Food Chemistry 45 (1992) 319–322

Mineral content modifications in Manchego-type cheese during ripening

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(Received 23 May 1991; revised version received and accepted 7 February 1992)

The change in contents of copper, iron and zinc during the ripening of a Manchego-type cheese in cold storage (temperatures below 10°C) was studied for a period of 6 months. The determinations were performed with an atomic absorption spectrophotometer. A two-factor variance analysis showed the existence of statistically significant differences ($p < 0.001$) in the contents of iron, copper and zinc between different portions and over a period of time, both when the concentrations are considered on a fresh weight and dry weight basis. However, certain differences with time were observed on using a Scheffè homogeneity test ($p < 0.05$), depending on whether the mineral content is expressed on a fresh weight or dry weight basis. The daily intake estimates calculated for the three elements were 5·94 μg/g day for copper, 31·1 μg/day for iron and 223·1 μg/day for zinc in Manchego cheese ripened for 6 months.

INTRODUCTION

Cheeses differ markedly not only in their external appearance and organoleptic characteristics, but also in their physicochemical characteristics and mineral contents. The latter in particular can be very variable in different cheeses, depending on the manufacturing process (Coppini *et al.*, 1979) and their distribution throughout the cheese can vary as a result of the ripening process to which they are subjected.

Manchego-type cheese is one of the most representative cheeses in Spain, and can be consumed at different degrees of ripeness, according to the consumer's taste.

What we have tried to do in this study is to determine how the mineral content is modified, more specifically copper, iron and zinc, throughout the ripening period of a Manchego-type cheese. We tried to verify whether there was some type of internal migration of these minerals from areas located at a greater or lesser depth in relation to the surface of the cheese.

MATERIALS AND METHODS

We studied the ripening process of a Manchego-type cheese in a commercial homogeneous batch from a cheese-factory stored (refrigeration at <10°C) from the time of its making, taking monthly samples up to the sixth month. In each monthly sampling two cheeses were extracted. From the centre of each cheese three portions were taken at different depths: the external, middle and internal. Five samples of 10 g each were obtained from each portion. This piecing system was used to assure a certain homogeneity in each portion.

For the analysis of the samples Gabrielli Favretto's (1990) method was followed with certain modifications. From each one of the portions, 10 g of sample were weighed into crucibles and, once the sample was desiccated, it was incinerated in a furnace at 450°C for one night. After cooling, 2 ml of nitric acid (2 N) was added, evaporated on a thermostatic plate and again placed in the furnace at 450°C for 1 h. The recovery of the ash was done with 5 ml nitric acid (2 N) and 20 ml nitric acid (0·1 N) in a volumetric flask (25 ml) and stored in polypropylene flasks under refrigeration.

The determinations were performed with a Perkin-Elmer Model 2380 Atomic Absorption Spectrophotometer. A 10 cm 1-slot burner head and standard air–acetylene flame, and wavelengths of 324·8 nm, 248·3 nm and 213·9 nm for copper, iron and zinc respectively were used. Simple element hollow cathode lamps were used for all elements. The instrument settings and other experimental conditions were in accordance with the manufacturer's specifications. The sensitivity obtained was 0·045 mg/litre; 0·052 mg/litre and

Food Chemistry 0308-8146/92/$05.00

0·440 mg/litre for copper, iron and zinc respectively. The mean recoveries were copper = 92%, iron = 101% and zinc = 95%. For the calculation of the detection limit the criteria of the American Chemical Society (1980) and Mottola (1984) were followed. The concentration limits obtained (minimum concentrations detectable in fresh weight) were 0·015 mg/kg, 0·053 mg/kg and 0·675 mg/kg for copper, iron and zinc respectively.

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 and Figures 1–3 show the mean concentrations per day and portion, of copper, iron and zinc at fresh and dry weight.

A two-factor variance analysis was done to determine if there were statistically significant differences established between the portions and the different times at which the samples were taken. It was verified that differences existed both between the portions and the times in the concentrations of the three minerals under study, expressed both in fresh and in dry weight ($p < 0{\cdot}001$). After this, Scheffè's multiple range analysis was done ($p < 0{\cdot}05$) from which it was possible to distinguish groups by portion in the mean times and by times in the mean portion, which are shown in Tables 1 and 2.

