facultad de Ciencias, Universidad de Burgos, Plaza Misael Bañuelos s/n, Burgos, 09001, Spain
[b] AOTECH (Advanced Optical Technologies S.L.), Escuela Ing. De Bilbao, Plaza Ingeniero Torres Quevedo, 1, 2°, 48013, Bilbao, Spain
[c] Departamento de Matemáticas y Computación, Facultad de Ciencias, Universidad de Burgos, Plaza Misael Bañuelos s/n, Burgos, 09001, Spain

ARTICLE INFO

Keywords:
Sensitivity and specificity
DMCEN
PLS2-Class modelling
Process control
Kneading
Rolling

ABSTRACT

Biscuits are a highly demanded product worldwide. Its success makes their manufacture process a challenging task, needing new strategies to maintain the high production levels and a high-quality standard. This is determined by two key processes: the kneading and the rolling. This manuscript aims to reflect the improvements that the application of a novel soft multiclass compliant classification method (PLS2-CM) entails regarding the traditional chemometric class modelling. With this new approach, the intention is to detect possible deficiencies in biscuit doughs (excess of water, lack of water or little kneading time) during both industrial processes by using NIR spectroscopy.

In PLS2-CM, the coding of the classes is done using an Error Correcting Code Matrix (ECOC), which implies to employ several binary learners so that their number and structure are not predetermined beforehand but are function of the data set to be modelled. The optimization criterion in PLS2-CM is the sensitivity and specificity matrix evaluated by the Diagonal Modified Confusion Entropy (DMCEN), a new index inspired by the Shannon's entropy that is more sensitive to changes in the elements of that matrix than the usual total efficiency. The results obtained according to this index are better with this new soft classification method than the ones obtained when using other soft class modelling techniques such as soft independent modelling of class analogy (SIMCA) or unequal dispersed classes (UNEQ).

In this work it is shown that it is possible to completely distinguish a correct kneaded dough from another defective one with a specificity equal to 1 during the kneading process, but the class corresponding with water deficit dough, accepts a very high percentage (80 % in training and 92 % in prediction) of the excess-water dough spectra. Despite that, after the fermentation and during the rolling process, the same doughs are modelled with complete sensitivity and specificity in prediction (100 %), which indicates that the physico-chemical changes produced during the fermentation are decisive to characterize the absence of defects in biscuit doughs kneading by NIR spectroscopy.

1. Introduction

Biscuits consumption all over the globe is elevated. In fact, global snacks consumption increased in more than 2.5 million tons in the past two years, reaching almost 65 million in 2021 and reporting sales of 474,000 million dollars worldwide [1]. With these production levels, it is clear that controlling the production processes of this food to assess the quality of the final product is truly important.

One of the key aspects in the manufacture of these highly consumed snacks, are the kneading, fermentation and rolling processes, since they are the ones that influence the most the quality of the final product. As a crucial control step of these manufacture processes, an expert in the food sector is always demanded to assess the appropriateness of the biscuit doughs in each stage. Nevertheless, new computational methods and machine learning techniques are being improved or developed in pastry and bakery sectors in order to enhance their industrial control of processes [2–4]. In that sense, the advances of the *in situ* methods stand out for its great interest in the last few years, and therefore, so does near infrared (NIR) spectroscopy, since it has been proven to be one of the most efficient and versatile techniques in the *in-line* processes for this type of analysis [5,6]. The flexibility of NIR spectroscopy in the food industry to evaluate the quality of raw materials and the final products is

* Corresponding author.
E-mail address: mcortiz@ubu.es (M.C. Ortiz).

https://doi.org/10.1016/j.chemolab.2024.105092
Received 29 November 2023; Received in revised form 9 February 2024; Accepted 19 February 2024
Available online 20 February 2024

widely recognized for being a fast and non-destructive technique, and with no sample preparation, what makes it increasingly demanded by the food industry. Quality control in bakery and pastry industries using NIR is usually based either in the nutritional characteristics and/or physicochemical parameters determination of the food products [7–9], or in food manufacturing process monitoring that outline some of those characteristics and the quality of the final product [3,10]. However, the use of classification algorithms has also gained relevance lately [2].

The purpose of the present study is to show the feasibility of detecting possible deficiencies in the kneading and rolling processes through NIR spectroscopy reproducing the expertise of a professional in the industrial sector. It is aimed to monitor the correct manufacture of biscuit doughs during two different elemental processes: the kneading and the rolling processes, having the objective that there is not a person continually supervising them. In order to do that, the intention is to detect if the dough is correct, if it has an excess or lack of water, or whether it needs more kneading time during these industrial operations.

It was decided to monitor those processes by detecting these deficiencies given that rheological tests have quite a few shortcomings. The evaluation of dough quality is mainly based on rheological properties, whereas the quality of the final product usually relays in the specific volume and texture [10]. Nevertheless, rheological methods are unavoidably influenced by the bakeries and the operating conditions, having as a result the possibility of not adequately predicting the quality of the food. Furthermore, all the trials involved require large amounts of resources and are also affected by expert judgements (based on subjective evaluations) [10,11]. In addition, detecting errors in the amount of water or the little kneading time is essential, and it is a logical reasoning because, on the one hand, the correct amount of water allows the flour components to hydrate and the semicrystalline polymers (starch) to achieve glass transition going from a glassy to a rubbery state [10–12]. On the other hand, the contribution of mechanical energy during kneading and rolling processes results in the progressive growth of the gluten netting since it causes new synergies between the gluten proteins through disulphide bonds. Despite that, if that energy is not adequate, protein depolymerization occurs [10,12,13]. For all that, it has been considered a good choice to monitor the ideality of the biscuit doughs by detecting these possible defects with NIR spectroscopy together with a class modelling algorithm.

Additional to study the suitability of biscuit doughs by this approach, in order to detect the possible aforementioned defects an efficient and innovative soft multiclass compliant classification method (PLS2-CM) was used, that for a k-class model, k = 4 in this case, it allows each spectrum to be assigned to one, several, or none of them, avoiding the lack of flexibility of a classifier, such as Partial Least Squares-Discriminant Analysis (PLS-DA) or Support Vector Machine (SVM), which necessarily assign each one of all objects to one class. Recently it has been generalized the two-class class modelling using a PLS regression (PLS-CM) [14–18], into a k-classes case (PLS2-CM) [19] considering the ECOC codification of the responses and using DMCEN [20] to evaluate its performance, that in this work was better than the one obtained when using SIMCA or UNEQ.

Thanks to this new soft multiclass compliant classification method, it is possible to determine that, correctly kneaded doughs can go to the fermentation chamber, and those whose kneading time is not enough, can be kneaded for a longer time to correct that deficiency (still rectifiable before fermentation). On the other hand, after fermentation, the rolling process will automatically differentiate all possible defects in the doughs, being able to solve in this case, the problems with the amount of water. If the dough had excessive water, the defect would be compensated by adding more flour, while if it had a lack of water, it would be discarded so to be reused and corrected in a second kneading process (preventing defective doughs from being moulded and baked, with all the savings that this entails).

2. Materials and methods

2.1. NIR spectroscopy. Spectrophotometer configuration and measurements

The experiments were carried out in an industry of the bakery sector in Spain, in Lugar da Veiga S.L.L [21].

As introduced in the previous section, two processes have been monitored with the objective that there is no need for a qualified person to continually supervise those processes.

The kneading process is characterized by the mixing of all the ingredients that make up the final product, until they reach the most homogeneous dough possible. Rigorously, dough kneading refers to the subsequent development of the gluten network [22]. In that sense, NIR spectra were collected from the beginning (from the mixture of ingredients) until attain the final dough. After the kneading, the doughs were fermented for 1 h and were then laminated in order to moulding them into a biscuit shape.

