Chemical and microbiological analysis of goat's milk, cheese and whey by near infrared spectroscopy

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Introduction

Current food legislation requires the dairy industry to perform a number of checks to ensure food safety and product quality. Moreover, the dairy industry's payments to farmers in many cases reflect the bacteriological and nutritional quality of the product. Although most of the required milk analyses can be performed using instrumental methods, these methods rely on the use of expensive equipment (Milkoscan, Fossomatic, Bactoscan) to ensure a thorough analysis.

A number of published studies address the use of near infrared (NIR) spectroscopy in determining the chemical composition of cheese[1–3] and milk from goats,[4–6] sheep[7,8] and cows,[9] although most have been carried out on experimental dairy farms. In contrast, the study reported here used industrial samples, seeking to reproduce real working conditions in the industrial or interprofessional laboratory.

The purpose of the present study was to obtain NIR calibration equations for the determination of quality parameters in goat's milk, cheese and whey.

Material and methods

Experimental material

A total of 123 samples of goat's milk, 109 samples of whey and 190 samples of goat's milk cheese, all from the dairy company Fromandal, S.A., were taken on a weekly basis over one year (January 2000 to January 2001) in order to obtain maximum seasonal variability.

Chemical analysis

Samples were analysed in duplicate to determine, for all three products, the fat content (Gerber for milk and whey, Van Gulik for cheese), total solids (oven-dried at 103 ± 2°C, using marine sand for cheese) and protein content (Kjeldahl). In milk samples, casein (Kjeldahl) and lactose content (Milko-Scan) were also measured. Somatic cell counts (SCC; Fossomatic) and bacterial counts (bacteria mL^{-1}; Bactoscan) were performed.

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NIR analyses and chemometric treatment of the data

All NIR spectra were collected using a Foss NIRystems 6500 SY-I scanning monochromator, fitted with a spinning cup, working in reflectance mode in the spectral range 400–2500 nm. Milk and whey measurements were made in folded-transmission gold reflector cups, with a pathlength of 0.1 mm. Two spectra were measured per sample, the mean spectrum being used for subsequent analysis. Cheese samples were analysed unground in small ring cups.

Spectroscopic and chemical data were subjected to chemometric treatment using WinISI ver. 1.04 software.[10] Calibration equations were obtained and evaluated according to Shenk and Westerhaus[10] and Williams and Sobering.[11] MPLS (modified partial least squares) was used for regression purposes; the wavelength range studied was 1100–2500 nm (at 2 nm intervals); SNV and Detrending treatments were applied to correct for scatter. Several first and second derivative treatments were also tested. The following statistical parameters were used to select the best calibration equations: standard error of the calibration set (*SEC*), standard error of cross validation (*SECV*), coefficient of determination for the calibration process (R^2) or the cross-validation process (r^2) and ratios *RPD* ($DT \cdot SECV^{-1}$) and *RER* (Range$\cdot SECV^{-1}$), using bibliography-recommended values of over 3 for *RPD* and over 10 for *RER*.[11]

Results and discussion

The NIR calibration equations obtained afforded a high degree of accuracy in predicting the chemical composition of goat's milk cheese (Table 1), with r^2 values of around 0.9 for all parameters. Similarly, calibration errors were very small and were lower in all cases than those reported (using the DESIR method) by Díaz *et al*.[4] (0.26% for fat, 0.15% for protein, 0.29% for casein and 0.09% for lactose) and by Angulo[5] (0.42% for fat, 0.20% for protein and 0.60% for total solids); error values were also lower than those obtained in liquid samples by Albanell *et al*.[6] (0.24% for fat, 0.18% for protein and 0.34% for total solids).

The equation obtained for the somatic cell count (Table 1), a major health-related parameter, afforded satisfactory precision. Tsenkova *et al*.,[9] in a study of cow's milk, obtained an NIR prediction model for SCC with an r^2 value of 0.35, much lower than the 0.81 obtained here.