It was seen (Table 1) that there was a clear differentiation in the concentrations of iron (Fig. 2) and zinc (Fig. 3) between the external portion and the other two portions which formed one homogeneous group in the majority of the sampling points studied throughout the time, expressed both on a dry and fresh basis. This difference, which was so marked between the external portion and the rest, could be due to a superficial contamination of iron and/or zinc in the process of the making of the cheese (perhaps because electroplate and iron materials were used for pressing the curd), since

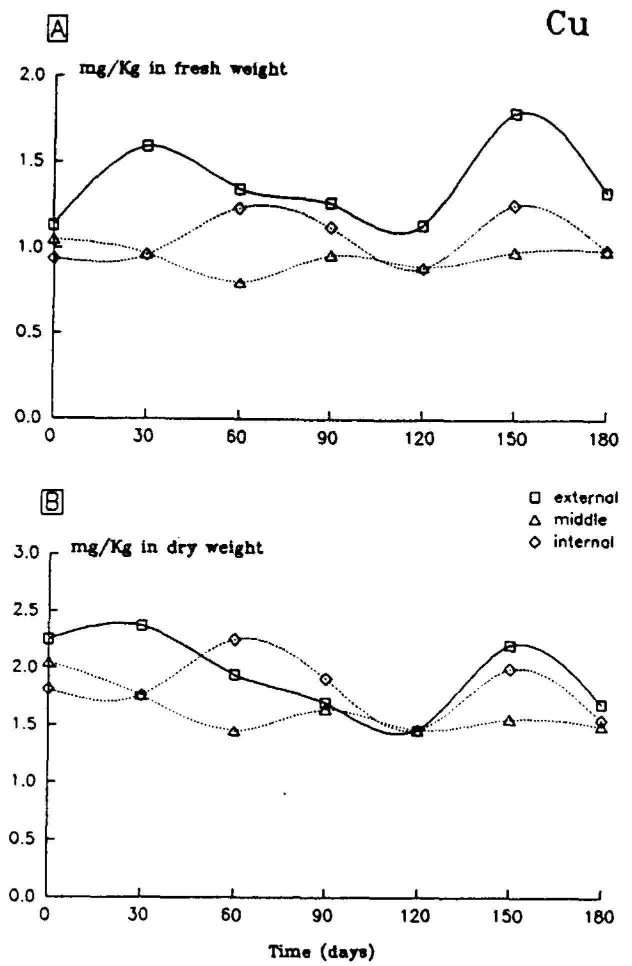

Fig. 1. Copper content change during the cheese ripening in portions: (A) fresh weight; (B) dry weight.

Table 1. Content of moisture, copper, iron and zinc (mean ± SD) expressed in mg/kg dry weight throughout ripening process and portions

Days	Moisture (%)	Copper	Iron	Zinc
0	49·2 ± 1·0	2·04 ± 0·43^{e}	13·36 ± 12·45^{c}	74·9 ± 26·5^{e}
30	41·1 ± 6·1	1·96 ± 0·34de	8·80 ± 4·23^{ab}	67·4 ± 18·6^{d}
60	40·4 ± 6·8	1·88 ± 0·42^{d}	7·80 ± 3·47^{ab}	63·3 ± 16·7^{bc}
90	36·2 ± 7·6	1·74 ± 0·20^{c}	9·20 ± 3·41^{ab}	67·5 ± 27·5^{d}
120	33·7 ± 8·1	1·46 ± 0·07^{a}	7·73 ± 3·31^{a}	60·9 ± 23·9^{b}
150	31·2 ± 8·7	1·92 ± 0·30^{d}	9·23 ± 5·25^{b}	65·9 ± 33·3^{cd}
180	30·2 ± 6·6	1·58 ± 0·12^{b}	8·01 ± 4·19^{ab}	57·8 ± 21·7^{a}
Portions				
External	29·0 ± 10·0	1·94 ± 0·40^{z}	15·63 ± 7·17^{y}	98·0 ± 13·2^{y}
Middle	41·4 ± 4·9	1·63 ± 0·27^{x}	6·05 ± 0·83^{x}	48·8 ± 5·1^{x}
Internal	41·9 ± 4·3	1·82 ± 0·31^{y}	5·80 ± 0·60^{x}	49·8 ± 6·2^{x}

