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Calcium, magnesium, manganese, sodium and potassium variations in Manchego-type cheese during ripening

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Changes in the contents of calcium (Ca), magnesium (Mg), manganese (Mn), sodium (Na) and potassium (K) during the ripening of a Manchego-type cheese during storage at temperatures below 10°C were studied over a period of six months. The determinations were performed by atomic absorption spectrophotometry. A two-factor variance analysis showed the existence of statistically significant differences ($p < 0{\cdot}001$) in the contents of Ca, Mg, Mn, Na and K between different portions and over a period of time, when the concentrations were considered both on a fresh-weight and a dry-weight basis. However, certain differences in the formed groups according to time were observed using a Scheffe homogeneity test ($p < 0{\cdot}05$), depending on whether the mineral content was expressed on a fresh-weight or on a dry-weight basis. The daily intake estimates calculated for the five elements were 47 mg/day for Ca, 2 mg/day for Mg, 2μg/day for Mn, 71 mg/day for Na and 8 mg/day for K in Manchego-type cheese ripened for 6 months.

INTRODUCTION

The physicochemical characteristics and mineral contents are very variable in different types of cheese as a function of factors such as the initial composition of the milk (García Olmedo *et al*, 1981), the manufacturing process (Coppini *et al.*, 1979; Moreno-Rojas *et al.*, 1991) and the ripening conditions (Le Graet & Brulé, 1988).

Manchego or Manchego-type cheese is one of the most popular indigenous cheeses in Spain and can be consumed at several stages of ripening: fresh some days after manufacture, half cured after a few weeks, cured for 2–3 months, matured for 3–6 months, or matured for 1 year (Fox, 1987). Its nutritional contribution may be different at the various stages of ripening due to the internal migrations of minerals throughout the ripening period. In a previous work, the influence of ripening period on the copper, iron and zinc contents was studied (Moreno-Rojas *et al.*, 1992).

The purpose of this study was to determine if the calcium, magnesium, manganese, sodium and potassium concentrations are modified during the ripening of a Manchego-type cheese. We tried to discover whether there was internal migration of these minerals from areas located at a greater or lesser depth from the surface of the cheese.

MATERIALS AND METHODS

A mixture of milk was used (22% goat's milk and 78% cow's milk). The mixture was pasteurized and subsequently placed in the curdling vat in which 3350 litres of milk with a 3·9% fat content and 15·5° Dornic acidity were processed. An addition to the milk of 70 g ferment (Bioferment Dac Homo), 280 g discolouring agent, 175 cm^3 lisozlime, 670 g $CaCl_2$ and 800 cm^3 rennet (Proinalsa) was made. After the formation of curds, these were pressed into plastic moulds. The pressed curd was placed in brine with a 20% salt content, pH 5·3 and 13° Dornic, in which it remained for 40 h.

The ripening process in a Manchego-type cheese from a homogeneous batch stored under identical conditions (at <10°C) was studied from the start of ripening, at monthly intervals for six month. At each monthly sampling, two cheeses were analysed (each of 3 kg weight, 24 cm diamter 10 cm high. Three portions were taken at different depths from each cheese: external (including rind), middle and internal. Five samples of 10 g each were obtained from each portion.

The samples were analysed by the method of Gabrielli Favretto (1990), with certain modifications. A 10 g sample of each portion was weighed into crucibles, dried at constant weiht and incinerated in a furnace at 460°C for 16 h. After cooling, 2 ml of 2 N HNO_3 were added, the sample dried on a thermostatic plate and again placed in the furnace at 460°C for 1 h. The ash was dissolved in 5 ml 2 N HNO_3, diluted to volume in a 25 ml volumetric flask with 0·1 N HNO_3 and stored in polypropylene flasks under refrigeration. For Ca, the solution was diluted 1:100 and lanthanum (chloride $LaCl_3$ 7 H_2O) was added to give 0·27% in the final solution.

Analyses were performed using a Perkin-Elmer Model 2380 atomic absorption spectrophotometer, using an air–acetylene flame. Single-element hollow cathode lamps were used for all elements except for Na and K which were determined by emission using the same instrument. For each element being determined, the analyses included duplicate analyses of samples, one spiked recovery analysis and one standard reference material (non-fat milk powder, NBS 1549) from the National Institute of Standards and Technology (NIST). For calculation of the detection limit (3SD), the definition and criteria of the IUPAC were followed (Long & Winefordner, 1983; Analytical Methods Commitee, 1987).

