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Chemometric studies of fresh and semi-hard goats' cheeses produced in Tenerife (Canary Islands)

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Abstract

The concentrations of fat, protein, dry matter, percentage of fat on dry matter, Na, K, Ca, Mg, Fe, Cu, Zn, Se and pH were determined in 200 goat's cheeses (100 fresh and 100 semi-hard cheeses) produced on the island of Tenerife. All parameters analysed, except Fe, Cu and Ca, presented significant differences between fresh and semi-hard cheeses. Factor and discriminant analyses made the separation of cheeses possible according to their type. Using discriminant analysis, moderate classifications were obtained according to the season of production and the type of goat's diet; however, poor classifications were observed using the region of production as a criterion for comparison.

Keywords: Fresh and semi-hard cheeses; Tenerife island; Multivariate analysis; Season and region of production; Goat's diet

1. Introduction

An important development in the production of cheese has recently occurred in the Canary Islands, particularly on the island of Tenerife, because of the incorporation of modern technology. The production of goat's milk in the Canary Islands is about 84 million litres/year. Most of this milk (85%) is used for the production of cheese (Consejería de Agricultura, Pesca y Alimentación, 2002).

The local government, in agreement with European Union legislation, has established the criteria for quality, food labelling and geographical origin in order to obtain the "Protected Denomination of Origin" (PDO) label. Cheeses with PDO must be obtained from defined milks produced in a well-defined geographical area. Also, the process of elaboration must ensure the sensory characteristics of the cheese. In the Canary Islands, there are two PDOs for cheese, "Queso majorero" and "Queso palmero". There are no complete studies about the characterization of the goat's cheese produced in Tenerife.

Application of chemometric classification studies to analytical parameters is commonly used for the determination of the geographic origin or quality brand of food products (Favretto, Pertoldi Marletta, Gabrielli Favretto, & Vojnovic, 1987, 1994; Gabrielli Favretto, Pertoldi Marletta, Bogoni, & Favretto, 1989; Martín-Hernández, Amigo, Martín-Alvarez, & Juárez, 1992; Rodríguez Rodríguez, Sanz Alaejos, & Díaz Romero, 1999). The use of these methods could confirm the authenticity of the cheeses from a PDO, and also differentiate them from cheeses imported from other regions. Analytical parameters must be previously determined using standardised methods to apply the chemometric methods of classification.

The lack of technical and scientific information about these cheeses, together with their high commercial potential, has led us to study them in order to make them

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better known and improve their quality. Thus, the aim of this paper was to define the profile of the major chemical compounds and metals of fresh and semi-hard goat cheeses produced in Tenerife. Several pattern recognition approaches, factor analysis and linear discriminant analysis were applied to separate the samples of cheeses according to different categories, such as region or season of production and goat's diet.

2. Material and methods

2.1. Samples

Samples were taken from 25 cheese factories situated in different parts grouped in two zones (north and south) of Tenerife, the cheeses sampled being representative of the cheeses produced in the island (Fig. 1). Twenty-three of factories were small factories, which make cheese from raw goat's milk and have their corresponding health inspection certificate as establishments of limited production, while two were of the large industrial type. The sampling was carried out on four occasions: summer-1999, winter-2000, autum-2000, and spring-2001. Twenty-five samples of fresh cheeses and 25 semi-hard cheeses were taken in each sampling. A total of 200 whole cheeses (100 fresh cheeses + 100 semi-hard cheeses) were collected. The samples were stored under refrigeration. A representative portion of the sample was cut and homogenized before the application of the analytical methods.

Fresh cheeses were produced following the traditional cheese-making method. The majority of the artisan businesses added the rennet directly after milking, without controlling the temperature. In the larger factories, the temperature was controlled and the milk arrived refrigerated. Most farmers used kid rennet; the second most used were various commercial rennets. The coagulation time was usually about 30 min. After that the curd was cut into batches in very small grains (rice size); this was transferred into the cheese-moulds where it was pressed. For this study, the factories matured the cheeses at 10–15 °C and 80–85% relative humidity for 45 days, while small producers did not control these two parameters. Throughout this ripening period, the cheeses were turned over daily or every second day and, when necessary, the surface was brushed to control/limit the growth of mould.

