Near infrared spectroscopy as a tool for the evaluation of milk quality for Grana Padano cheese production

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Introduction

An increasing percentage of milk produced in European countries is used for manufacturing cheese.[1] In particular, more than 75% of milk collected in Italy is used for cheese production and 55% is processed for PDO (protected designation of origin) products like Grana Padano.[2] The amount of Grana Padano cheese produced from a given amount of milk depends on milk quality, and for a maximum cheese yield, milk must firstly have a high content of casein and fat[3,4,5] and secondly an 'excellent' aptitude for coagulation.[6] Indeed, favourable conditions of milk reactivity with rennet, curd formation rate and curd strength, as well as good syneresis, have a positive effect on the whole cheese-making process and consequently on the ripening development of the cheese.[7]

Modern, automated, online methods, based on near infrared (NIR) spectroscopy have previously been used to evaluate milk clotting[8,9] and to provide additional information to cheese producers in an effort to increase the efficiency of cheese production.[10,11] The aim of the study presented here was to further investigate the potential of NIR spectroscopy to measure milk clotting, in order to obtain additional information useful to predict cheese yield at milk collection.

Materials and Methods

Samples

Forty eight raw milk samples were collected from July to October 2008. For each sampling, milk was taken from 2 tanks for creaming, and was divided into several copper vats to produce Grana Padano cheese. Samples were representative of the milk collected daily for use in Italian cheese-making. Fat and total casein percentage, α_{s1}-, β- and κ-casein quantity, α-lactoalbumin and β-lactoglobulin concentration were determined by official methods of analysis.[12] Cheese yield was calculated by weighing the final product and was expressed as a percent ratio between cheese weight (CW) and milk weight (MW).

Near infrared spectroscopy

Milk samples were heated to the renneting temperature (35 ± 2°C) and the milk coagulation properties were assessed. The rennet solution (chymosin 20 ± 5%, REMCAT 130 IMCU.g^{-1}, Naturen, CHR Hansen, Milan) was diluted (1.6 ml.100 ml^{-1}) in sodium acetate-3-hydrate (0.07 M)/acetic acid (1 M) buffer (pH 5.5) and 200 μL of the solution was added to 10 mL of milk.

The milk coagulation properties were calculated from photon absorbance at 890 nm using an Optigraph instrument (Ysebaert, Frepillon, France).[13] Milk samples were monitored for 60 min after rennet addition. Three parameters were obtained from the observed curves: milk coagulation time (CT), indicated by the maximum of the first derivative of the signal; curd firmness (CF), determined 30 min after the addition of the rennet, and the aggregation rate (AR), calculated from the slope of the linear region of the curve.

Data processing

Qualitative analysis of milk samples was performed with principal component analysis (PCA) to determine whether individual characteristics of each sample had an influence on the prediction of cheese yield. Models for the prediction of cheese yield were developed using a partial least squares (PLS) regression and validated by cross-validation. Prior to PLS regression, all data were standardised, i.e. first mean centered then scaled to unit variance. PCA and PLS regression were carried out using The Unscrambler 9.2 (Camo, Oslo, Norway).

Results and Discussion

The complete dataset (48 samples) was subjected to PCA to detect sample patterns and grouping. The first three principal components (PCs) explained 85% of the total variance, with PC1 and PC2 accounting for

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60% and 16%, respectively. Samples were separated along PC1 according to fat, total casein content, milk coagulation time, curd firmness and aggregation rate (determined by Optigraph), α-lactoalbumin and β-lactoglobulin content (Figure 1). The main variables influencing sample distribution along the PC2 were α_{s1}-, β- and κ-caseins (Figure 1). Samples were separated along PC1 according to the day of sampling, probably due to seasonal variations.[14,15] Milk samples taken in October showed the best chemical characteristics, notably high fat and casein content[16,17] and milk coagulation time (a parameter closely linked to the casein content). Indeed, the October samples had a higher cheese yield than those samples collected in summer (8.55 vs 8.18).

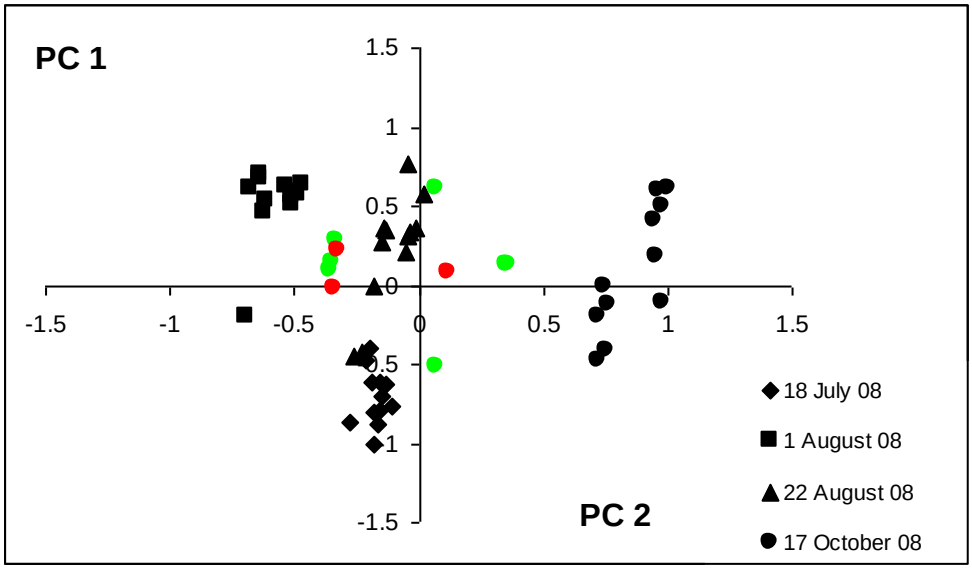

Figure 1. Scores-plot of the 48 milk samples**.** Fat, total casein content, milk coagulation time, curd firmness and aggregation rate, α-lactoalbumin and β-lactoglobulin = green indicators; α_{s1}-, β- and κ-casein amount = red indicators.

