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Characterization and biochemical changes during the ripening of a Spanish craft goat's milk cheese (Armada variety)

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The gross and mineral composition, and some physico-chemical parameters were determined in 15 batches of Armada goat's milk cheese (a Spanish craft variety), as well as in the milk used for its manufacture. Some biochemical changes during the ripening process have been also investigated. The milk used in the elaboration of Armada cheese had higher lactose, fat, protein and ash contents than previously reported by other authors, whilst iron content was lower than recent results for goat's milk from other countries. Armada cheese showed a high total solids content and a low NaCl and ash content. Water activity (A_w) values decreased progressively during ripening, reaching very low final values (0.895 on average). Lactose disappeared almost completely within the first 7 days of ripening, when the cheese had the lowest pH values (about 4.50). L-Lactic acid dominated in the curd, but during the ripening process both isomers (D- and L-) tended to balance. Variations in mineral content during ripening were only found for magnesium, calcium, phosphorus and zinc: they showed a significant reduction in the first days of ripening coincidental with a decrease in pH values.

INTRODUCTION

Goat's milk production in Spain was around 450 million litres in 1991 (Anon, 1994), from which only 12% was dedicated to the specific elaboration of goat's cheese. Such a low percentage represents an obstacle to the profitability of the production of this kind of milk.

Despite the existence of a large variety of goat's cheeses in Spain (Anon., 1990), only a few types are produced on an industrial scale, probably because of the scarcity of knowledge of their manufacturing methods, and their biochemical and microbiological characteristics. Only Majorero cheese (Fontecha *et al.*, 1990; Martín-Hernández *et al.*, 1992), Ibores (Más-Mayoral *et al.*, 1991), Cendrat del Montsec (Carretero *et al.*, 1992), Gredos (Medina *et al.*, 1992) and Valdeteja (Carballo *et al.*, 1994) have been extensively studied. There is also some information about the final chemical composition of Cádiz and Málaga (Marcos *et al.*, 1983), Babia-Laciana (Argumosa *et al.*, 1992) and Palmero (Gómez *et al.*, 1991) cheeses, the available technical information of the rest of the varieties being almost non-existent.

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Among these latter, the Armada cheese, made in the north of Spain with whole raw milk by artisanal methods, is included. Its excellent organoleptic characteristics and good acceptance in local markets suggest that it would achieve national and international markets, if a manufacturing technology were developed to produce uniform product of constant quality on a large scale. That demands a comprehensive knowledge of biochemical and microbiological aspects of the artisanal product ripening. The objective of this work is the study of the biochemical characteristics of Armada cheese, and of the milk used in its manufacture, as well as some biochemical changes during the ripening process. This technical information is of great interest for the eventual manufacture of this cheese on an industrial scale in controlled conditions.

MATERIALS AND METHODS

Cheesemaking and sampling

Armada cheese is traditionally manufactured with raw whole goat's milk, treated with a small amount of whey from previous batches, and coagulated at 30°C by the addition of about 15 ml of commercial calf rennet (strength 1/10 000) per 100 litres of milk. No starter cultures are inoculated into the milk. After 60 min, the curd, now compact, is cut and transferred to cheese-cloths. These are made into bundles and hung for 48 h to drain the whey. Bundles are then opened and the salt added and the curd is given a rigorous kneading ('sobadol'). It is then transferred to clean cheese-cloths and hung for 3 days more, after which it is kneaded and hand-moulded to produce its characteristic square shape. Subsequently, cheeses are wrapped again in cheese-cloths and hung from the ceiling, where the ripening process takes place in natural conditions with a temperature of 10–15°C and a relative humidity of 70–85%, depending on the time of year. Cheeses of approximately 20 cm diameter and 20 cm high are obtained.

The study of the biochemical characteristics of the ripened cheese and the milk used in its manufacture was done on 15 batches.

For the study of the biochemical changes during ripening, four batches of cheese were prepared, from which curd samples (0 days) and 7, 15, 30, 60 and 120 days-old cheese samples were taken (each sample was made up of one whole cheese).

Samples were transported to the laboratory under refrigeration (below 4°C) and prepared according to the FIL-IDF 50:B (1985) standard. The cheeses, after discarding the rind, were divided into three portions (surface, main and depth) as described by Oria (1986). The surface portion consists of approximately 3 cm immediately next to the more external portion of cheese; the main portion is made up of the 3 cm adjacent to the surface portion towards the inner of the cheese; and finally, the depth portion is the more internal part of cheese.