The NIR calibration equation obtained for total bacteria in milk (Table 1) accounted for 58% of the variability due to this parameter and thus enables classification of samples into high, medium and low bacteria mL^{-1} content.[12] The value obtained for the calibration set ($n = 93$) can be considered low, given the difficulty of testing this parameter; however, use of a larger calibration set would probably ensure greater accuracy.

Table 1. Calibration statistics obtained for quantitative analysis of goat's milk.

Parameter	Mean	Range	*SD*	*SEC*	*SECV*	r^2	*RPD*	*RER*
Fat	4.99	4.0–6.4	0.701	0.18	0.20	0.92	3.44	11.76
Total solids	13.50	11.7–15.6	0.967	0.19	0.22	0.95	4.40	17.73
Protein	3.76	3.3–4.6	0.277	0.05	0.07	0.94	3.90	17.46
Casein	3.60	3.1–4.3	0.275	0.05	0.07	0.93	3.83	17.27
Lactose	4.37	4.0–4.7	0.158	0.04	0.05	0.89	3.02	12.43
Bacteria $mL^{-1}10^{-3}$	890.83	20.0–3500	762.0	354.0	499.3	0.58	1.53	6.97
SCC 10^{-3}	2495.10	1343–4168	624.6	169.1	276.9	0.81	2.26	10.20

Table 2. Calibration statistics obtained for quantitative analysis of whey.

Parameter	Mean	Range	*SD*	*SEC*	*SECV*	r^2	*RPD*	*RER*
Fat	0.941	0.70–1.35	0.127	0.07	0.08	0.66	1.69	8.64
Total solids	7.103	6.29–7.84	0.332	0.18	0.19	0.67	1.75	8.16
Protein	1.110	0.88–1.54	0.148	0.05	0.07	0.76	2.11	9.43

Table 3. Calibration statistics obtained for quantitative analysis of goatsmilk cheese.

Parameter	Mean	Range	*SD*	*SEC*	*SECV*	r^2	*RPD*	*RER*
Fat	32.2	28.3–37.0	1.94	0.49	0.57	0.92	3.40	15.3
Total solids	58.6	55.6–66.6	2.07	0.83	0.92	0.80	2.25	12.4
Protein	22.1	19.7–25.5	1.15	0.58	0.63	0.70	1.85	9.3

Equations obtained for whey also afforded satisfactory accuracy (Table 2). Calibrations for fat, total solids and proteins recorded very low *SECV* values and r^2 values—though around 0.7—were normal given the reduced range of variation for the three components analysed; this was also reflected in the values obtained for *RPD* and *RER*.

Table 3 shows calibration statistics obtained for predicting the chemical composition of goat's milk cheese. Predictive performance for the three parameters tested was satisfactory; *SECV* values were lower than those reported by Núñez *et al*.[1] using an interactance–reflectance probe (1.11% for fat, 1.33% for total solids and 0.71% for protein). However, Sorensen *et al*.,[2] in reflectance testing with unground cheese, obtained *SECV* values for fat and total solids lower than those recorded here (0.24% and 0.37%, respectively) while De Santis *et al*.,[3] using an interactance–reflectance probe, obtained an *SEC* value of 1.59% for protein, much higher than that recorded here.

Conclusions

These results confirm the viability of NIR technology for predicting chemical, microbiological and somatic cell count parameters in goat's milk and for predicting chemical composition of goat's milk cheese and whey. The chief benefits for the dairy industry of using this technology rather than other methods of chemical or instrumental analysis are the speed of analysis and, particularly, the versatility it offers; NIR not only measures the quality parameters required in milk analysis but also enables analysis of derived products such as whey and cheese.

Acknowledgements

This study formed part of Project CICYT-Feder IFD1997-0990 and was performed using equipment and infrastructure belonging to SCAI (Unidad NIR/MIR), University of Córdoba (Spain). The authors thank Ms Francisca Baena, Mr Alberto Sánchez de Puerta, Mr Antonio López and Ms Isabel Leiva of the Animal Production Department (ETSIAM-UCO) for technical assistance.

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