The measurements were carried out in-line to explore better the possible variations in the manufacture processes of the biscuits. The experimental procedure was made with the AONIR (AOTECH S.L [23]) integrated solution for real-time NIR measurements, including a NIR sensor, a measurement platform, and the precise software to integrate the hardware with the chemometric model outcome for real-time monitoring and control of the kneading and rolling processes. The spectra were recorded throughout the entire kneading industrial process of the biscuit doughs in a kneader and in an industrial dough roller for the rolling process, what implied 30 kg of dough per class. The spectrometer was configured automatically so that NIR reflectance was measured in a wavelength range from 900 to 1670 nm (125 wavelengths, accounting for a spectral resolution of 6 nm), with 50 scans per spectrum with an integration time of 10.8 ms and taking one spectrum every 10 s. Simultaneously, a pastry expert was aware of the evolution of both processes to ensure the reference status of the biscuit doughs. To study the possible defects, not only a correct dough was monitored (Class 1, correct doughs), but other three doughs corresponding to the three types of defects mentioned in the introduction section (Class 2, dough with excess of water; Class 3, dough with lack of water; and Class 4, dough with little kneading time). In that sense, the recorded spectra for the four doughs (four classes) were 576 during the kneading process and 431 during the rolling process (corresponding to the same biscuit doughs). The different number of spectra is due to the fact that the rolling process is shorter than the kneading process. The spectra distribution for each class is shown in Table 1.

2.2. NIR signals and spectral preprocessing

Just as mentioned beforehand, NIR spectra were registered during the kneading process in four different scenarios that conform the classes to be modelled. Fig. S1 in the supplementary material shows the

Table 1
Number of spectra per class, registered during the kneading and rolling processes.

	Classes			
	Class 1	Class 2	Class 3	Class 4
Kneading process				
Number of spectra	129	128	154	165
Training	90	90	108	116
Validation	39	38	46	49
Rolling process				
Number of spectra	126	126	110	119
Training	88	88	77	83
Validation	38	38	33	36

Abbreviations: Class 1, correct dough. Class 2, dough with excess of water. Class 3, dough with lack of water. Class 4 dough with little kneading time.

representation of these spectra for each class, while Fig. 1 shows these same spectra, but preprocessed. It can be observed that, apparently, the shape of the spectra is quite similar during the kneading. The majority components of the doughs are water and flour, which contains high amounts of carbohydrates [13], and for that reason, the most remarkable band is the one between 1400 and 1500 nm in the raw spectra (in the four possible situations during the kneading process) possibly related to the first overtone of the symmetric and asymmetric vibration stretch of the water molecule and the second overtone of the O–H bond of sugars, but it also can be associated with the presence of proteins (stretching vibration of the first overtone of the N–H bond). It can also be observed two bands at approximately 980 and 1200 nm, related with the O–H bond of sugars, the C–H of carbohydrates, and the bending mode, and the asymmetric stretch of the water molecule [24].

On the other hand, in Fig. S2 in the supplementary material can be found the recorded spectra during the rolling process, and in Fig. S3, the corresponding preprocessed ones.

By comparing Fig. S1 and Fig. S2 in the supplementary material, it is shown how both the physical appearance of the doughs and the physicochemical changes occurred during the fermentation process influence the NIR spectra. In the course of fermentation, yeasts take up nutrients for growth in the biscuits doughs (mainly carbohydrates), and its metabolism results in the evolution of glucose and the formation of carbon dioxide to leaven the doughs [25].

Smoothing, baseline corrections, and scatter corrections used to correct artefacts in analytical signals, depend strongly on the data [26] and the purpose of the analysis and can be applied in any order [27,28]. Reference [29] shows the pretreatment combination that optimizes the residual sum of squares in a PLS calibration model is different from the one that optimizes the figures of merit of the analytical method. In this latter case, the optimum is obtained by applying first Savitzky-Golay (SG) and after, standard normal variate (SNV). This same pretreatment (SG + SNV) has been also optimum in Ref. [30] and for NIR signals obtained with AONIR and a similar data matrix that the one in this manuscript when PLS-DA is applied [2]. As a consequence, both for kneading and rolling processes, NIR spectra were pre-processed by applying Savitzky-Golay procedure with a window width of 15 points using a second-degree polynomial and a second derivative, and afterwards by standard normal variate (SNV) in order to baseline corrections and resolution enhancement.

2.3. Sample distribution in training and in validation

Regarding the capability of prediction of a class model, cross-validation (CV) or a validation set (VS) are commonly used to evaluate it. Despite its popularity, CV has been criticized [31] and recently, has been theoretically demonstrated that it is not the correct way to evaluate the capability of prediction [32]. Therefore, in this work, both for the kneading and rolling processes, the NIR spectra of each one of the four classes were split in two subsets: training and prediction. In both cases, the 70 % of the spectra of each class were assigned to the training set and the remaining 30 % to the validation one, using the Kennard Stone

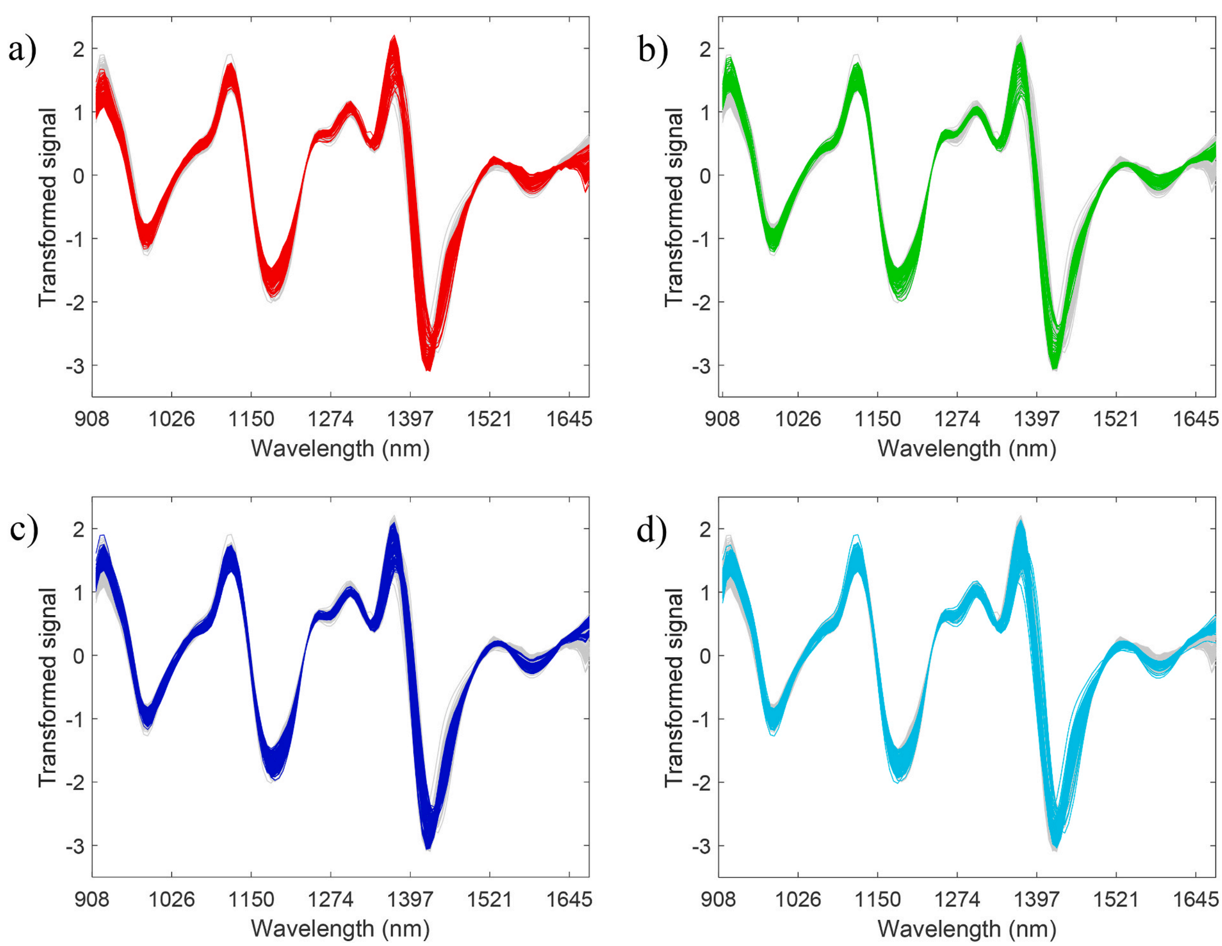

Fig. 1. NIR spectra recorded during the kneading process preprocessed by Savitzky-Golay and SNV for each class. a) Class 1: correct dough (in red), b) Class 2: dough with an excess of water (in green), c) Class 3: dough with deficit of water (in blue), and d) Class 4: dough with little kneading time (in cyan). In grey are represented all the remaining spectra corresponding to the other 3 classes. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

method [33] for the selection, as previously shown in Table 1.

