Use of FT-NIR spectroscopy in classifying grated Grana Padano cheese: preliminary results

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Introduction

Grated cheese fits into the category of convenience-foods[1-2] and their trade is in continuous increase due to some advantages such as it is simple to use, there is no waste, it is ready to consume, etc. Italian long ripened hard cheeses, and in particular Grana Padano and Parmigiano Reggiano at different age and deriving from productions of many kinds are used to preparing these products.. Packaging in modified atmosphere or under vacuum is used to preserve the original quality. Packed grated cheeses should be stored at low temperature (4°C) during the whole shelf-life in order to minimise chemical and microbiological modification phenomena.[3-4]

The aim of this work was to test the ability of FT-NIRS in discriminating grated Grana Padano cheeses deriving from different sources. The discriminating power of this technique was compared with that obtained by evaluating the indices more commonly used to assess the chemical and microbiological quality of these products.

Materials and methods

Samples

Seventy-eight samples packed under vacuum were collected from two different Italian companies (A; D), stored at low temperature and analysed at the expiry date.

Chemical and microbiological indices

Some microbiological (coagulase negative staphylococci,[5] enterococci,[6] yeasts and moulds,[7] aerobic and anaerobic sporeforming bacteria[8]) and chemical [pH, a_w by a CX-3 AQUA LAB apparatus (Decagon Devices, Inc. USA), moisture[9]] indices were determined.

PCA and Linear Discriminant Analysis (LDA)[10] were applied to evaluate the results.

NIR spectroscopy

FT-NIR spectra were collected in the full range from 4000 to 10000 cm^{-1} with a NIRLab N-200 [BÜCHI Italia S.r.l., Assago (MI)] apparatus (64 scans for each spectrum), using Petri's glass plates in transflectance mode, with 4 cm^{-1} resolution (1557 points).

PCA was applied to the whole spectrum,[11] and LDA was carried out using the absorbance values at six selected wavenumbers, chosen on the basis of their relation with the most important constituents. [12-13]

LDA was validated by leave one out evaluation set technique.

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Results and discussion

Chemical and microbiological indices

Figure 1 shows the results obtained by applying PCA on the data set of chemical and microbiological indices.

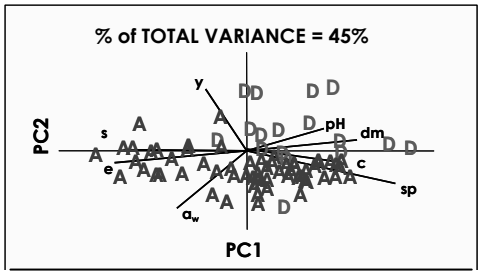

Figure 1 – PCA applied to microbiological and chemical indices. pH, dm (dry matter), aw, y (yeast and mould), s (staphylococci), e (enterococci), sp (aerobic sporeforming bacteria), c (anaerobic sporeforming bacteria) = variables; A = samples of grated Grana Padano supplied by packing company A; D = samples of grated Grana Padano supplied by packing company D.

The results obtained by PCA prompted us to apply LDA as a classification technique, as shown in Figure 2. The difference between the first and the second discriminant scores gives values lower than 0 for the samples classified in the category A, and it gives values higher than 0 for the samples classified in the category D. Only one A object and four D objects were misclassified. LDA was validated by leave one out evaluation set technique, and the results, expressed as percentage of cheeses correctly predicted, are reported in Table 1. Satisfactory discrimination among packing companies was obtained using the microbiological and chemical parameters with a correct total prediction of about 92%, also if category A was better predicted than category D.

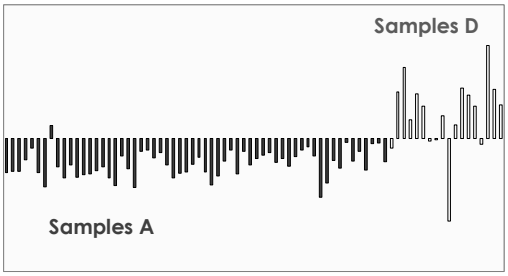

Figure 2 –Histogram for the discriminant scores obtained by LDA carried out on 8 variables and 78 objects.