Chemical analysis

The following methods were used for the determination of the basic composition of the milk: total solids, FIL-IDF 21B: 1987; protein, FIL-IDF 20A: 1986; fat, FIL-IDF 105: 1981; lactose, FIL-IDF 28A:1974; NaCl, FIL-IDF 12A: 1969; ash by incineration at 535 ± 15°C. The milk pH was measured directly with a pH meter PHM 82 Standard (Radiometer, Copenhagen, Denmark). The titratable acidity was measured using a phenolphthalein solution at 1% (0.5 ml per 10 ml of milk) as indicator.

Total solids, fat, protein, salt, ash and lactose were analysed in cheese according to the FIL-IDF standards, 4A:1982, 5B:1986, 25:1964, 17A:1972, 27:1964, and 43:1967. D- and L-Lactic acids were determined by the method of Noll (1974). pH and titratable acidity were measured using AOAC methods 14022 (1975) and 16228 (1975), respectively. Water activity was measured in a DECAGON CX-1 Water Activity System apparatus (Decagon Devices Inc., Pullman, USA).

Main and trace elements in milk and cheese were analysed with a Perkin-Elmer Model 3110 Atomic Absorption Spectrophotometer using a multi-element hollow-cathode lamp as described by Juárez and Martínez-Castro (1979) and Juárez and Martín-Hernández (1983). Phosphorus content in milk and cheese was determined by colorimetry following the FIL-IDF standards 42: 1967 and 33C: 1987, respectively.

Statistical analysis

In order to investigate the differences in the biochemical parameters during ripening, one-way analysis of variance with the confidence intervals test at 95% level, was carried out using the Statgraphics 3.0 computer programme (Statistical Graphics Corporation, Rockville, Maryland, USA).

RESULTS AND DISCUSSION

Biochemical characteristics of Armada cheese and of the milk used in its manufacture

Table 1 shows the mean values of the different components and physicochemical parameters determined in the milk used in the elaboration of Armada cheese, and in the cheese at the end of the ripening process. In general, lactose, fat, protein and ash contents of the milk used for the manufacture of Armada cheese turn out to be higher than those found by other authors in goat's milk from other countries (Grandpierre *et al.*, 1988; Simos *et al.*, 1991). Only Martín-Hernández *et al.* (1988) have described similar values for Spanish goat milk, although with a lower protein content than that found

Table 1. Biochemical parameters of Armada cheese ($n = 15$) and of the milk used in its manufacture ($n = 15$)

Parameter	Milk	Cheese
Total solids	15.81 ± 1.51^a	78.85 ± 2.84^a
Protein	4.35 ± 0.71^a	37.14 ± 3.61^c
Fat	5.58 ± 0.80^a	56.66 ± 3.95^c
Lactose	4.83 ± 0.23^a	—
Ash	0.87 ± 0.07^a	3.74 ± 0.72^c
Salt	0.10 ± 0.01^a	2.18 ± 0.55^c
pH	6.59 ± 0.10	4.96 ± 0.33
Titratable acidity	0.17 ± 0.02^b	1.75 ± 0.25^d
Aw	—	0.877 ± 0.039
Sodium	1.28 ± 0.07^1	8.35 ± 2.27^1
Calcium	1.55 ± 0.07^1	5.98 ± 1.32^1
Potassium	2.36 ± 0.15^1	2.21 ± 0.37^1
Magnesium	0.13 ± 0.01^1	0.32 ± 0.09^1
Phosphorus	1.15 ± 0.14^1	6.47 ± 0.78^1
Iron	0.34 ± 0.01^2	3.80 ± 1.0^2
Zinc	4.35 ± 0.27^2	36.1 ± 12.10^2
Copper	0.27 ± 0.09^2	1.72 ± 0.65^2
Manganese	0.051 ± 0.001^2	0.89 ± 0.32^2

[a] Expressed as g/100 g.
[b] Expressed as g lactic acid/100 g.
[c] Expressed as g/100 g TS.
[d] Expressed as g lactic acid/100 g TS.
[1] Expressed as g/kg TS.
[2] Expressed as mg/kg TS.

by us. This circumstance is due to the fact that the milk used to make the Armada cheese comes from indigenous unimproved breeds of low milk production which, however, give milk with high total solids. Regarding the mineral content, our results are within the range described by some authors for goat's milk, although calcium, phosphorus and potassium contents are in the upper limit of this range. In relation to iron content, data available in the literature are varied, and in most cases higher than the values found by us.