2.4. PLS2-CM

PLS2-CM is very versatile, and it adapts to the characteristics of each data set thanks to its coding and decoding of classes. The structure that this method follows can be summarized in the following steps.

Step 1. The codification of classes is done by applying to the label vector of the objects an Error Correcting Code matrix (ECOC). This codification is not fixed beforehand but is part of the method optimization, which leads to select the most appropriate one for the current data.
Step 2. Through PLS2 a regression model between the NIR spectrum and the code of class of each object is obtained. PLS2 can manage the lack of orthogonality of the codified responses by means of an ECOC matrix.
Step 3. The decoding is made using critical values at a confidence level established *a priori* and without using any probability distribution predefined for the predicted values via PLS2. Also, critical Q and T^2 statistics values are employed to define if the model is valid to apply the PLS2 regression to a new spectrum.
Step 4. Each sample is assigned to the class whose code matches with the code that class has in the ECOC matrix.
Step 5. The optimization criterion is the sensitivity and specificity matrix evaluated by the Diagonal Modified Confusion Entropy (DMCEN) [20], a new index that is more sensitive to changes in the elements of that matrix than the usual efficiency.

The details of the previous steps can be consulted in Ref. [19], but a description will be made below, applying it to the case of kneading data to ease its reading and the interpretation of the results.

According to Table 1, the NIR spectra of the kneading process that were assigned to the training set form a matrix $\mathbf{XT}_{404x125}$, whereas the validation ones, form the $\mathbf{XV}_{172x125}$ matrix. There are also two column vectors corresponding to the labels of the objects from the training and validation sets, respectively, $\mathbf{LT}_{404x1}$ and $\mathbf{LV}_{172x1}$. The labels, belong to the {1, 2, 3, 4} set, and they denote the class to which each object belongs according to the notation in Table 2. So, the five steps to be applied to the kneading process go as follows.

2.4.1. Step 1 for the PLS2-CM

The codification ECOC matrix is a $\mathbf{M}_{kxc} = (m_{ij})$ matrix with $m_{ij} \in \{-1,1\}$ being k the number of classes (in this case, four), and c the length of the codeword. Each row of the ECOC matrix is the codeword of the class and each column is a binary learner. The ECOC matrices come from problems in the communication engineering, but their use in multiclass classification problems has gained importance since the pioneering study made by Dietterich in 1995 [34].

Table 2 shows an example of this type of matrix for $k = 4$ and $c = 5$. In it, the class of doughs with lack of water is codified by the (−1, −1, 1, −1, 1) vector, corresponding with each binary learner values for dough spectra with lack of water. From now on this ECOC matrix will be used for the description of the different steps of the PLS2-CM procedure.

Table 2
Example of an ECOC matrix for $k = 4$ and $c = 5$.

Class	Label	Binary learner				
		f_1	f_2	f_3	f_4	f_5
Class 1	1	1	1	1	1	1
Class 2	2	−1	−1	−1	1	1
Class 3	3	−1	−1	1	−1	1
Class 4	4	−1	1	−1	1	−1

Abbreviations: Class 1, correct dough. Class 2, dough with excess of water. Class 3, dough with lack of water. Class 4 dough with little kneading time.

From the vector of labels $\mathbf{LT}_{404x1,}$ the row vector that corresponds to its class is assigned to the i-th object, for instance, if $\mathbf{LT}(i) = 3$, then, the vector $\mathbf{YT}(i) = (-1, -1, 1, -1, 1)$ will be assigned to the i-th object. In this way, a $\mathbf{YT}_{404x5}$ matrix is built with the code assigned to each class and which is the response matrix associated with the NIR spectra matrix, $\mathbf{XT}_{404x125}$. Each column of $\mathbf{YT}$ are the values of one "binary learner". That is, they are the values of a binary function that models two $\mathbb{A}$ and $\mathbb{B}$ superclasses. As an example, in the f_2 case, $\mathbb{A}$ is composed by classes 1 and 4 (correct dough, and dough with little kneading time, respectively) when $\mathbb{B}$ is formed by classes 2 and 3 (dough with excess of water and with lack of water, respectively). However, f_1, models the class of correct doughs versus the union of the other three remaining classes.

Some additional information about how to build and work with ECOC matrices can be consulted in Ref. [19] and in the supplementary material (Section 4.2.1).

2.4.2. Step 2 for the PLS2-CM

With the $\mathbf{XT}_{404x125}$ and $\mathbf{YT}_{404x5}$ autoscaled matrices, a PLS2 regression model is built [35], varying the number of LV from 3 to 9.

As is known, the PLS2 regression model is a compromise between variances and correlation, which is obtained by maximising a geometric mean or, equivalently, their product, Eq. (1)

$$max_{(r,q)}\left\{var(\mathbf{XTr})[corr(\mathbf{XTr},\mathbf{YTq})]^2 var(\mathbf{YTq})\right\} \quad \text{subject to } \|\boldsymbol{r}\| = \|\boldsymbol{q}\| = 1 \tag{1}$$

where $\mathbf{r}$ and $\mathbf{q}$ are the vectors that define a linear combination both for predictor and response variables respectively. The maximisation of the product var($\mathbf{XTr}$)[corr($\mathbf{XTr}$,$\mathbf{YTq}$)]^2 var($\mathbf{YTq}$) tends to look for directions with large variance in NIR spectra, $\mathbf{XT}$, and also in its codification $\mathbf{YT}$, avoiding those with small variance or little correlation with each other. This PLS2 structure adapts the regression both to the class of the spectra and to each ECOC matrix.

Together with the PLS2 model, the critical values T^2_{crit} and Q_{crit} are available for the T^2 and Q statistics at the confidence level that is desired. With them, the PLS_{BOX} is defined by Eq. (2)

$$PLS_{BOX} = \{\mathbf{x} \mid T^2(\mathbf{x}) < T^2_{crit}\} \bigcup \{\mathbf{x} \mid Q(\mathbf{x}) < Q_{crit}\} \tag{2}$$

being $\mathbf{x}$ a NIR spectrum from $\mathbf{XT}$ matrix in training, or from the $\mathbf{XV}$ matrix in validation. A more restrictive PLS_{BOX} could be obtained by using the intersection of both sets in Eq. (2). When $\mathbf{x} \notin PLS_{BOX}$, the built PLS2 model is not applied to a spectrum, $\mathbf{x}$, and in consequence, the spectrum is not assigned to any of the classes. If the PLS_{BOX} defined in Eq. (2) is employed, the number of non-assigned spectra is lesser that if the intersection of the two sets defined by the critical values of T^2 and Q were used.

This is truly useful when the spectra are being recorded *in-line*, as it allows detecting unusual and anomalous spectra registered by the NIR sensor. If the frequency of such recordings is high, the possibility of sensor failure should be considered. In any case, the surely incorrect assignment of an anomalous spectrum to one of the classes is completely avoided.

Another additional advantage of using the PLS2 regression model, is that the PLS_{BOX} is common to every binary learner of each ECOC matrix, five, in the case of the matrix in Table 2.

2.4.3. Step 3 for the PLS2-CM

As a result of *steps 1* and *2,* and once that the spectra that are not in the PLS_{BOX} were rejected, the 224 $\widehat{\mathrm{YT}}$ matrices from the predicted values by the PLS2 model for each one of the five binary learners of the ECOC matrix used (Table 2) are obtained. The number of the $\widehat{\mathrm{YT}}$ matrices corresponds to 32 selected ECOC matrices for each one of the 7 LVs used (see supplementary material of section 2.4.1). For instance, take the supposition that matrix $\mathbf{M}$ from Table 2 has been used, which is one of the 12 optimal ones for $c = 5$. Consider f_2, and the two superclasses $\mathbb{A}$ and $\mathbb{B}$. Through the univariate kernel density [36], which does not assume any *a priori* probability, the density function is calculated for the f_2 values in each superclass. Fig. 2 shows an ideal sketch of these two density functions, in blue for the superclass $\mathbb{A}$ and in red for the superclass $\mathbb{B}$.