The sensitivities (μg/ml) obtained for Ca, Mg, Mn, Na and K, were 1·38; 0·089, 0·034, 6·42 and 6·70, respectively. The minimum concentrations detectable in cheese, on a fresh-weight basis (μg/g), were: 93·7, 12·2, 0·023, 100, and 50·0 for Ca, Mg, Mn, Na and K, respectively. Mean recoveries in Non-Fat Milk Powder (NBS 1549) were Ca, 102·%; Mg, 101%; Mn, 98·5%; Na, 104%; and K, 96·3%.

Statistical analysis

Data obtained from the chemical analysis of the samples were evaluated statistically using a two-factor variance analysis, with Scheffè multiple range test (Snedecor & Cochran, 1971).

RESULTS AND DISCUSSION

Table 1 shows the moisture content (%), and the mean concentrations (on a dry-weight basis) of Ca, Mg, Mn, Na and K, per time and per portion. Figures 1 to 6 show the changes in moisture and mineral content during ripening in portions, at fresh and dry weight.

A two-factor variance analysis was done to determine if there were statistically significant differences in mineral concentrations between portions and between times at which the samples were taken. It was shown that differences existed between both the portions and the times in the concentrations of minerals studied, expressed both on a fresh or on a dry-weight basis ($p < 0.001$). After this, Scheffè's multiple range analysis was performed ($p < 0.05$) from which it was possible to form two kinds of group: by portions from the concentrations of the average of times; and by times from the concentrations in the mean portions. Both are shown in Table 1.

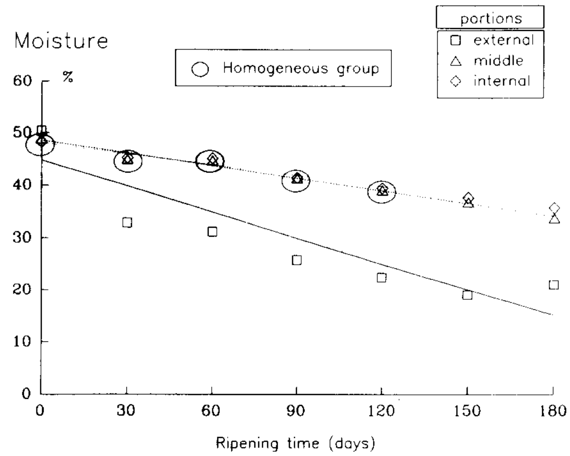

Fig. 1. Changes in the moisture content in different portions of the cheese during ripening.

Changes in moisture content

The percentage of moisture decreased in the three portions during ripening (Fig. 1). By means of Scheffè multiple range analyses it was verified that the middle and internal portion showed a similar trend from the beginning until day 120 of ripening and started to differ in moisture content ($p < 0.05$) from day 150. It should also be mentioned that at the start of ripening (day 0), the percentage of moisture in the external portions was slightly higher than that of the other two portions, which did not happen again throughout the ripening period. Through ripening there was a loss of water by evaporation from the external portion which rapidly dried up, unlike the other two portions which lost their moisture slowly towards the external area, which had a lower moisture content. It should also be taken into account that the high fat content of the cheese in the area of the dried rind has a hydrophobic effect which makes it difficult for the water to reach deeper areas.

Changes in mineral content

Calcium

Throughout ripening, a slight increase in the calcium content of the external portion was observed (Fig. 2(A)). Although no clear trend in the other two portions on a fresh-weight basis was observed, there was a slight decrease on a dry-weight basis (Fig. 2(B)). It was observed that the three portions formed one homogeneous group at the beginning, but not in the other stages except for the association of the middle and internal portions as from day 90 on both a fresh- and a dry-weight base. These changes seemed to indicate a slight migration of calcium towards the external portion, which agrees with the results of Matche and Fanni (1978) and Le Graet *et al.* (1983) who reported extensive migration of calcium to the rind in Camembert cheeses. Le Graet and Brulé (1988) remarked that this phenomenon only occurred in the presence of fungal flora and that there was no migration when antifungals were used so that, in cheese in which there was a higher growth in the rind (as in Camembert), the migrations