Armada cheese composition at the end of the ripening process is characterized by a high total solids, and a low salt and ash content, in comparison with other goat cheeses studied.

pH values (4.96 ± 0.33) as well as titratable acidity (1.75 ± 0.25 g of lactic acid/100 g of total solids) were similar to those found in the majority of hard goat cheeses. Water activity (A_w) was low (0.877 ± 0.039), but comparable to that of Gomera cheese (Millán *et al.*, 1992) and Valdeteja cheese (Carballo *et al.*, 1994). Calcium content (5.98 ± 1.32 g/kg TS) was lower than current data in literature for enzymatic coagulation cheeses and much higher than for acid-coagulation cheeses. The phosphorus content (6.47 ± 0.78 g/kg TS) was similar to that commonly described for other hard goat cheeses but, on the other hand, sodium content was low (8.35 ± 2.27 g/kg TS), probably as a consequence of the slight salting. Among trace elements, zinc is the main element, consistent with the majority of goat's cheeses studied. Iron content turn out to be especially low, in agreement with the low iron level found in milk.

Changes in the gross composition and water activity during cheese ripening

Mean values for total solids, fat, protein, NaCl, ash and water activity during ripening are presented in Table 2.

Total solids content increased considerably during the first 60 days of ripening, reaching very high values, around 80%, comparable with those obtained by Fontecha *et al.* (1990) for artisanal Majorero cheese and Carballo *et al.* (1994) for Valdeteja cheese. Fat and protein contents were similar for all batches with final mean values of 59.27 and 35.0 g/100 g TS, respectively.

NaCl and ash contents of the three portions increased steadily during the first week of ripening as a consequence of the salting process. The salt content evolution throughout ripening was fairly irregular owing to the salting technique used. Cheeses are individually salted by the addition of solid salt during the kneading operations and each sample is made up of one entire cheese. It is then possible that all the cheeses do not attain the same exact quantity of salt, and it is also possible that the losses in salt with the whey, which still drops out from the curd while in cheese-cloth before giving them their final shape, are also different for every cheese.

At the end of ripening, the salt concentration was low, as described for washed curd Majorero cheese (Martín-Hernández *et al.*, 1992) and Valdeteja cheese (Carballo *et al.*, 1994).

The importance, during ripening, of the salt content, expressed as g of salt/100 g of moisture, is determined by its influence on certain chemical reactions (Thomas

Table 2. Changes in gross composition and water activity during the ripening of Armada goat's milk cheese[1]

	Portion[2]	Ripening time (days)					
		0	7	15	30	60	120
Total solids (TS, %)	Surface		53.31 ± 3.37^{a}	61.89 ± 1.16^{b}	69.99 ± 4.03^{c}	79.44 ± 4.53^{d}	80.32 ± 3.34^{d}
	Main	48.18 ± 2.13^{a}	52.63 ± 3.39^{a}	61.13 ± 1.27^{b}	69.27 ± 3.83^{c}	78.21 ± 3.73^{d}	79.34 ± 3.55^{d}
	Depth		51.89 ± 3.06^{a}	60.66 ± 1.50^{b}	68.17 ± 3.40^{c}	74.97 ± 2.56^{d}	76.95 ± 2.17^{d}
Protein (% TS)	Main	32.5 ± 3.81^{a}	32.5 ± 1.58^{a}	33.5 ± 1.18^{a}	34.3 ± 2.76^{a}	33.7 ± 1.07^{a}	35.0 ± 2.95^{a}
Fat (% TS)	Main	61.98 ± 2.30^{a}	59.21 ± 3.95^{a}	62.00 ± 3.95^{a}	60.65 ± 3.09^{a}	60.19 ± 2.23^{a}	59.27 ± 2.45^{a}
Salt (% TS)	Surface		3.55 ± 1.10^{a}	2.32 ± 1.26^{a}	3.29 ± 0.63^{a}	3.11 ± 0.28^{a}	2.69 ± 0.60^{a}
	Main	0.40 ± 0.09	3.26 ± 1.01^{a}	1.93 ± 1.11^{a}	2.65 ± 0.71^{a}	2.85 ± 0.78^{a}	2.54 ± 0.64^{a}
	Depth		3.14 ± 1.08^{a}	1.59 ± 087^{b}	1.88 ± 0.30^{ab}	1.94 ± 0.45^{ab}	2.00 ± 0.47^{ab}
S/M[3]	Surface		3.81 ± 1.21^{a}	3.78 ± 2.24^{a}	7.97 ± 2.87^{ab}	12.6 ± 3.69^{b}	11.3 ± 3.38^{b}
	Main	0.36 ± 0.06	3.58 ± 1.07^{a}	3.05 ± 1.84^{a}	6.22 ± 2.61^{ab}	9.52 ± 3.38^{b}	10.0 ± 3.33^{b}
	Depth		3.35 ± 1.14^{ab}	2.46 ± 1.42^{a}	4.09 ± 0.98^{abc}	5.89 ± 1.47^{bc}	6.68 ± 1.46^{c}
Ash (% TS)	Surface	4.32 ± 0.14^{a}	6.10 ± 0.57^{b}	4.65 ± 1.46^{ab}	5.31 ± 0.58^{ab}	5.29 ± 039^{ab}	4.27 ± 0.33^{a}
	Main	4.32 ± 0.14^{ab}	5.82 ± 0.59^{b}	3.66 ± 1.10^{a}	3.76 ± 0.84^{a}	3.85 ± 0.75^{a}	3.19 ± 0.24^{a}
	Depth	4.32 ± 0.14^{ab}	5.53 ± 0.59^{b}	3.34 ± 0.93^{ac}	2.75 ± 0.53^{c}	2.81 ± 0.58^{c}	2.79 ± 0.15^{c}
A_w	Surface		0.967 ± 0.004^{ab}	0.957 ± 0.017^{ab}	0.918 ± 0.018^{bc}	0.874 ± 0.038^{c}	0.866 ± 0.048^{c}
	Main	0.990 ± 0.003^{a}	0.970 ± 0.011^{ab}	0.971 ± 0.014^{ab}	0.941 ± 0.017^{bc}	0.904 ± 0.031^{c}	0.895 ± 0.039^{c}
	Depth		0.966 ± 0.004^{abc}	0.969 ± 0.010^{ab}	0.960 ± 0.008^{bc}	0.943 ± 0.012^{cd}	0.922 ± 0.022^{d}