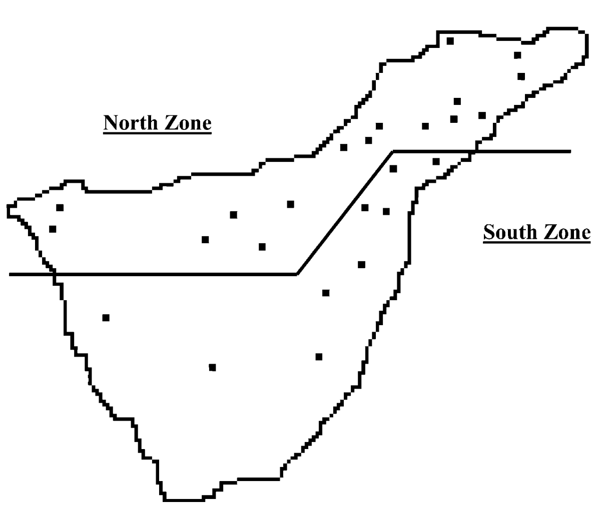

Fig. 1. Situation of cheese factories selected in the island of Tenerife.

2.2. Analytical methods

2.2.1. Determination of fat, protein, dry extract and pH

Cheese samples were homogenized and an aliquot was introduced to the apparatus for analysis, Instalab 600 NIR Product Analyser (Dickey-john Corporation), which was periodically calibrated according to the FIL-IDF methods: total solids (FIL-IDF 4A, 1982); protein (FIL-IDF 20B, 1993); fat (FIL-IDF 5B, 1986). The pH was measured with a pH meter (pH-metro inoLab pH Level 1 WTW, Wissenschaftlich-Technische Werkstatten GmbH and Co.KG) with an pH-electrode, SenTix 60. All determinations were done in duplicate.

2.2.2. Determination of minerals

Two grams of homogenized cheese, 10 ml of nitric acid and 1 ml of perchloric acid were introduced to vessel-tubes, which were left overnight. Next morning the temperature of each mixture was increased slowly, using a digestion block, to 160–170 °C until fumes of perchloric acid appeared. After 1 ml of 6 N hydrochloric acid was added, heating was continued at 160 °C for 5 min to reduce the Se(VI) to Se(IV). After cooling to room temperature, this solution was quantitatively transferred and adjusted to 10 ml with Milli-Q water. Major elements (Na, K, Ca and Mg) were analysed by dilution (1:10) with Milli-Q water of the concentrated solution. All results were the averages of three determinations.

The mineral concentrations were determined by flame emission spectrometry (Na and K) and atomic absorption spectrometry with flame air/acetylene (Fe, Cu, Zn) and nitrous oxide/acetylene (Ca and Mg) and with hydride generation (Se). Bovine liver (NBS 1577a), as a reference material, was routinely analysed in order to perform quality control of the measurements, except for Se. Quality control for Se was checked using cheese samples spiked or not spiked with known amounts of Se standard. Acceptable mean recoveries (10 replicates) were obtained for all the minerals: Fe, 99.5 ± 5.0%; Cu, 98.1 ± 3.8%; Zn, 97.6 ± 1.6%; Na, 105 ± 8.2%; K, 98.8 ± 2.5%; Ca, 101.0 ± 5.8%, Mg, 107.8 ± 2.0%, Se, 98.5 ± 2.6%.

2.3. Statistical analysis

All the statistics were performed by means of the SPSS version 10.0 software for Windows. The Kolmogorov–Smirnov's test was applied to verify if the variables had a normal distribution ($p < 0.05$). Mean values obtained for the variables studied in the different groups were compared by one-way ANOVA, assuming that there were significant differences among them when the statistical comparison gives $p < 0.05$.