Table 1. Moisture content (%) and calcium, magnesium, manganese, sodium and potassium concentrations (mean ± SD) expressed in mg/kg a dry-weight basis with ripening and per portions

	n	Moisture	Ca	Mg	Mn	Na	K
Days[1]							
0	30	49·2 ± 1·0^{g}	149 45 ± 126 3^{e}	610 ± 89^{d}	0·7 ± 0·28^{d}	128 62 ± 108 79^{a}	271 6 ± 98^{c}
30	30	41·1 ± 6·1^{f}	140 19 ± 876^{cd}	583 ± 57^{cd}	0·6 ± 0·14^{c}	135 69 ± 416 2^{a}	268 9 ± 288^{c}
60	30	40·4 ± 6·8^{a}	144 39 ± 118 0^{d}	562 ± 23^{bc}	0·6 ± 0·08^{c}	169 27 ± 462 9^{b}	261 0 ± 570^{b}
90	30	36·2 ± 7·6^{d}	139 86 ± 157 0^{bc}	597 ± 49^{d}	0·6 ± 0·16^{c}	240 50 ± 569 2^{c}	235 9 ± 549^{a}
120	30	33·7 ± 8·1^{a}	131 53 ± 157 6^{a}	523 ± 41^{a}	0·5 ± 0·11^{a}	280 39 ± 790 2^{d}	261 1 ± 749^{b}
150	30	31·2 ± 8·7^{b}	135 42 ± 243 2^{ab}	555 ± 61^{ab}	0·6 ± 0·17^{b}	300 84 ± 957 2^{e}	238 3 ± 785^{a}
180	30	30·2 ± 6·6^{a}	136 96 ± 187 4^{bc}	591 ± 98^{cd}	0·5 ± 0·13^{a}	241 59 ± 767 7^{c}	240 1 ± 610^{a}
Portions[2]							
External	70	29·0 ± 10·0^{x}	153 99 ± 131 5^{y}	592 ± 68^{y}	0·8 ± 0·16^{y}	154 92 ± 671 8^{x}	187 3 ± 490^{x}
Middle	70	41·4 ± 4·9^{y}	131 54 ± 130 9^{x}	569 ± 75^{x}	0·5 ± 0·08^{x}	238 97 ± 996 9^{y}	285 4 ± 239^{y}
Internal	70	41·9 ± 4·3^{y}	133 53 ± 139 5^{x}	564 ± 57^{x}	0·5 ± 0·06^{x}	247 63 ± 983 9^{y}	288 7 ± 214^{y}

[1] For the average of portions.
[2] For the average of days.
[a,b,c,d,e] Scheffe homogeneous groups ($p < 0{\cdot}05$) between times.
[x,y,z] Scheffe homogeneous groups ($p < 0{\cdot}05$) between times.

would be more apparent than in the present case. Román Esteban (1990), showed a trend similar to ours in Manchego-type cheese although the levels found by him were slightly lower.

Magnesium
From the Scheffè analyses performed and the trends calculated it was presumed that there were no statistically significant differences between the middle and internal portions with time, with certain exceptions. The external portion differed from the other two as from day 30 of ripening at fresh weight (Fig. 3(A)). The trend of the magnesium content expressed on a dry-weight basis does not show any clear differentiation between the three portions throughout rlpening time (Fig. 3(B)).

The concentrations found by Román Esteban (1990)

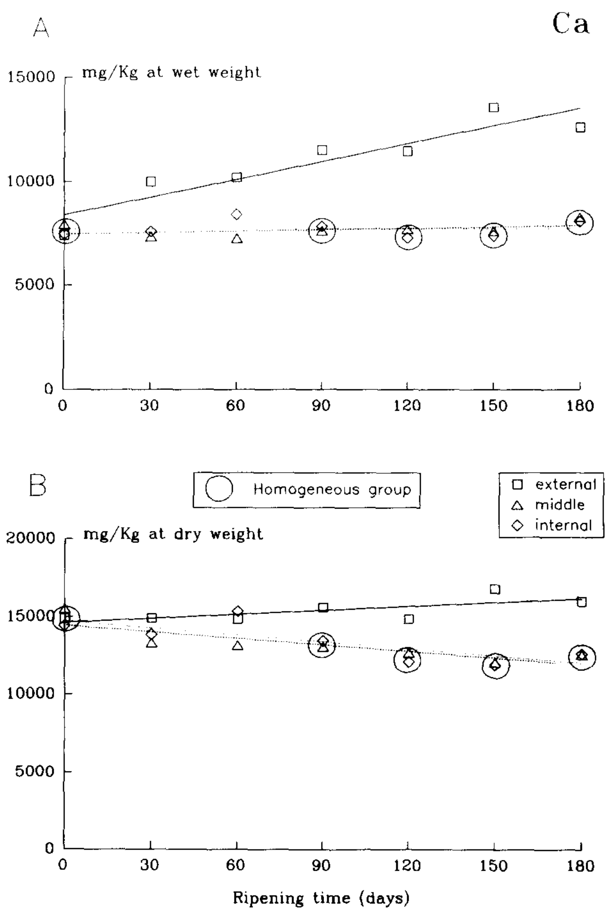

Fig. 2. Changes in the calcium content in different portions of the cheese during ripening. (A) Wet weight, (B) dry weight.