[1]Average values ± standard deviation of four cheese batches.
[2]Portions were obtained as described by Oria (1986).
[3]S/M expressed the salt content as a percentage of moisture.
[a–d] Means in the same row and parameter group during the ripening without a common superscript are significantly different ($P < 0.05$).

& Pearce, 1981; Schroeder *et al.*, 1988) and upon the growth and activity of lactic acid bacteria. In our case, it showed a considerable increase, averaging values above 4% from the first 15 days of ripening onwards. In the 120 day-old cheese, salt/moisture concentrations were 11.3, 10.1 and 6.7 g/100 g of water in superficial, main and depth portions; these results agree with those described for other ripened goat cheeses, namely, the artisanal Majorero (Fontecha *et al.*, 1990), Ibores (Más-Mayoral *et al.*, 1991), Gomera (Millán *et al.*, 1992) and Valdeteja (Carballo *et al.*, 1994).

As was expected, the A_w values decreased progressively and constantly throughout the ripening process, from an initial value in the main portion of 0.99 to 0.90 on average. In comparison with literature, only Majorero cheese (Fontecha *et al.*, 1990) has lower A_w values.

Changes in lactose, D- and L-lactic acids, titratable acidity and pH during cheese ripening.

Table 3 shows the evolution of the mean values of lactose, D- and L-lactic acids, titratable acidity and pH during cheese ripening.

Lactose content decreased until its almost complete disappearance within the first 7 days, whereas D- and L-lactic acids increased. This rapid disappearance could be partially explained by the technological manufacturing process, provided that the kneading operations caused a more intense whey draining; furthermore, due to the fact that cheeses are not salted until a few days after coagulation, the lactic acid flora growth and activity would not be limited during the time elapsed until salting, thus contributing to the disappearance of lactose. A similar change of lactose was also observed in Valdeteja cheese, but in this case the complete disappearance occurred within the first 17 days of ripening (Carballo *et al.*, 1994).

D- and L-Lactic acid change during ripening is a consequence of the microbial changes that take place in this type of cheese (Tornadijo, 1995). In the curd, the higher L-lactic acid content is related to the predominant action of lactococci. During ripening, both isomers (D- and L-) tend to balance, although the D-form can predominate in some cases. The reduction of lactococci and the setting up of secondary flora (mainly lactobacilli) that could transform L-lactate into D-lactate (Thomas & Crow, 1983) could provide an explanation for such change. A similar trend for D- and L-lactic acids has been described for Romano cheese (Deiana *et al.*, 1984), Cheddar (Jordan & Cogan, 1993) and Valdeteja (Carballo *et al.*, 1994).