^{a,b,c,d,e} Scheffè homogeneous groups ($p < 0{\cdot}05$) between times.
^{x,y,z} Scheffè homogeneous groups ($p < 0{\cdot}05$) between portions.

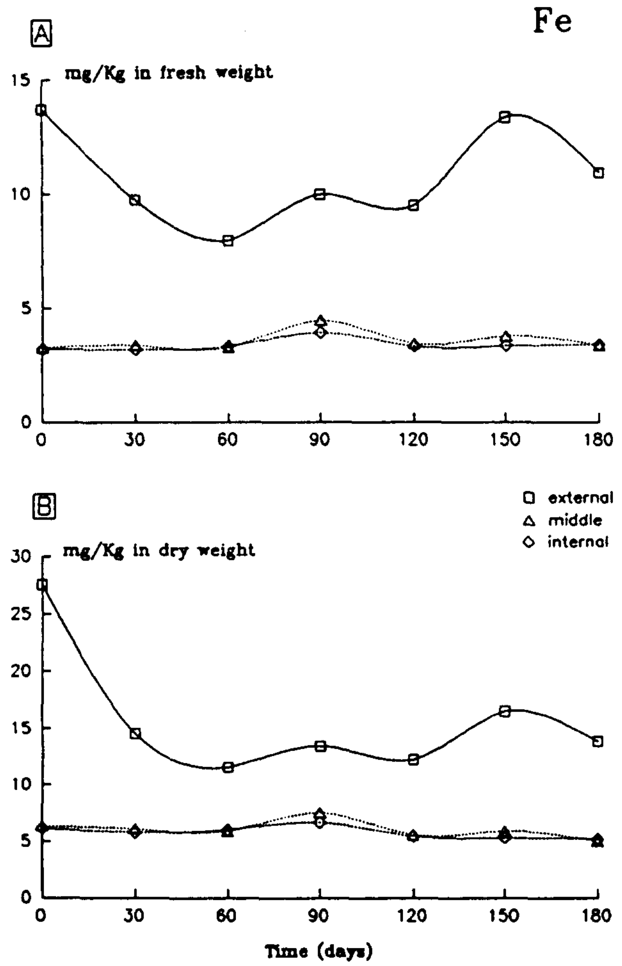

Fig. 2. Iron content change during the cheese ripening in portions: (A) fresh weight; (B) dry weight.