By fixing the γ_i y δ_i probabilities (that do not have to be equal to every f_i, i = 1, …, 5), the critical values cv_i ($\mathbb{A}$) and cv_i ($\mathbb{B}$) are computed with the previously fitted distribution so that Eq. (3) is fulfilled,

$$\begin{aligned} P\{\hat{y}_i \in f_i(\mathbb{A}) | \hat{y} \leq cv_i(\mathbb{A})\} = \gamma_i \\ P\{\hat{y}_i \in f_i(\mathbb{B}) | \hat{y} \leq cv_i(\mathbb{B})\} = \delta_i \end{aligned} \tag{3}$$

where P stands for probability, and $\hat{y}_i$ is the value of the i-th binary learner calculated by the PLS2 model for a spectrum from the training set or the validation one. Notice that the definitions in Eq. (3) involves that γ_i would be a large value close to one, whereas δ_i would be close to zero.

Both critical values cv_i ($\mathbb{A}$) and cv_i ($\mathbb{B}$) define the +1 or −1 assignment to each spectrum, that is, they assign the spectrum to one of the superclasses. There are two possible situations: i) that cv_i ($\mathbb{A}$) is greater than cv_i ($\mathbb{B}$), which is the particular case shown in Fig. 2a for the binary learner f_2 in Table 2 ii) that cv_i ($\mathbb{B}$) is greater than cv_i ($\mathbb{A}$), Fig. 2b for the same f_2. In Fig. 2a, when a $\hat{y}_i$ value belongs to the interval marked in red, a +1 (**x** ϵ $\mathbb{B}$) is assigned to the corresponding spectrum **x**, while if it belongs to the interval marked in blue, a −1 (**x** ϵ $\mathbb{A}$) is assigned. Finally, if it belongs to the intersection of the two intervals, **x** ϵ $\mathbb{A} \cap \mathbb{B}$, the two values, +1 and −1 are assigned. Opposite to that, if the relative position of both critical values is that of the second case (Fig. 2b), the assignment to the superclasses is as explained in first instance, but there is the possibility that the value of $\hat{y}_i$ is external to both intervals. In that particular case, the value assigned would be a 0 (this indicates that the corresponding spectrum **x** does not belong to either of the two superclasses).

2.4.4. Step 4 for the PLS2-CM

After the previous steps and having used an ECOC matrix of length of codework c to encode the classes, either one or more vectors of dimensions c (formed by −1 and +1), or a vector with some null coordinate, are assigned to each vector **x** (NIR spectrum). Furthermore, it can also happen that **x** $\notin$ PLS_{BOX} in which case, all the coordinates of the vector are zero. This vector (or vectors) is the code estimated by PLS2 for the spectrum **x**. As a consequence, the spectrum **x** will be assigned to the class (or classes) whose row in the ECOC matrix matches the estimated code.

2.4.5. Step 5 for the PLS2-CM

In the training phase, the actual class to which each spectrum belongs is compared with the one assigned in the previous step. In this way we have the sensitivity and specificity matrix, **S**=(s_{jm}). If j ≠ m, s_{jm}, is the specificity of class model m respect class j, and if j = m, then s_{jm} is the sensitivity of class. In this case, there are 224 matrices of dimensions 4 × 4 because there are 4 classes (S_{4x4}). These matrices are function of the ECOC matrix and the number of LV of each PLS2 model. To decide which is the best model, the **S** matrices must be compared. There are few indices to evaluate these matrices when there are more than two classes. For classifiers such as SVM or PLS-DA, the most commonly used is the total efficiency, which is not very sensitive to changes in the elements of **S**. The analysis of this issue together with the proposal of a new DMCEN index and its evaluation is addressed and can be consulted in Ref. [20]. DMCEN, uses the entropy concept defined by Shannon as a measure of the order/information generated by a classifier in the training set (or validation set). It can take values from zero to one, and the lower the DMCEN value is, the better the performance of the model is.

In this way, the PLS2-CM class model is obtained, which provides the minimum DMCEN by varying the ECOC matrix for coding the responses and the number of LV in the PLS2 regression. This k-classmodel is formed by the ECOC matrix and the PLS2 regression and will be applied to the **XT** test set to evaluate its capability of prediction.

2.5. Software

PLS2-CM has been programmed in MATLAB [37]. The PLS2 regressions and the "Sav-Gol" and "SNV" functions from PLS-Toolbox [38] were built and applied working also under MATLAB version 9.9.0 (R2020b). DMCEN was calculated using an ad-hoc MATLAB code, available in Ref. [39], that calculates the global DMCEN and, for each class given an **S** matrix. PARVUS was used to build SIMCA and UNEQ models [40].

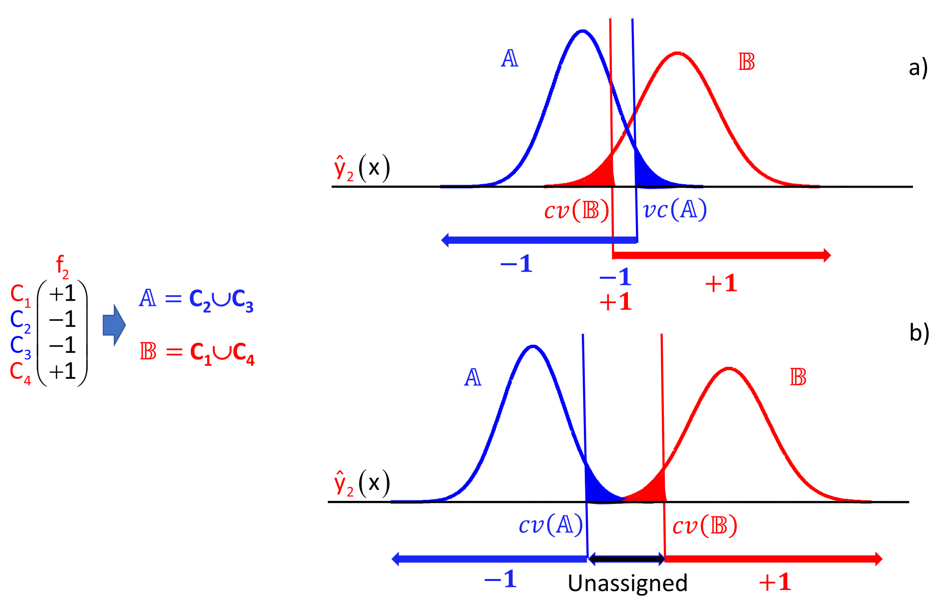

Fig. 2. Ideal sketch of the two density functions for decoding f_2. a) when cv_i ($\mathbb{A}$) is greater than cv_i ($\mathbb{B}$), and b) when cv_i ($\mathbb{B}$) is greater than cv_i ($\mathbb{A}$). In blue for the superclass $\mathbb{A}$ and in red for the superclass $\mathbb{B}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3. Results and discussion

Before analysing PLS2-CM results and, following the usual strategy in the control of processes, a preliminary exploratory analysis (Principal Component Analysis, PCA) has been performed separately for the kneading and rolling processes. 4 Principal Components (PCs) were selected in the first case and 5 in the second one. The models were made considering only the class of the correct doughs, projecting then the remaining classes. By representing the Q statistic for each one of the samples (Fig. S4 in the supplementary material) and the Hottelling's T^2 (Fig. S5 in the supplementary material) it can be seen that there is a clear difference between the correct doughs (represented in red) and the other three ones (each one of them above the confidence limit), but it is not possible to differentiate the defect that each of the doughs presents, with the exception of the class with little kneading time in the case of the rolling process. That is to say, it can be confirmed the necessity of using a soft multiclass compliant classification method.