For the multivariate analysis, the type of goat's diet was divided into two groups: diet with <50% of fibre and diet with >50% of fibre. Besides, the samples obtained in summer-1999 and autumn-2000 were also grouped as a dry season, and the samples of winter-2000 and spring-2001 as a rainy season. The multivariate techniques applied were the following: (1) factor analysis, using principal components as method for extraction of the factors, was used to summarize the information in a reduced number of factors; (2) linear discriminant analysis (LDA), which is a supervised method used for classification purposes. This method maximises the variance between categories and minimises the variance within categories. Two processes can be applied in LDA: (1) stepwise LDA that selected the quantitative variables that enhance discrimination of the groups established by the dependent variable and (2) introduction of all independent variables. The objective of this second process was to use all the information although the system obtained is more complex (Ferrán Aranaz, 2001).

3. Results and discussion

3.1. Physicochemical characterisation

Table 1 shows the concentrations of the chemical compounds (fat, protein, dry matter, fat/dry matter, Na, K, Ca, Mg, Fe, Cu, Zn and Se) and pH for both types of goat's cheese, fresh and semi-hard, produced in Tenerife. The results of the variance analysis for the comparison of the mean values are also included in this table. Semi-hard cheeses presented higher ($p < 0.05$) mean levels of dry matter, protein, fat and percentage of fat on the dry matter than the fresh cheeses, which is a consequence of the normal drying process during ripening. The results obtained for protein and percentage of fat on dry matter contrasted with those reported by Franco, Prieto, Bernardo, González Prieto, and Carballo (2003) who did not find differences in the protein and fat content in dry matter during 60 days of ripening. The protein results can be explained because the losses of soluble proteins in the milk whey during ripening are compensated by the increase of concentrations of nutrients in the drying process. The mean value of pH in semi-hard cheeses was lower ($p < 0.05$) than in fresh cheeses, which is due to the normal acidification, particularly important in the first days of ripening (Franco et al., 2003), as a consequence of lactose hydrolysis. Ca, Fe and Cu presented no significant differences between the mean concentrations observed for both types of cheeses. Thus, the losses of these metals in the whey balance the tendency to increase their concentrations for the normal drying during ripening. On the other hand, the semi-hard cheese had higher ($p < 0.05$) Na, K, Mg and Se mean concentrations and a lower ($p < 0.05$) Zn mean concentration than the corresponding mean values in fresh cheese. High amounts of Zn were lost, which is probably a consequence of association with the albumins and other proteins of whey.

Table 1
Phyisicochemical parameters analysed in fresh and semi-hard cheese from Tenerife

Parameter	Fresh cheese	Semi-hard cheese	p
Fat (%)	20.9 ± 2.5	30.0 ± 4.4	0.00
Protein (%)	19.6 ± 1.0	20.1 ± 1.7	0.02
Dry matter (DM) (%)	53.3 ± 1.9	62.1 ± 4.7	0.00
Fat/DM (%)	39 ± 3	48 ± 4	0.00
pH	6.33 ± 0.49	5.49 ± 0.48	0.00
Na (g/kg)	6.0 ± 2.8	10.9 ± 4.5	0.00
K (g/kg)	1.7 ± 0.2	2.0 ± 0.8	0.00
Ca (g/kg)	9.8 ± 1.7	10.2 ± 3.1	0.27
Mg (g/kg)	0.47 ± 0.08	0.56 ± 0.18	0.00
Fe (mg/kg)	2.2 ± 0.5	2.1 ± 0.5	0.22
Cu (mg/kg)	0.80 ± 0.27	0.86 ± 0.26	0.13
Zn (mg/kg)	6.5 ± 2.5	4.7 ± 1.8	0.00
Se (μg/kg)	73 ± 2	152 ± 51	0.00

3.2. Factor analysis

Factor analysis was applied to all the samples of cheeses studied. Four factors were chosen (70.7% of the total variance) because their eigenvalues were greater than 1, and therefore, they explain more variance than the original variables. A Varimax rotation was carried out to minimize the number of variables influencing each factor and to facilitate the interpretation of the results (Table 2). The first factor that explains the higher percentage of variance (35.0%) is heavily associated with the dry matter and fat content, which are the variables with a higher weight in the system. The second factor is related to Ca and Mg concentrations, and the third factor is negatively and positively associated with Fe and protein, respectively. The fourth factor is related to Cu. Representing the score plots for all the cheese samples on the first and second factor (Fig. 2), it can be observed that both types of cheeses are separated graphically from each other. Only one fresh cheese was grouped as a semi-hard cheese and two semi-hard cheeses were included with the fresh cheeses.