Table 1 - Prediction of origin of grated Grana Padano cheese samples by LDA by using microbiological and chemical indices.

Category	No. of prediction for category A	No. of prediction for category D	% Correctly predicted
A	59	2	96.72
D	4	13	76.47
Overall			92.31

NIR spectroscopy

Multivariate statistical methods allowed the evaluation of the whole spectral information (Figure 3). Spectroscopic data express the absorbance of the cheese matrix which is the result of bacterial activity, differences in chemical and physico-chemical properties, modifications related to the grating process, sampling period and sample size, etc.. The separation between the two categories occurs on the first component axis.

To verify whether the separation between categories could be obtained when using a reduced number of variables, without a noticeable loss of information, six variables were selected on the basis of their relation with the most important constituents. The selected wavenumbers were related with water (5187, 8990 cm $^{-1}$), protein (5862, 8095 cm^{-1}), and fat (5700, , and 8277 cm^{-1}) absorptions.[12-13]

The principal components were recalculated on the reduced data set (78 objects and six variables).

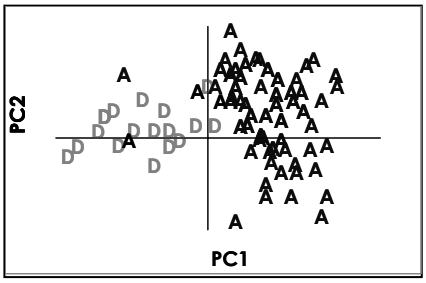

Figure 3 – PCA applied to the whole spectrum

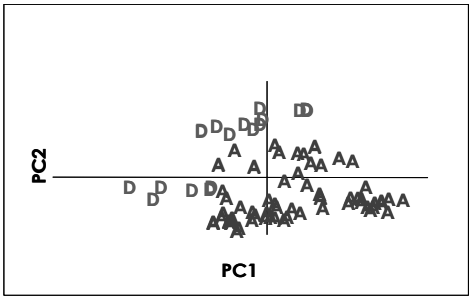

Figure 4 – PCA applied to the reduced data set (78 objects and six variables)

It is worth noting (Figure 4) that a satisfactory separation between the two categories was achieved also by using the six selected wavenumbers.

LDA was applied to the reduced data set (Figure 5). Using this technique, 98% of grated samples A and 94% of grated samples D were correctly classified.

After validation by leave one out technique, the percentage of correctly predicted objects was satisfactory. The results, expressed as the percentage of samples correctly categorised, are reported in Table 2. In particular, the value obtained for category A (98.36%) was comparable to that obtained by classification, and the value obtained for category D (88.23%) was significantly increased in comparison with that obtained using microbiological and chemical indices. The total prediction power obtained by FT-NIR spectroscopy was 96.15%.

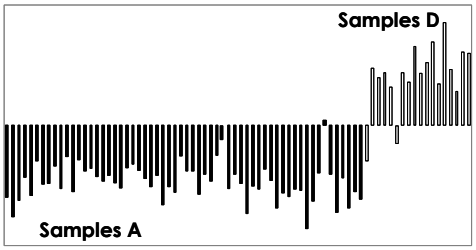

Figure 5 – Histogram for the discriminant scores obtained by LDA carried out on 6 variables and 78 objects

Category	No. of prediction for category A	D	% Correctly predicted
A	60	1	98.36
D	2	15	88.23
Overall			96.15

Table 2 - Prediction of origin of grated Grana Padano cheese samples by LDA by using spectroscopic data.

Conclusions

Statistical analysis applied to FT-NIR data was able to classify samples with a good discrimination in two groups, on the basis of the spectra characteristics. FT-NIRS showed a better total prediction power (percentage of correct prediction = about 96%) than microbiological and chemical indices (percentage of correct prediction = about 92%). NIR results suggested the potential strong influence of the grating and packaging technology used rather than that of individual parameters related to product characteristics.

The availability of samples derived from several packing companies could improve and confirm these preliminary results. In this way spectral information could be associated with defined technological steps.

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