Differences in concentration of whey proteins (especially β-lactoglobulin) drove the separation of samples along PC2, which may be due to genetic polymorphism of albumin synthesis in the mammary gland (i.e. many samples show a β-lactoglobulin genotype of type B).[18] This condition results in the formation of a stable casein network and has a positive influence on cheese yield.

PLS regression was applied to predict cheese yield. Regression coefficients showed that the variables contributing most to the prediction of cheese yield were fat and casein content, milk coagulation time, curd firmness and aggregation rate, α-lactoalbumin and β-lactoglobulin; confirming the PCA results. Calibration and validation curves are shown in Figure 2 and the statistical parameters related to the PLS regression are summarised in Table 1.

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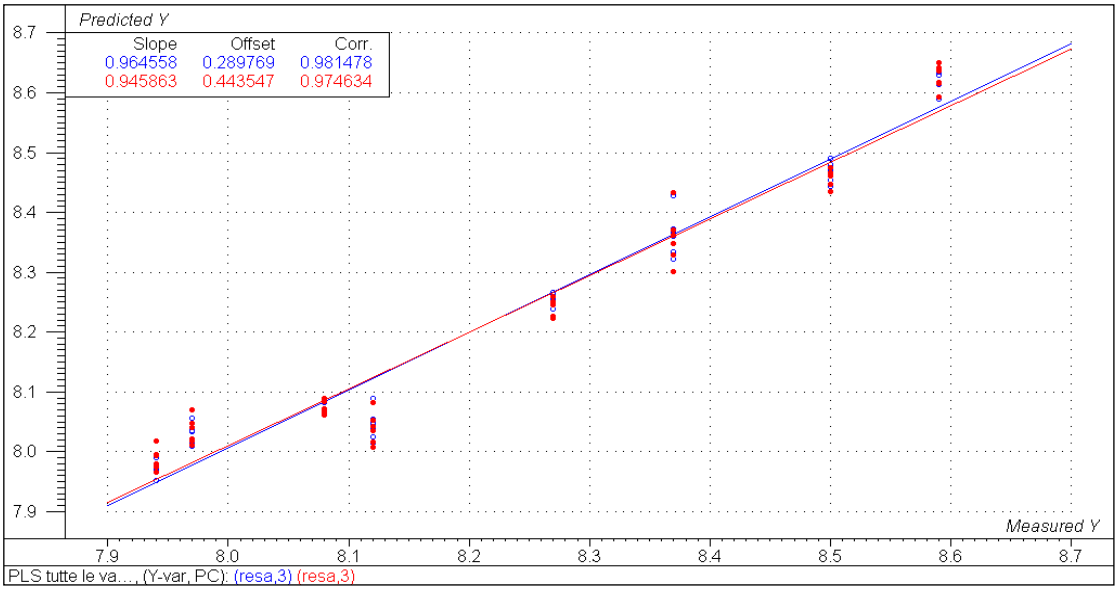

Figure 2. Linear regression relationship between predicted and measured values for cheese yield prediction (48 milk samples). Blue line = calibration curve; red line = validation curve.

The PLS predictive equation was characterised by high correlation coefficients (r) in both calibration (r = 0.98) and cross-validation (r = 0.97), and a low standard deviation (SD = 0.23). The root mean square error of prediction (RMSEP) was 0.057 and the ratio of performance to deviation (RPD) was 4.89. The PLS model was a valid means of cheese yield prediction: RPD values from 5 to 10 identify a model is adequate for quality control; 2.5 to 5 indicate usefulness for screening in breeding programs; 1.0 means that standard error of prediction (SEP) and the SD are the same and the instrument is not capable of predicting the parameter accurately.[19]

These results showed that good cheese yield predictions depend on foreknowledge of milk chemistry and coagulation propensity. Furthermore, NIR spectroscopy appeared to be suitable as a quick and non-intrusive method for evaluating rennet milk coagulation.[20]

Table 1. Statistical parameters associated with calibration and cross-validation curves for cheese yield.

Parameter	Sample set	
	Calibration	Cross-Validation
Number of samples	48	48
Range	7.95–8.64	7.96–8.65
Mean	8.23	8.23
Standard Deviation (SD)	0.22	0.22
r	0.98	0.97
RMSEC	0.04	
RMSEP		0.05
Slope	0.96	0.94
Bias	-0.001	-0.001

Conclusion

These results confirmed the close relationship between total casein content, casein sub-fractions and cheese yield. NIR spectroscopy, combined with the appropriate chemometric tools, offered a fast and accurate method for the prediction of cheese yield.

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