Table 2
Factor matrix obtained after a Varimax rotation

Eigenvalues	4.55	2.41	1.21	1.02
Variance (%)	35.01	18.56	9.33	7.82
	Factor			
	1	2	3	4
DM	**0.922**	0.169	−0.111	−0.021
Fat	**0.921**	0.090	0.030	0.018
Fat/DM	0.886	−0.002	0.171	0.007
pH	−0.731	−0.105	0.070	−0.097
Se	0.717	0.322	0.022	0.070
Zn	−0.459	0.368	−0.034	−0.038
Ca	−0.058	**0.887**	0.001	0.039
Mg	0.174	**0.873**	0.002	0.043
K	0.162	0.821	−0.132	−0.036
Na	0.479	0.608	0.133	0.015
Fe	−0.052	0.073	**−0.764**	0.293
Protein	−0.020	0.025	**0.742**	0.373
Cu	0.103	0.013	−0.005	**0.895**

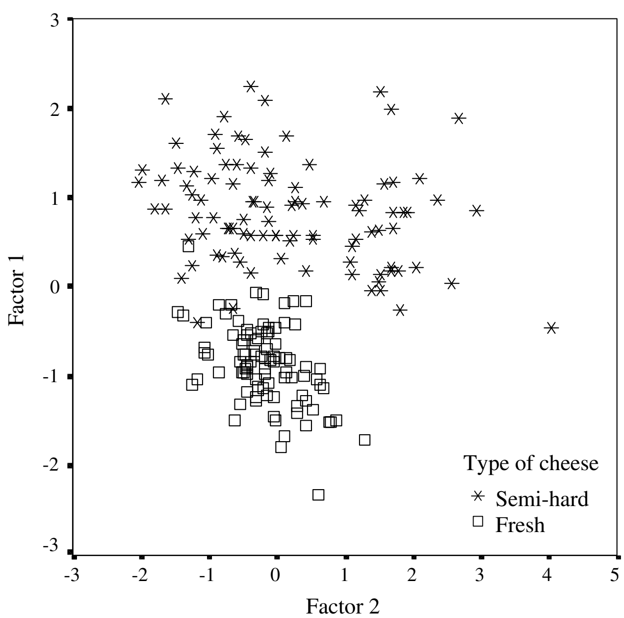

Fig. 2. Scores of the cheese samples on axes representing the first two factors differentiating the type of cheese.

3.3. Discriminant analysis

Several studies of discriminant analysis (DA), each one considering different qualitative variables (type of cheese, season of production, region of production and type of goat's diet) and 13 quantitative variables (fat, protein, dry extract, percentage of fat on dry extract, pH, Na, K, Ca, Mg, Fe, Cu, Zn and Se) were performed. Considering the type of cheese criterion (fresh–semi-hard cheeses), and after application of the stepwise DA of the data (Table 3), a high percentage (97.4%, and 97.4% after cross-validation) of correct classification

Table 3
Results of the discriminant analysis according to type of cheese (stepwise)

	Type of cheese	Predicted group	
		Fresh	Semi-hard
Initial group	Fresh	95 (99.0%)	1 (1.0%)
	Semi-hard	4 (4.0%)	95 (96.0%)
Cross-validation	Fresh	95 (99.0%)	1 (1.0%)
	Semi-hard	4 (4.0%)	95 (96.0%)

97.4% samples well classified; (97.4% after cross-validation).

was obtained. Only one fresh cheese and four semi-hard cheeses were erroneously classified. The quantitative variables selected were: Na, Zn, Se, fat, protein, percentage of fat matter on dry extract and pH. When the DA was applied to all the variables, the classification did not improve, with 97.4% of the total cheeses correctly classified (with a cross-validation of 97.4%).