The evolution of titratable acidity was similar to that of lactic acid, average values of 1.97 ± 0.29 g of lactic acid/100 g TS being observed in the main portion at the end of the ripening process.

The rapid disappearance of lactose coincided with an important decline in pH during the first few days, reaching a minimum value at the 7th day of ripening. From 15 days onwards, a certain rise was noticed so as to reach final values of about 5, similar to those observed for other goat's cheeses as Palmero (Gómez *et al.*, 1991), Gredos (Medina *et al.*, 1992), Cendrat del Montsec (Carretero *et al.*, 1992), Feta (Mallatou *et al.*, 1994) and Valdeteja (Carballo *et al.*, 1994). The slight increase of pH does not correspond to what could be expected for a cheese in which the presence of moulds and yeasts is relatively important (Tornadijo, 1995). However, the high concentrations of salt/moisture could limit the action of its enzymes. It is well known that the activity of the proteases of some moulds is reduced when salt concentration rises above 0.5% (Kinsella & Hwang, 1977). Moreover, the small increment of pH throughout ripening could also be determined by a higher buffer capacity of the curd, which seems to influence this parameter as much as the quantity of basic and acid compounds produced. In other cheese varieties it has been proved (Lucey *et al.*, 1993) that the curd buffer capacity is maximal at pHs around 4.5–5 (those presented in Armada cheese); furthermore, it has been also observed that in low initial pH cheeses, the pH

Table 3. Changes of lactose, D- and L-lactic acid contents, pH and titratable acidity during the ripening of Armada goat's milk cheese[1]

		Ripening time (days)					
	Portion[2]	0	7	15	30	60	120
Lactose (% TS)	Main	2.40 ± 1.08^a	0.03 ± 0.06^b	—	—	—	—
D-Lactic (% TS)	Main	0.20 ± 0.36^a	1.57 ± 0.10^b	1.28 ± 0.03^{bc}	0.93 ± 0.34^{cd}	0.66 ± 0.12^d	0.73 ± 0.06^d
L-Lactic (% TS)	Main	0.84 ± 0.35^{ac}	1.50 ± 0.10^b	1.18 ± 0.05^{ab}	0.81 ± 0.18^{ac}	0.70 ± 0.12^c	0.79 ± 0.27^{ac}
pH	Surface		4.60 ± 0.16^b	4.81 ± 0.27^{ab}	4.99 ± 0.14^{ab}	4.99 ± 0.16^{ab}	5.13 ± 0.18^a
	Main	5.17 ± 0.37^a	4.52 ± 0.17^b	4.49 ± 0.16^b	4.55 ± 0.12^b	4.69 ± 0.41^{ab}	4.92 ± 0.11^{ab}
	Depth		4.50 ± 0.17^{ab}	4.41 ± 0.16^b	4.42 ± 0.18^b	4.91 ± 0.63^{ab}	5.07 ± 0.32^{ab}
Titratable acidity[3]	Surface		2.56 ± 0.39^b	1.99 ± 0.41^{ab}	2.02 ± 0.27^{ab}	1.97 ± 0.27^{ab}	2.08 ± 0.25^{ab}
	Main	1.66 ± 0.36^a	2.47 ± 0.31^b	2.08 ± 0.36^{ab}	1.69 ± 0.36^a	1.67 ± 0.34^a	1.97 ± 0.29^{ab}
	Depth		2.45 ± 0.28^b	2.19 ± 0.40^{ab}	1.70 ± 0.35^a	1.58 ± 0.36^a	1.81 ± 0.34^{ab}

[1]Average values ± standard deviation of four batches.
[2]Portions were obtained as described by Oria (1986).
[3]Expressed as g lactic acid/100 g TS. — = none detected.
[a–d] Means in the same row and parameter group during the ripening without a common superscript are significantly different ($P < 0.05$).