Both for the construction of the models of $k = 4$ classes for kneading and rolling processes, a length of the codeword, c, between 3 and 7 has been used. Therefore, for each value of c, the number of ECOC matrices to be considered in the optimization have been 12, 3, 12, 4 and 1 respectively (see supplementary material). The PLS2 models have been built by varying the number of LV from 3 to 9. As explained beforehand, this leads to evaluate 224 PLS2 regressions to obtain the minimum DMCEN. In order to define the PLS_{BOX} (see Eq. (2)), the critical values T^2_{crit} and Q_{crit} of the T^2 and Q statistics have been chosen at the 95 % significance level. The critical values of the distributions of the binary learner f_i, $i = 1, \ldots c$, has been obtained regarding Eq. (3), establishing $\gamma_i = 0.99$ and $\delta_i = 0.01$.

3.1. Kneading process

In this case, the PLS2 model (with 7 LV and the ECOC matrix from Table 2) provides the DMCEN value that is 0.1378 in training, and 0.1232 in validation. The similarity between both DMCEN values, indicates that the k-class model is not overfitted. The number of non-assigned spectra to any of the four classes has been six, (3, 0, 1, 2 belonging to the classes 1, 2, 3 and 4 respectively). The corresponding sensitivity and specificity matrices are shown in Table 3 ((a) in training, and b) in prediction).

The sensitivities in training go from 0.9333 to 0.9556, and in prediction, from 0.9744 to 1.0000, that is, the model of each class correctly accepts the spectra that belong to that class, both in fitting and in prediction. The models of the correct doughs and the ones with little kneading time are entirely specific in training and in prediction, which means that they do not accept any spectrum from the other two remaining classes (those with water problems). In training, just the specificity of the class with little kneading time regarding the class with an excess of water is different from one, in fact, the model of the class with little kneading time accepts mistakenly only one spectrum of the class with an excess of water. In summary, correct-kneading and time-deficit kneading are perfectly modelled by the 4-class model during the kneading process and this, will let correctly kneaded doughs to go to the fermentation chamber, and those whose kneading time is not enough, can be kneaded for a longer time to correct that deficiency.

Different from that, it does not occur the same for the specificity of the other two classes between them: the kneading with excess or deficit of water. The model for the kneading with an excess of water accepts a 13.89 % of spectra corresponding to the kneading with lack of water in fitting and a 19.57 % in prediction. But, in a completely asymmetrical way, the kneading model with lack of water incorrectly accepts an 80.00 % and a 92.11 % of the spectra with excess of water in fitting and in prediction, respectively. In other words, 76 spectra out of the 90 that constitute the class with an excess of water have also been assigned to the class with lack of water, while only 13 out of 108 of that class have also been assigned to the class with an excess of water (considering that some spectra can be unassigned).

3.2. Rolling process

The optimal ECOC matrix to encode the recorded spectra during the rolling process is the one showed in Table 4, with a code length of 4.

The PLS2 model for these four binary learners has 3 LV and the DMCEN value is 0.0142 in training and 0 in prediction. In this case there are 7 spectra that are not assigned to any class, two from class 1 (correct dough), three from class 2 (dough with excess of water) and two from class 3 (dough with lack of water). That is the reason why the sensitivity of the k-class-model for these classes is 0.9773, 0.9659 and 0.9740 respectively, whereas the sensitivity for the class with little kneading time is equal to one.

None of the classes have spectra assigned to another class, as occurred between classes 2 and 3 during the kneading. The specificities of the model of each class regarding the other three ones is equal to one. In prediction, all the sensitivities and specificities are equal to one.

The models obtained with PLS2-CM and the NIR spectra can completely distinguish the four classes, one from the others: correct or deficient kneading, and each one of the deficiencies (excess of water, lack of water or little kneading time) from the others. That will allow to solve possible defects in the doughs (if it were the case) before moulding and baking them to obtain the biscuits. The excess of water would be solved by adding more flour, whereas if there was a lack of water, the dough would be discarded to be reused in a second kneading (it is assumed that a short kneading time at this stage could have been solved

Table 4
ECOC matrix for the 4-class model using the NIR spectra obtained during the rolling process.

Binary learners	f_1	f_2	f_3	f_4
Class 1	1	1	1	1
Class 2	−1	−1	−1	1
Class 3	−1	1	1	−1
Class 4	1	−1	1	−1

Abbreviations: Class 1, correct dough. Class 2, dough with excess of water. Class 3, dough with lack of water. Class 4, dough with little kneading time.

Table 3
Kneading process. Sensitivity and specificity matrices a) in training and b) in prediction, of the 4-class model using the NIR spectra obtained during the kneading process.

a) Training		Class model C_1	C_2	C_3	C_4	b) Prediction		Class model C_1	C_2	C_3	C_4
True class	C_1	0.9333	1.0000	1.0000	1.0000	True class	C_1	0.9744	1.0000	1.0000	1.0000
	C_2	1.0000	0.9556	0.2000	0.9889		C_2	1.0000	0.9737	0.0789	1.0000
	C_3	1.0000	0.8611	0.9352	1.0000		C_3	1.0000	0.8043	1.0000	1.0000
	C_4	1.0000	1.0000	1.0000	0.9483		C_4	1.0000	1.0000	1.0000	0.9796

Abbreviations: C1, correct dough. C2, dough with excess of water. C3, dough with lack of water. C4, dough with little kneading time.

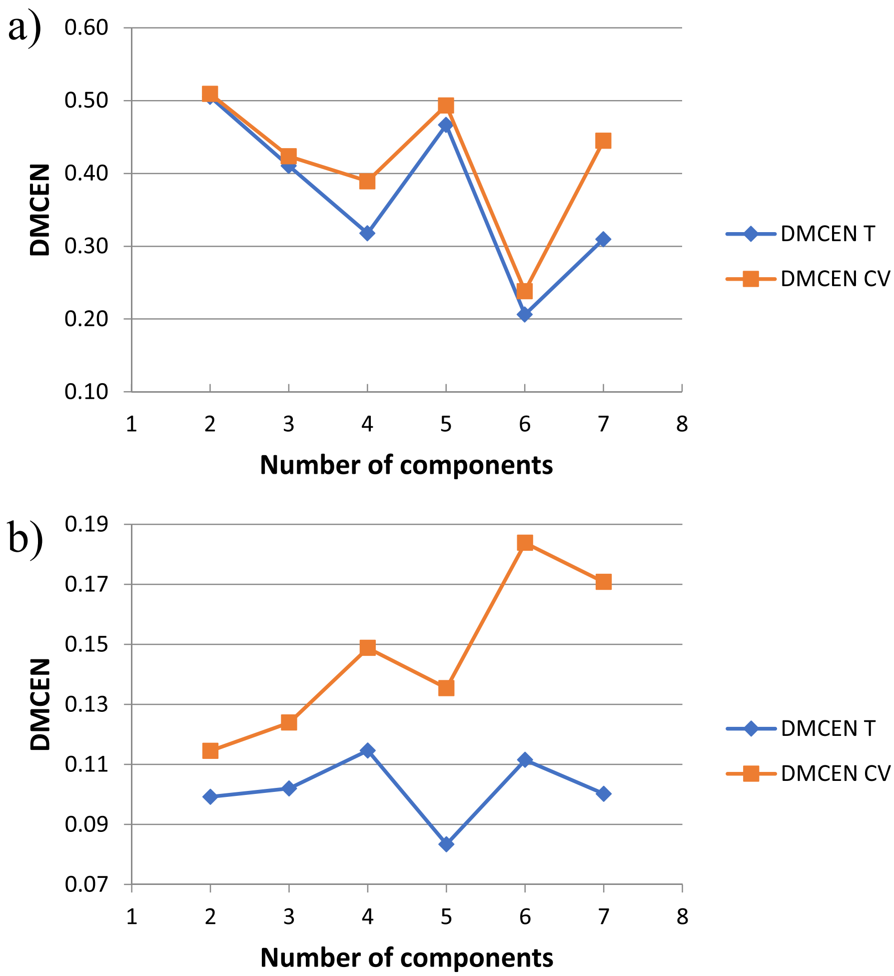

Fig. 3. DMCEN values as functions of the number of principal components in the inner space in SIMCA model for a) the kneading process and b) the rolling process.

already during the kneading process). All of this leads to great savings in energy and financial expenses, as well as avoiding food waste.