A subsequent analysis of the fresh and of the semi-hard cheeses analysed, in an independent manner, was carried out using the season of production as a criterion for comparison. For the fresh cheeses, the correct classifications with stepwise DA were 75.8%, and 65.3% after cross-validation with seven variables selected (Zn, K, dry extract, Cu, Ca, Mg and Fe). These percentages improved when all the quantitative variables were included (81.6% and 70.4% after cross-validation) (Table 4). The scores plot for all the fresh cheeses of the representation of the first two discriminant functions is shown in Fig. 3. A tendency to differentiate the cheeses as a function of the season of production can be observed in this figure. A new discriminant analysis, with all the variables, was also developed, grouping the seasons into rainy and dry seasons, improving the classification to 90.5% (81.2% after cross-validation). Only one cheese produced in a rainy season was included in a dry season.

A stepwise DA was applied to the semi-hard cheeses in order to distinguish them as a function of season of production (Table 4). Similar results to those found for fresh cheeses were obtained (74.7% and 68.7% after cross-validation). Stepwise DA selected four variables (Ca, Zn, Se and percentage of fat on dry matter); these percentages changed when all the quantitative variables are included (81.6% and 70.4% after cross-validation). Representing the semi-hard cheeses in the plane defined by the two first discriminant functions, a tendency to separate the cheeses according to the season of production was also observed (Fig. 4). When the study was carried out using the two seasons, rainy and dry, the correct classification decreased to 69.4% (63.3% after cross-validation).

Similarly, a DA (stepwise and all the variables) was carried out on the fresh and semi-hard cheeses to differentiate them by region of production. The results of

Table 4
Results of the discriminant analysis according to season of production (all variables)

	Season	Predicted group			
		Summer 1999	Winter 2000	Autum 2000	Spring 2001
Initial group fresh cheese[a]	Summer 1999	18 (90.0%)	0 (0%)	2 (10.0%)	0 (0%)
	Winter 2000	0 (0%)	21 (84.0%)	1 (4.0%)	3 (12.0%)
	Autum 2000	2 (8.0%)	2 (8.0%)	17 (68.0%)	4 (16.0%)
	Spring 2001	1 (4.0%)	2 (8.0%)	1 (4.0%)	21 (84.0%)
Initial group semi-hard cheese[b]	Summer 1999	21 (84.0%)	2 (8.0%)	1(4.0%)	1 (4.0%)
	Winter 2000	0 (0%)	18 (72.0%)	4 (16.7%)	3 (12.0%)
	Autum 2000	0 (0.0%)	1 (4.2%)	22 (91.7%)	1 (4.2%)
	Spring 2001	0 (0.0%)	1 (4.2%)	4 (16.7%)	19 (79.2%)

[a] 81.1% samples well classified; (67.4% after cross-validation).
[b] 81.6% samples well classified; (70.4% after cross-validation).

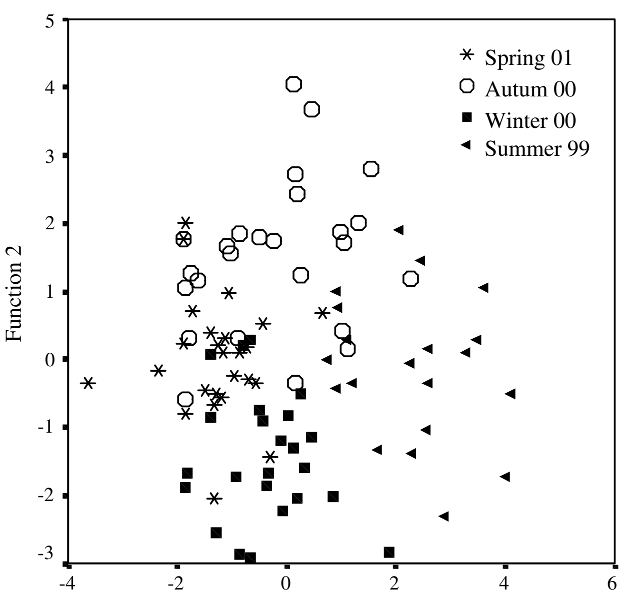

Fig. 3. Scatter diagram of the fresh cheese samples on the axes representing the first two-function discriminant differentiating by season of production.