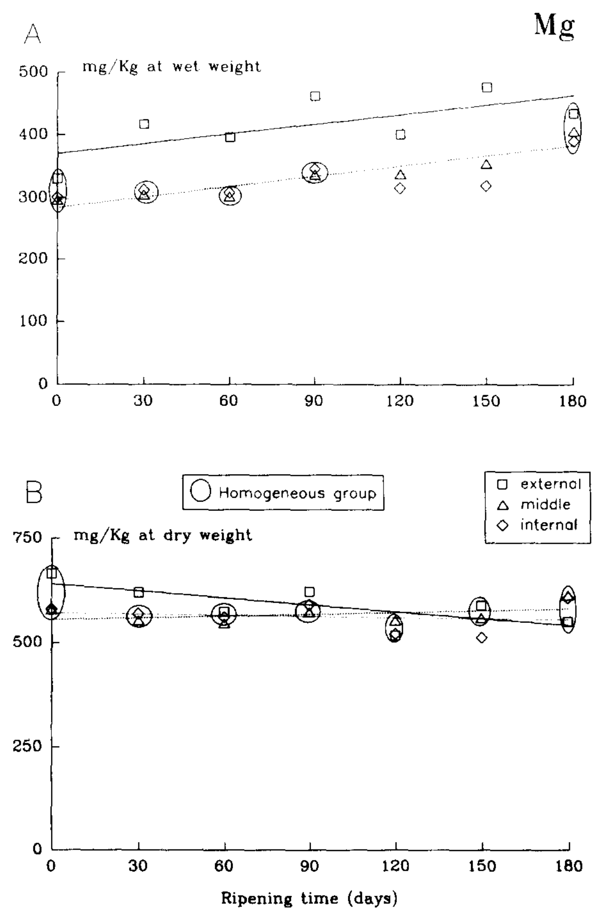

Fig. 3. Changes in the magnesium content in different portions of the cheese during ripening. (A) Wet weight, (B) dry weight.

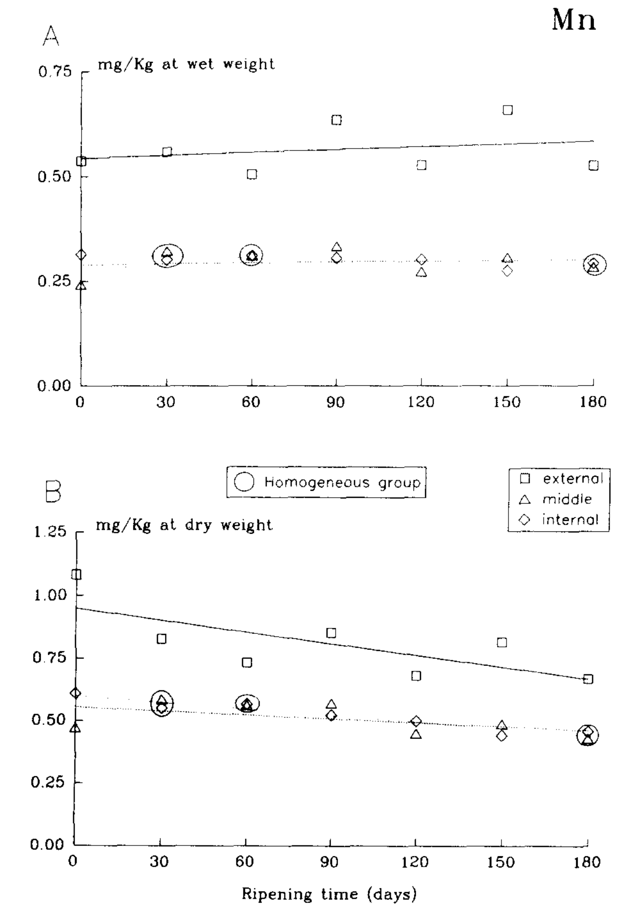

Fig. 4. Changes in the manganese content in different portions of the cheese during ripening. (A) Wet weight, (B) dry weight.