3.3. Comparison with SIMCA and UNEQ

The PLS2-CM is very versatile, and it adapts to the characteristics of each data set thanks to its coding and decoding of classes. It has been introduced in this work as a soft multiclass compliant classification method that allows to assign an object to one, more than one, or even none of the classes. In chemometrics, SIMCA and UNEQ are commonly used as soft classifiers [41], having in common that each class is modelled separately. To evaluate the performance of the proposed method, it has been decided to compare the results obtained with those provided by SIMCA and UNEQ. These two methods will also provide a sensitivity-specificity matrix as a result of the classification, that will be evaluated by DMCEN. As a reminder, the lower DMCEN, the better the model performance is.

3.3.1. SIMCA results

The SIMCA models have been built with the same number of components per class and three cancellation groups have been used to perform CV procedure. The optimal model will be chosen according to the lowest DMCEN obtained in CV. This also applies to UNEQ. It has been worked at 95 % confidence level for class spaces, and the class boundary was determined according to the confidence limit.

As can be seen in Fig. 3a, in the case of the kneading process, and in

Table 5
Kneading process. DMCEN and sensitivity and specificity matrices of SIMCA model using 6 PCs. a) in training and b) in CV, of the 4-class model using the NIR spectra obtained during the kneading process.

a) Training. DMCEN = 0.2062						b) CV. DMCEN = 0.2384					
		Class model						Class model			
		C_1	C_2	C_3	C_4			C_1	C_2	C_3	C_4
True class	C_1	0.7555	1.0000	1.0000	1.0000	True class	C_1	0.7555	1.0000	1.0000	1.0000
	C_2	1.0000	0.7888	0.7667	1.0000		C_2	1.0000	0.6222	0.8148	1.0000
	C_3	1.0000	0.8889	0.8333	1.0000		C_3	1.0000	0.8889	0.7467	1.0000
	C_4	1.0000	1.0000	1.0000	0.7391		C_4	1.0000	1.0000	1.0000	0.7217

Abbreviations: C1, correct dough. C2, dough with excess of water. C3, dough with lack of water. C4, dough with little kneading time.

Table 6
Rolling process. DMCEN and sensitivity and specificity matrices of SIMCA model using 2 PCs. a) in training and b) in CV, of the 4-class model using the NIR spectra obtained during the rolling process.

a) Training. DMCEN = 0.0992						b) CV. DMCEN = 0.1145					
		Class model						Class model			
		C_1	C_2	C_3	C_4			C_1	C_2	C_3	C_4
True class	C_1	0.8863	1.0000	1.0000	1.0000	True class	C_1	0.8409	1.0000	1.0000	1.0000
	C_2	1.0000	0.8863	1.0000	1.0000		C_2	1.0000	0.7841	1.0000	1.0000
	C_3	1.0000	1.0000	0.7272	1.0000		C_3	1.0000	1.0000	0.7532	1.0000
	C_4	1.0000	1.0000	1.0000	0.8072		C_4	1.0000	1.0000	1.0000	0.7349

Abbreviations: C1, correct dough. C2, dough with excess of water. C3, dough with lack of water. C4, dough with little kneading time.

Table 7
Prediction results for SIMCA model. DMCEN and sensitivity and specificity matrices for a) Kneading process, and b) Rolling process of the 4-class model.

a) Kneading. DMCEN = 0.2062						b) Rolling. DMCEN = 0.0775					
		Class model						Class model			
		C_1	C_2	C_3	C_4			C_1	C_2	C_3	C_4
True class	C_1	0.8205	0.9778	0.9667	1.0000	True class	C_1	1.0000	1.0000	1.0000	1.0000
	C_2	1.0000	0.8684	0.6316	1.0000		C_2	1.0000	1.0000	1.0000	1.0000
	C_3	1.0000	0.8478	0.8478	0.7609		C_3	1.0000	1.0000	0.8182	1.0000
	C_4	1.0000	1.0000	1.0000	0.8000		C_4	1.0000	1.0000	1.0000	0.8889

Abbreviations: C1, correct dough. C2, dough with excess of water. C3, dough with lack of water. C4, dough with little kneading time.

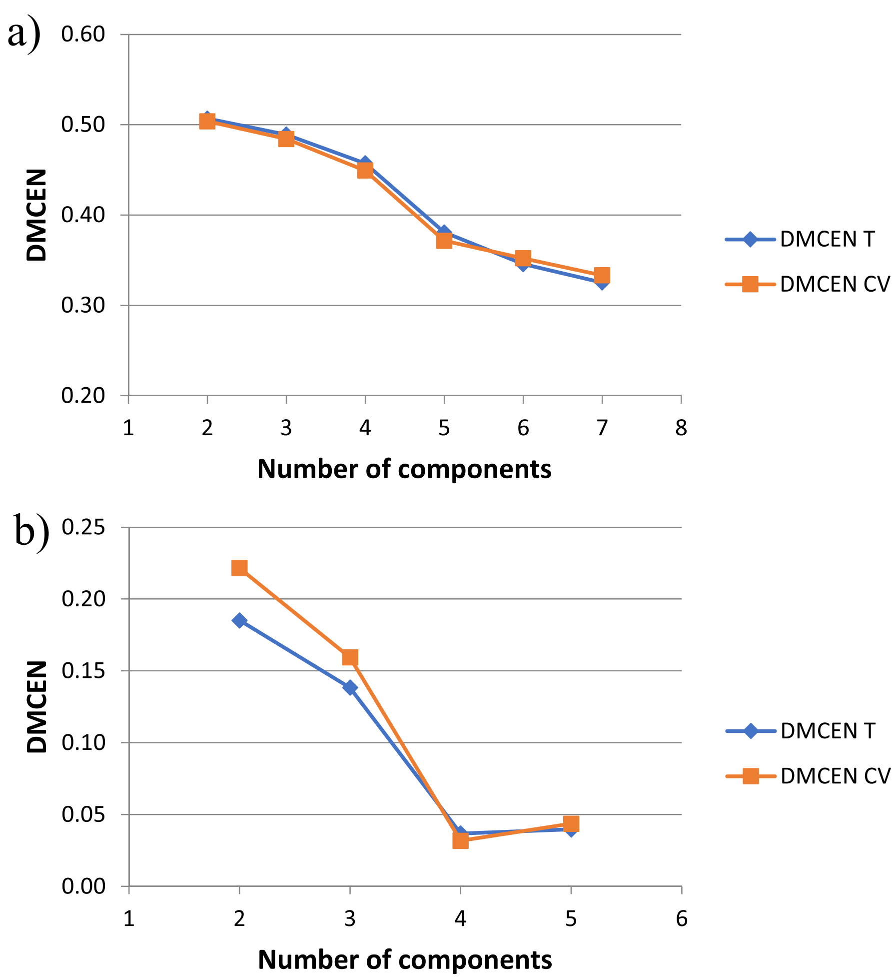

Fig. 4. DMCEN values as function of the number of principal components used before building the UNEQ model for a) the kneading process and b) the rolling process.

Table 8
Prediction results for UNEQ model. DMCEN and sensitivity and specificity matrices for a) Kneading process, and b) Rolling process of the 4-class model.

a) Kneading. DMCEN = 0.2614						b) Rolling. DMCEN = 0					
		Class model						Class model			
		C_1	C_2	C_3	C_4			C_1	C_2	C_3	C_4
True class	C_1	0.9744	1.0000	0.9744	1.0000	True class	C_1	1.0000	1.0000	1.0000	1.0000
	C_2	0.9737	1.0000	0.2105	1.0000		C_2	1.0000	1.0000	1.0000	1.0000
	C_3	0.9130	0.8043	0.9783	0.2826		C_3	1.0000	1.0000	1.0000	1.0000
	C_4	0.9800	1.0000	0.2200	0.9800		C_4	1.0000	1.0000	1.0000	1.0000

Abbreviations: C1, correct dough. C2, dough with excess of water. C3, dough with lack of water. C4, dough with little kneading time.

Fig. 3b in the case of rolling process, the lowest DMCEN was obtained in CV using 6 and 2 PCs, respectively. On the one hand, Table 5 shows the sensitivity and specificity matrix obtained with those 6 PCs, both in training (DMCEN = 0.2062) and in CV (DMCEN = 0.2384), whereas on the other hand, Table 6 reflects the DMCEN value and the corresponding sensitivity-specificity matrices when 2 PCs are selected in the rolling process case.