Table 4. Changes in the main and trace element content during the ripening of Armada goat's milk cheese[1]

	Ripening time (days)					
	0	7	15	30	60	120
Na[2]	0.68 ± 0.32	13.0 ± 4.27^{a}	6.15 ± 4.03^{a}	9.80 ± 3.43^{a}	10.5 ± 3.90^{a}	9.52 ± 3.27^{a}
Ca[2]	13.0 ± 1.96^{a}	8.23 ± 1.19^{b}	6.50 ± 1.66^{b}	5.60 ± 1.28^{b}	5.19 ± 1.79^{b}	5.69 ± 1.15^{b}
K[2]	2.20 ± 0.29^{a}	2.97 ± 0.52^{b}	2.02 ± 0.37^{a}	2.32 ± 0.43^{ab}	2.24 ± 0.31^{ab}	2.12 ± 0.22^{a}
Mg[2]	0.72 ± 0.20^{a}	0.52 ± 0.20^{ab}	0.37 ± 0.14^{b}	0.32 ± 0.12^{b}	0.27 ± 0.09^{b}	0.27 ± 0.06^{b}
P[2]	9.30 ± 0.48^{a}	6.95 ± 0.61^{b}	6.04 ± 0.94^{b}	5.50 ± 0.73^{b}	5.67 ± 1.28^{b}	6.16 ± 0.86^{b}
Fe[3]	4.84 ± 0.83^{a}	4.82 ± 0.74^{a}	4.00 ± 0.49^{ab}	3.28 ± 0.14^{b}	3.08 ± 0.53^{b}	3.61 ± 0.67^{ab}
Cu[3]	1.55 ± 0.27^{a}	1.54 ± 0.20^{a}	1.36 ± 0.14^{a}	1.31 ± 0.12^{a}	1.12 ± 0.05^{a}	1.36 ± 0.36^{a}
Zn[3]	67.1 ± 19.46^{a}	47.0 ± 10.80^{ab}	35.9 ± 8.13^{bc}	29.1 ± 2.21^{bc}	25.6 ± 1.22^{c}	29.7 ± 0.5^{bc}
Mn[3]	1.36 ± 0.41^{a}	1.25 ± 0.43^{a}	1.20 ± 0.35^{a}	1.13 ± 0.36^{a}	1.15 ± 0.44^{a}	1.23 ± 0.38^{a}
Ca/P	1.40 ± 0.18^{a}	1.19 ± 0.08^{ab}	1.06 ± 0.10^{bc}	1.01 ± 0.12^{bc}	0.90 ± 0.11^{c}	0.92 ± 0.07^{c}

[1]Average values ± standard deviation of four batches.
[2]Expressed as g/kg TS.
[3]Expressed as mg/kg TS.
$^{a-c}$Means in the same row and parameter group during the ripening without a common superscript are significantly different ($P < 0.05$).

increment during ripening is smaller than in those with higher initial values (Lucey & Fox, 1993).

Changes in the mineral content during ripening

The main and trace average mineral contents in Armada cheese during ripening are listed in Table 4.

With regard to main minerals, the most important, quantitatively, was sodium, followed by phosphorus and calcium. Sodium and potassium showed a similar changes with final values of 9.52 and 2.12 g/kg TS, respectively.

Magnesium, calcium and phosphorus contents showed a significant decline in the first days, coincidental with a decrease in pH values, with a subsequent stabilization towards the end of ripening, averaging final values of 0.27, 5.69 and 6.16 g/kg TS; these values are intermediate between those obtained for acid and enzymatic coagulation cheeses. The reduction in calcium, phosphorus and magnesium content as pH decreases is a usual phenomenon, since low pH values favour the migration of these minerals from casein micelles towards the soluble fraction, thus increasing losses with the whey. Calcium and phosphorus retention in cheese is important, not only from the nutritive point of view, but also because of the considerable contribution of such elements to the maintenance of the micellar structure of casein and therefore, to the cheese texture, as well as to the curd buffer capacity (Lucey & Fox, 1993).

In the Armada cheese, the calcium reduction was always more important than phosphorus reduction. This circumstance is probably owing to the greater effect that the acidification of the curd exerts on calcium (Creamer *et al.*, 1988; Kimura *et al.*, 1992), provided that it is situated in the micelles totally in ionic form linked to residues loaded with casein, citrate and esterified and non-esterified phosphate, whilst 40% of the casein micelle phosphate is esterified to αs_1-, αs_2-, β- and κ-casein, and cannot be solubilized (Walstra & Jenness, 1984). In addition, ionic calcium has a lower molecular weight than ionic phosphate, a fact that could favour its higher mobility (Kindstedt & Kosikowski, 1988).

In relation to the trace mineral elements, significant variations were only found for zinc content, which decreased during the first days of ripening. The fact that in milk 85% of this element is linked to the casein micelle (Parkash & Jenness, 1967; Favier & Dorsainvil, 1987) causes its losses to increase as pH is reduced, as happens with magnesium, calcium and phosphorus.

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