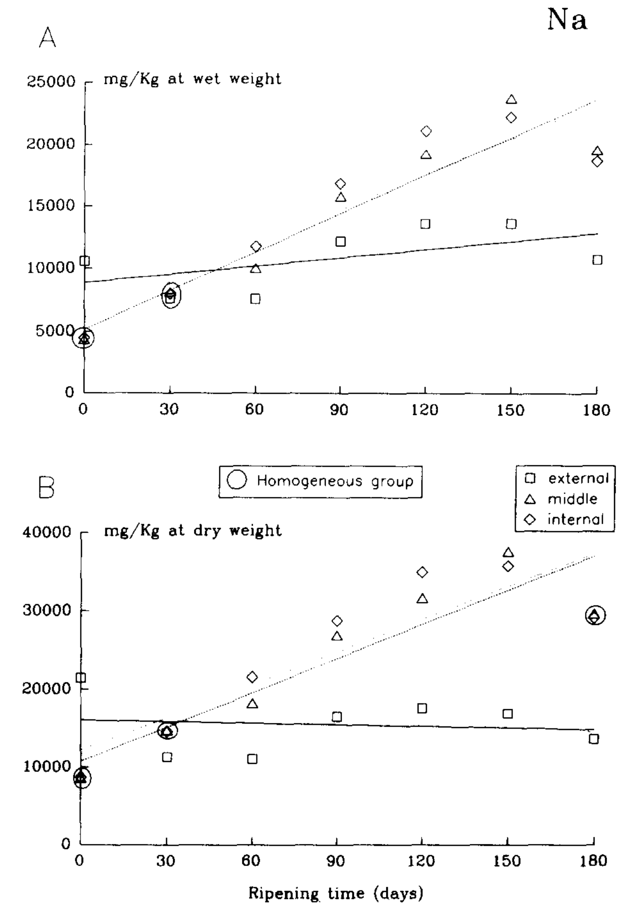

Fig. 5. Changes in the sodium content in different portions of the cheese during ripening. (A) Wet weight, (B) dry weight.

were very similar and, in view of the evolution of the portions formed by him, this would also seem to imply slight differences between portions all through ripening.

Manganese

Changes in the manganese content during ripening are shown in Fig. 4. There was a similar concentration in the middle and internal portions, which formed a homogeneous group in some of the time periods investigated and, in every case, always at lower concentrations than those of the external portion. Manganese content decreased with time in the external portion with slight fluctuations in the middle and internal portions. The concentrations found in the external portions were similar to those found by Román Esteban (1990) in this same portion. The internal portions showed lower concentrations when compared to his, although the trends per portion in both studies were very similar.

Sodium

During ripening, a similar trend was observed (Fig. 5), both on a fresh- and dry-weight basis. The middle and internal portions had similar sodium contents which increased with time and even formed a homogeneous group at 0 days, 30 days (fresh and dry weight) and at 180 days (dry weight). It is also of interest to note how, at 30 days, a point of equilibrium in the sodium content on a fresh-weight basis was produced when the three portions formed a single homogeneous group. The salting of the cheese started a diffusion of the salt from the surface area towards the inside, where its concentration was lower, reaching its equilibrium at around 30 days. The sodium concentration was lower in the external portion than in the other two, remaining so throughout the rest of the ripening time. The fact that the external portion showed lower concentrations than the other two portions after 30 days of ripening was due to a drying up of the rind, which caused a migration of the sodium to areas with a higher moisture content. Román Esterban (1990) found similar changes in this element and his research demonstrated a point of equilibrium between the external and internal portions at 60 days, the concentrations found being very similar to those found by us.

Potassium

During ripening a similar trend for the middle and external portions was observed (Fig. 6) although at no time did they belong to the same homogeneous group, and they showed higher concentrations than for the external portion; these portions showed a negative trend and differed more and more after salting and were more easily noticeable on a dry-weight basis. The levels found were similar to those reported by Román Esteban (1990), as well as the trend and relationship between portions. This author also reported a greater