All the remaining sensitivity-specificity matrices for each model depending on the number of PCs, as well as the DMCEN value in training and CV can be consulted in the supplementary material (Tables S2–S11).

Once the optimal number of PCs has been selected, the sensitivity-specificity matrix in prediction is obtained together with its DMCEN value. Table 7 shows the results obtained: a) for the case of kneading, and b) for the case of rolling using the same prediction set employed in PLS2-CM.

3.3.2. *UNEQ results*

The same strategy as in SIMCA has been applied with UNEQ, that is, the optimal model has been selected in each case based on the best DMCEN in CV. With UNEQ is necessary to have, at least, three times as many objects as variables per class, that is why PCs are previously done to reduce the dimensionality of the problem. In this way, for the case of kneading, 7 PCs were selected, and for the rolling, 4 (Fig. 4a and b, respectively). The sensitivity-specificity matrices for all models can be consulted, once again, in the supplementary material, both in training and in CV (Tables S12–S17 for the kneading process and Tables S18–S21 for the rolling process). On the other hand, Table 8 shows the prediction results for these matrices for the selected models and for both processes using the same prediction set employed in the PLS2-CM.

3.3.3. *Comparative analysis regarding DMCEN*

Finally, as a summary, Fig. 5 represents the DMCEN values in prediction for each industrial process and each chemometric strategy. Observing that figure, one can conclude that the method that presents the best performance is the proposed one, the PLS2-CM.

By doing a more detailed analysis, it can be said that in prediction UNEQ offers in general a greater sensitivity, but worse specificity, while SIMCA gives more importance to specificity, and consequently, worse sensitivity is obtained. This is why the use of DMCEN is essential, otherwise it would be difficult to evaluate which results are better. Based on the results of the PLS2-CM, it can be said that this soft multiclass compliant classification method has been made possible to detect deficiencies in the biscuits manufacture process, and above all, and in comparison with traditional methods, it has made possible to increase the information regarding the failures (misclassifications) of the chemometric models. The DMCEN values obtained with PLS2-CM (0.1232 and 0.0000 for kneading and rolling processes, respectively) is always better than the ones obtained with SIMCA and UNEQ model.

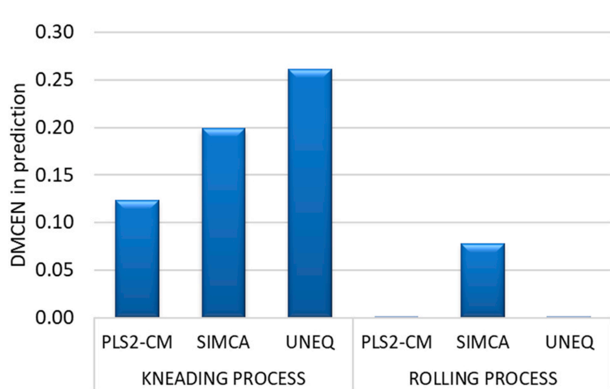

Fig. 5. Summary results for DMCEN in prediction with an external data set for each process and each chemometric strategy.

4. Conclusions

In this work, *in-line* NIR spectra were used together with PLS2-CM in order to detect three possible defects related to the amount of water and the mechanical energy that can occur during the kneading process in the manufacturing of biscuits. It was considered this as a more convenient way to evaluate their quality than taking into account their rheological properties. The four following classes were considered: correct dough, dough with an excess of water, with lack of water and with little kneading time.

With the spectra recorded during the kneading, the class models allow not only to fully distinguish the correct doughs from the other three classes with defects with the perfect specificity (equal to 1), but also the model with little kneading time is completely specific regarding the other three. On the contrary, the kneading model with lack of water accepts a high percentage (92 %) of the spectra corresponding to the kneading with excess of water. Nevertheless, after the fermentation, in the rolling process, the same doughs, are modelled with complete specificity.

In summary, NIR spectroscopy along with PLS2-CM has been proven to be an effective technology to detect the most common deficiencies in the kneading process also reaching the conclusion that the identification of the most common deficiencies is not complete until the fermentation ends. The great advantage of using a unique model for the four classes such as PLS2-CM is that it allows to increase the information about the failures of the model. Either due to the way in which the spectra are assigned to several classes (the asymmetry observed in the classes with excess and deficit of water in the kneading process) or due to the non-assignment to any of them (spectra out of PLS_{BOX} for the data coming from the rolling process). This information would be masked by a forced assignment of all spectra to a single class as occurs with a classifier. The results obtained with the applied method have been proven to be better than those achieved when using traditional methods such as SIMCA or UNEQ.

Funding

This work has been funded by the Ministerio de Comercio, Industria y Turismo under Project PHOTONICS4BAKERY (AEI-010500-2021b-111) Junta Castilla y León, Consejería de Educación under Project BU052P20 cofinanced with Regional European Funds.

CRediT authorship contribution statement

D. Castro-Reigía: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation. **M.C. Ortiz:** Writing – review & editing, Visualization, Validation, Supervision, Project administration, Funding acquisition, Formal analysis, Conceptualization. **S. Sanllorente:** Writing – review & editing, Validation, Supervision. **I. García:** Supervision, Resources, Methodology, Funding acquisition. **L.A. Sarabia:** Conceptualization, Formal analysis, Investigation, Software, Supervision, Validation, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

Acknowledgments

The authors thank Lugar daVeiga S.L.L. for allowing the measurements in their facilities and the entities for financial support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemolab.2024.105092.

References

[1] Consumo per cápita de snacks a nivel mundial, por segmento, en 2021. https://es.statista.com/estadisticas/1350295/consumo-per-capita-de-snacks-a-nivel-mundial-por-segmento/. (Accessed 27 November 2023).

[2] D. Castro-Reigía, I. García, S. Sanllorente, L.A. Sarabia, J.M. Amigo, M.C. Ortiz, Bread fermentation monitoring through NIR spectroscopy and PLS-DA. Determining the optimal fermentation point in bread doughs, J. Food Eng. 361 (2024) 111738, https://doi.org/10.1016/j.jfoodeng.2023.111738.

[3] X. Chang, X. Huang, W. Xu, X. Tian, C. Wang, L. Wang, S. Yu, Monitoring of dough fermentation during Chinese steamed bread processing by near-infrared spectroscopy combined with spectra selection and supervised learning algorithm, J. Food Process. Eng. 44 (9) (2021) e13783, https://doi.org/10.1111/jfpe.13783.

[4] J.M. Amigo, B.M. Jespersen, F. van den Berg, J.J. Jensen, S.B. Engelsen, Batch-wise versus continuous dough mixing of Danish butter cookies. A near infrared hyperspectral imaging study, Food Chem. 414 (2023) 135731, https://doi.org/10.1016/j.foodchem.2023.135731.

[5] J.U. Porep, D.R. Kammerer, R. Carle, On-line application of near infrared (NIR) spectroscopy in food production, Trends Food Sci. Technol. 46 (2) (2015) 211–230, https://doi.org/10.1016/j.tifs.2015.10.002.

[6] H. Huang, H. Yu, H. Xu, Y. Ying, Near infrared spectroscopy for on/in-line monitoring of quality in foods and beverages: a review, J. Food Eng. 87 (3) (2008) 303–313, https://doi.org/10.1016/j.jfoodeng.2007.12.022.

[7] J.A. Cayuela-Sánchez, J. Palarea-Albaladejo, T.P. Zira, E. Moriana-Correro, Compositional method for measuring the nutritional label components of industrial pastries and biscuits based on Vis/NIR spectroscopy, J. Food Compos. Anal. 92 (2020) 103572, https://doi.org/10.1016/j.jfca.2020.103572.

[8] C. Quintelas, C. Rodrigues, C. Sousa, E.C. Ferreira, A.L. Amaral, Cookie composition analysis by Fourier transform near infrared spectroscopy coupled to chemometric analysis, Food Chem. 435 (2024) 137607, https://doi.org/10.1016/j.foodchem.2023.137607.