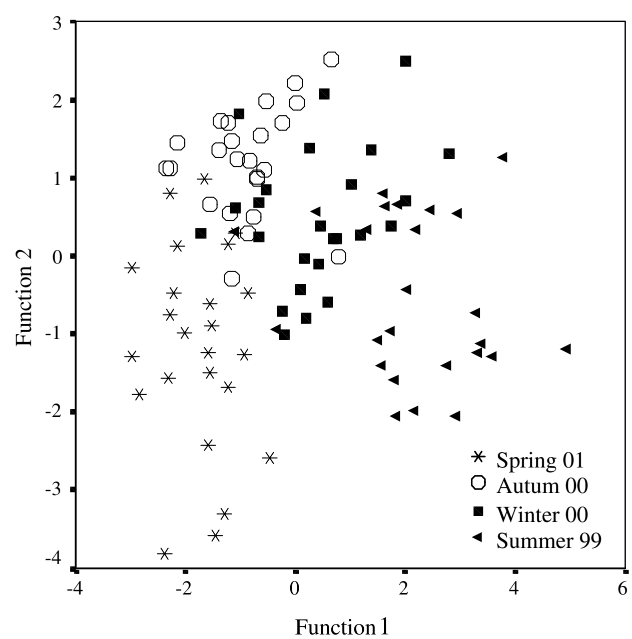

Fig. 4. Scatter diagram of the semi-hard cheese samples on the axes representing the first two-function discriminant differentiating by season of production.

the classification, by applying both processes, showed low percentages of correct classifications for both types of cheeses. The correct classification using all the variables was 69.5% (54.7% after cross-validation) for fresh cheeses and 69.4% (59.2% after cross-validation) for semi-hard cheeses. Thus, considering the chemical parameters determined, the fresh and semi-hard cheeses analysed here were relatively homogeneous, which does not permit a satisfactory classification on the basis of the region of production.

A subsequent DA on the fresh and semi-hard cheeses from Tenerife was carried out using all the variables and types of goat's diet as criteria for comparison. Table 5 shows that the correct classifications were moderate for the fresh cheeses (80.5%, and 71.3% after cross-validation), and relatively low for the semi-hard cheeses

Table 5
Results of the discriminant analysis according to the type of goat's diet (all variables)

	Goat's diet	Predicted group	
		<50% fibre	>50% fibre
Initial group Fresh cheese[a]	<50% fibre	37 (80.4%)	4 (19.6%)
	>50% fibre	8 (19.5%)	33 (80.5%)
Initial group semi-hard cheese[b]	<50% fibre	33 (68.8%)	15 (31.3%)
	>50% fibre	14 (33.3%)	28 (66.7%)

[a] 80.5% samples well classified; (71.3% after cross-validation).
[b] 67.8% samples well classified; (60.0% after cross-validation).

(67.8%, and 60.0% after cross-validation) using all the variables. When the stepwise DA was applied the variables selected were: Fe, fat, protein, percentage of fat on dry matter, and pH for fresh cheeses and only Fe for semi-hard cheeses. The correct classification of the fresh cheeses were 75.0% and 72.8% after cross-validation and, for the semi-hard cheeses, 70.7% (70.7% with cross-validation). Thus, the type of goat's diet seems to influence the chemical composition of the cheeses, particularly the fresh cheese, produced using goat's milk.

4. Conclusions

The factor and linear discriminant analyses make it possible to distinguish the fresh and semi-hard cheeses, and the linear discriminant analysis classified the fresh and semi-hard cheeses moderately well according to the season of production and the type of goat's diet.

The seasonal variations and the influence of the type of the goat's diet on the chemical composition of cheeses are of interest because they demonstrate that these artisan cheeses have a high degree of biodiversity. Thus, it is necessary to define and unify the characteristics of these cheeses in order to establish a future "Protected Denomination of Origin".

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