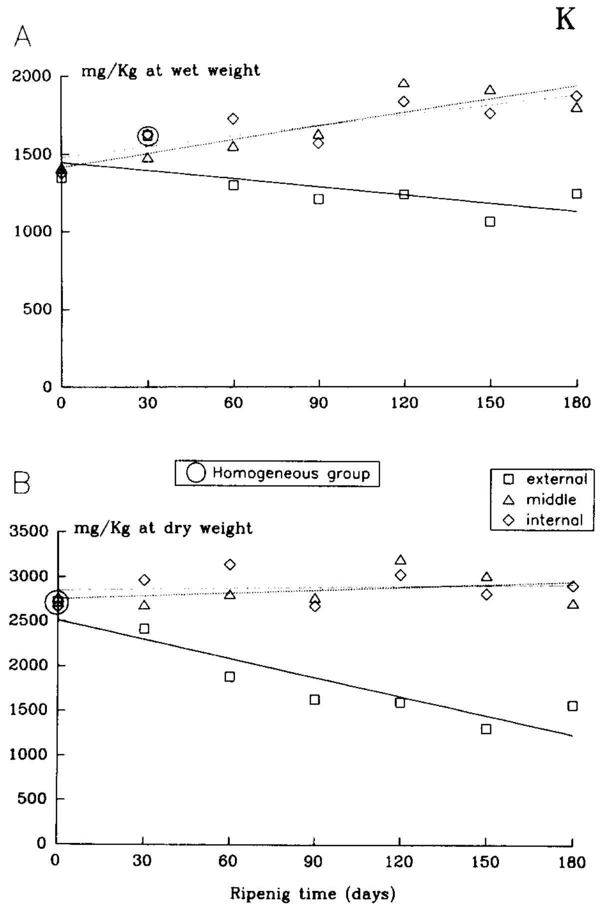

Fig. 6. Changes in the potassium content in different portions of the cheese during ripening. (A) Wet weight, (B) dry weight.

concentration of potassium in the internal portion than in the external one from the tenth day of ripening.

Relationships between elements

A study was made of correlations between the elements investigated, both on a dry- and fresh-weight basis, per portion and with moisture. There were significant correlation coefficients ($p < 0.001$) between all the elements, except between Mg and K. It should also be noted that the sign of the correlation coefficients was positive between Ca, Mg and Mn, and between Na and K, and negative between the first three elements and the two latter ones which indicates that the ripening process affects Ca, Mg and Mn in a similar way, but produces an opposite effect on Na and K. This phenomenon may be due to the different degree of mobility of the different elements which, in the case of Ca, Mg and Mn is small as they are to a great extent related to the solid phase of the cheese (Renner, 1989; Moreno-Rojas *et al.*, 1992), whilst the Na and the K are generally dissolved and emigrate towards areas with a lower concentrations.

Daily intake estimates

Estimates of the consumption of matured cheese are approximately 5·30 g per person/day in Spain in a total diet of 1387 g (Instituto Nacional de Estadística, 1985). Referring to the mean concentrations of the five elements analysed in cheese at 6 months, the daily intake estimates are: 47 mg/day for calcium, 2 mg/day for magnesium, 2 μg/day for manganese, 71 mg/day for sodium and 8 mg/day for potassium. The densities of nutrients of the minerals studied in cheese for a adult male, with an energy intake of 1800 kcal/day (NRC, 1989) are 889% for calcium, 91% for magnesium, 6–16% for manganese, 450–2163% for sodium and 36% for potassium.

This density of nutrients shows that Manchego-type cheese is an excellent source of calcium; it is well-balanced in magnesium and deficient in manganese (like other dairy products). However, unlike milk, it has a high percentage of sodium and a low percentage of potassium (this modification being produced during manufacture of the cheese) and therefore should not be consumed in excess by people suffering from hypertension. Also, although the ripening of the cheese does not produce significant changes in the densities of the nutrients studied, people with hypertension would find it more beneficial to consume unripened cheese, with the rind removed, as the sodium intake could be reduced compared to that produced by the consumption of ripened Manchego-type cheese.

The intake of Ca in Spain is fairly low, 883 mg/day (Instituto Nacional de Estadística, 1985), partly due to the limited consumption of cheese (11·8 g/day, Instituto Nacional de Estadística, 1985) which, however, is a food widely accepted by Spanish society unlike other dairy products such as milk itself and yoghurt, which are little consumed in Spain (336 ml milk/day and 15·62 g yoghurt/day per person, Instituto Nacional de Estadística, 1985). Considering this greater acceptance of cheese, its consumption should be encouraged as an ideal source of calcium, since cheese constitutes a more bioavailable form of calcium than milk (Fox, 1987) or dairy products in general, and more bioavailable than in salt tablet form (Dupuis *et al.*, 1985). The consumption of adequate amounts of calcium in milk and milk products during childhood and adolescence is a decisive factor in the prevention of osteoporosis (Renner *et al.*, 1991).

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