[9] L.K. Sørensen, Application of reflectance near infrared spectroscopy for bread analyses, Food Chem. 113 (4) (2009) 1318–1322, https://doi.org/10.1016/j.foodchem.2008.08.065.

[10] O. Parenti, L. Guerrini, S.B. Mompin, M. Toldrà, B. Zanoni, The determination of bread dough readiness during kneading of wheat flour: a review of the available methods, J. Food Eng. 309 (2021) 110692, https://doi.org/10.1016/j.jfoodeng.2021.110692.

[11] B.J. Dobraszczyk, M.P. Morgenstern, Rheology and the breadmaking process, J. Cereal. Sci. 38 (3) (2003) 229–245, https://doi.org/10.1016/S0733-5210(03)00059-6.

[12] B. Cuq, J. Abecassis, S. Guilbert, State diagrams to help describe wheat bread processing, Int. J. Food Sci. Technol. 38 (7) (2003) 759–766, https://doi.org/10.1046/j.1365-2621.2003.00748.x.

[13] S.P. Cauvain, L.S. Young, C.E. Stauffer, Principles of Dough Formation. Technology of Breadmaking, Springer, Boston, MA, 2007, pp. 299–332, https://doi.org/10.1007/0-387-38565-7_11.

[14] Ortiz, M.C. & Sarabia, L.A. Caracterización de vinos de Toro mediante técnicas quimiométricas de análisis multivariante. Anuario 1992' Instituto de Estudios Zamoranos C.S.I.C., 397-460. Free download on https://iezfloriandeocampo.com/anuarios/1992/. (accessed 27 November 2023).

[15] C. Ortiz, J.A. Sáez, J. López-Palacios, Typification of alcoholic distillates by multivariate techniques using data from chromatographic analyses, Analyst 118 (1993) 801–805.

[16] M.C. Ortiz, L.A. Sarabia, R. García-Rey, M.D. Luque de Castro, Sensitivity and specificity of PLS-class modelling for five sensory characteristics of dry-cured ham using visible and near infrared spectroscopy, Anal. Chim. Acta 558 (2006), https://doi.org/10.1016/j.aca.2005.11.038, 125-13.

[17] M.S. Sánchez, M.C. Ortiz, L.A. Sarabia, V. Busto, Class-modelling techniques that optimize the probabilities of false noncompliance and false compliance, Chemometr. Intell. Lab. Syst. 103 (2010) 123–142, https://doi.org/10.1016/j.chemolab.2010.05.007.

[18] M.C. Ortiz, L.A. Sarabia, M.S. Sánchez, Tutorial on evaluation of type I and type II errors in chemical analyses: from the analytical detection to authentication of products and process control, Anal. Chim. Acta 674 (2010) 123–142, https://doi.org/10.1016/j.aca.2010.06.026.

[19] O. Valencia, M.C. Ortiz, S. Ruiz, M.S. Sánchez, L.A. Sarabia, Simultaneous class-modelling in chemometrics: a generalization of Partial Least Squares class modelling for more than two classes by using error correcting output code matrices, Chemometr. Intell. Lab. Syst. 227 (2022) 104614, https://doi.org/10.1016/j.chemolab.2022.104614.

[20] O. Valencia, M.C. Ortiz, M.S. Sánchez, L.A. Sarabia, A modified entropy-based performance criterion for class-modelling with multiple classes, Chemometr. Intell. Lab. Syst. 217 (2021) 104423, https://doi.org/10.1016/j.chemolab.2021.104423.

[21] Lugar daVeiga. https://daveiga.es/(accessed 27 November 2023).

[22] N. Haegens, Mixing, Dough Making, and Dough Make-Up, Bakery products science and technology, 2014, pp. 307–324, https://doi.org/10.1002/9781118792001.ch17.

[23] AOTECH. Advanced Optical Technologies. https://www.aotech.es/(accessed 27 November 2023).

[24] Workman Jr., L. Weyer, Practical Guide to Interpretive Near-Infrared Spectroscopy, Crc Press, 2007, https://doi.org/10.1201/9781420018318.

[25] K. Kulp, K. Lorenz, Handbook of Dough Fermentations, vol. 127, Crc Press, 2003.

[26] M. Schoot, C. Kapper, G.H. van Kollenburg, G.J. Postma, G. van Kessel, L. M. Buydens, J.J. Jansen, Investigating the need for preprocessing of near-infrared spectroscopic data as a function of sample size, Chemometr. Intell. Lab. Syst. 204 (2020) 104105, https://doi.org/10.1016/j.chemolab.2020.104105.

[27] J. Engel, J. Gerretzen, E. Szymanska, J.J. Jansen, G. Downey, L. Blanchet, L. M. Buydens, Breaking with trends in pre-processing? Trends Anal. Chem. 50 (2013) 96–106, https://doi.org/10.1016/j.trac.2013.04.015.

[28] J. Gerretzen, E. Szymanska, J.J. Jansen, J. Bart, H.J. van Manen, E.R. van den Heuvel, L.M. Buydens, Simple and effective way for data preprocessing selection based on design of experiments, Anal. Chem. 87 (2015) 12096–12103, https://doi.org/10.1021/acs.analchem.5b02832.

[29] C. Mas, L. Rubio, L. Valverde-Som, L.A. Sarabia, M.C. Ortiz, Impact of the pretreatment of ATR-FTIR signals on the figures of merit when PLS is used, Chemometr. Intell. Lab. Syst. 201 (2020) 104006, https://doi.org/10.1016/j.chemolab.2020.104006.

[30] M.L. Oca, M.C. Ortiz, L.A. Sarabia, A.E. Gredilla, D. Delgado, 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, Talanta 99 (2012) 558–565, https://doi.org/10.1016/j.talanta.2012.06.035.

[31] K.H. Esbensen, P. Geladi, Principles of proper validation: use and abuse of re-sampling for validation, J. Chemometr. 24 (2010) 168–187, https://doi.org/10.1002/cem.1310.

[32] S. Bates, T. Hastie, R. Tibshirani, Cross-validation: what Does it Estimate and How Well Does it Do it?, 2022, https://doi.org/10.48550/arXiv.2104.00673 arXiv: 2104.00673vol. 4.

[33] R.W. Kennard, L.A. Stone, Computer aided design of experiments, Technometrics 11 (1969) 137–148, https://doi.org/10.1080/00401706.1969.10490666.

[34] T.G. Dietterich, G. Bakiri, Solving multiclass learning problems via error-correcting output codes, J. Artif. Intell. Res. 2 (1995) 263–286, https://doi.org/10.1613/jair.105.

[35] S. Wold, M. Sjöström, L. Eriksson, PLS-regression: a basic tool of chemometrics, Chemometr. Intell. Lab. Syst. 58 (2) (2001) 109–130, https://doi.org/10.1016/S0169-7439(01)00155-1.
[36] M.P. Wand, M.C. Jones, Kernel Smoothing, Monographs on Statistical an Applied Probability, vol. 60, Springer-Science-Business Media, New York, NY, USA, 1995.
[37] MATLAB, MATLAB Version: 9.9.0 (R2020b), The Mathworks Inc., Natick, Massachusetts, 2022. https://www.mathworks.com.
[38] B.M. Wise, N.B. Gallagher, R. Bro, J.M. Shaver, W. Winding, R.S. Koch, PLS Toolbox 8.8.1, Eigenvector Research Inc., Wenatchee, WA, USA, 2022.
[39] Sánchez M.S., Valencia O., Ruiz S., Ortiz M.C., Sarabia L.A. DMCEN a MATLAB Function to Evaluate the Entropy Improvement provided by a Multivariate K-Class-Model. Available online: dmcen - File Exchange - MATLAB Central (mathworks.com). (accessed 27 September 2023).
[40] M. Forina, S. Lanteri, C. Armanino, M.C. Casolino, M. Casale, P. Oliveri, V-PARVUS 2010. An Extendable Package of Programs for Explorative Data Analysis, Classification and Regression Analysis, Dip Chimica e Tecnologie Farmaceutiche, University of Genova, 2010. Available online: http://www.parvus.unige.it.
[41] R.G. Brereton, One-class classifiers, J. Chemometr. 25 (5) (2011) 225–246, https://doi.org/10.1002/cem.1397.