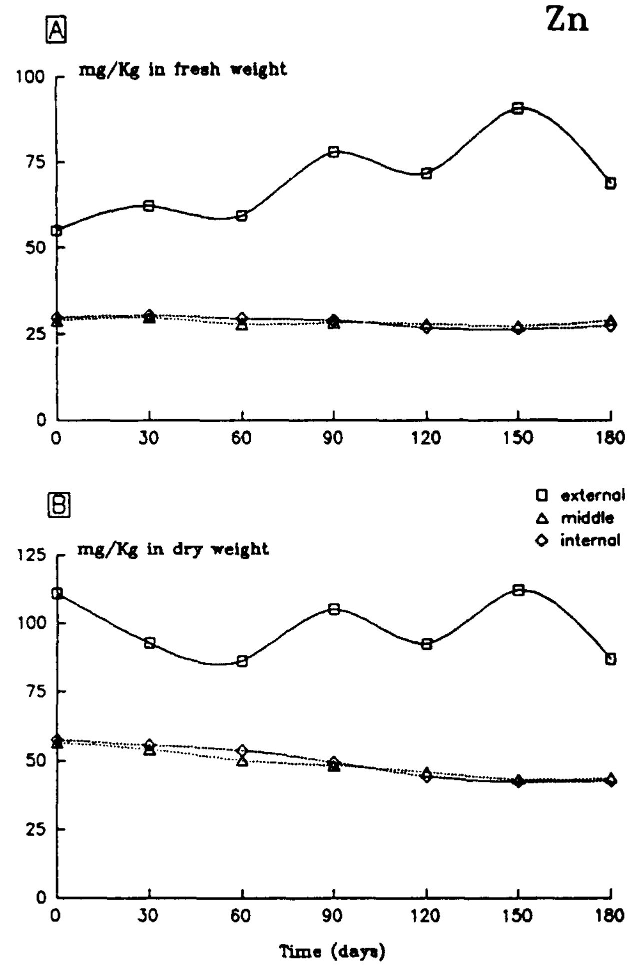

Fig. 3. Zinc content change during the cheese ripening in portions: (A) fresh weight; (B) dry weight.

the concentration of these minerals in the external portion is abnormally high in the whole ripening process.

With regard to the concentrations of copper, no lasting association between portions was observed. However, when expressed on a fresh weight basis (Fig. 1(A)), it was observed that, from the first moment, when the concentrations of the three portions were similar, a certain differentiation was noticed between the external portion and the other two portions, probably due to a more rapid drying of the rind. When the concentrations at dry weight are observed (Fig. 1(B)) this phenomenon is not noticeable.

The references consulted (Table 2) indicated very variable concentrations in the contents of these three trace elements in different cheeses. Gabrielli Favretto (1990) found mean concentrations in cheese of 0·54, 1·76 and 34·6 mg/kg for copper, iron and zinc respectively. Gabrielli Favretto & Pertoldi Marletta (1984) found, for copper, 0·31 mg/kg, and for iron 2·36 mg/kg, in cheese. The copper and iron concentrations obtained by Pertoldi Marletta & Gabrielli Favretto (1983) in cheese were 0·43 and 3·25 mg/kg respectively. Koops *et al.* (1986) indicated a content of zinc in Gouda cheese, 4 months' ripe, of 39·4 mg/kg.

Coppini *et al.* (1979) carried out a study of the maturation of Parmesan cheese at 6, 12 and 18 months made in different geographical areas of Italy. The mean values at 6 months for copper, iron and zinc were 0·99, 1·42 and 38·6 mg/kg of dry matter, respectively, developing in a very different manner in the other two periods depending on the geographical area.

Le Graet & Brulé (1988), in an investigation of the change of mineral content in Camembert-type cheese, studied three portions (rind, subrind and centre) for 19 days under different conditions. The copper content was not appreciably modified during the study period and was 0·50 mg/kg. The iron differed noticeably according to the conditions to which the cheeses were exposed although a marked increase in the concentration in the rind was observed. The latter developed in a clearly independent way with respect to the other two portions which behaved in a similar manner. Zinc also presented a different change in rind when compared to the other two portions which developed similarly.

The estimates made in Spain of the consumption of this type of product are approximately 5·30 g person/day in a total diet of 1387 g (Instituto Nacional

Table 2. Copper, iron and zinc in cheeses reported in references

Author (year): type of cheese	Cu	Fe	Zn
Coppini *et al.* (1979)			
Parmesan (dry weight)[a]			
6 month	8·50–11·40	10·50–17·90	35·5–40·2
12 month	8·60–10·60	10·60–17·20	31·8–35·7
18 month	9·40–11·70	9·80–18·50	34·3–36·8
Gabrielli Favretto (1990)			
Latteria	0·31–1·23	1·21–2·92	25·5–48·9
Gabrielli F. & Pertoldi M. (1984)			
Mozzarella	0·31 ± 0·05	2·36 ± 0·12	
Koops *et al.* (1986)			
Gouda			39·4
Le Graet & Brulé (1988)			
Camembert (19 days)			
Rind	0·50	2·67	57·6
Centre			20·4
Pertoldi M. & Gabrielli F. (1983)	0·43 ± 0·042	3·25 ± 0·348	

[a] Expressed in mg/kg dry weight, remainder fresh weight.

de Estadistica, 1985). Referring to the mean concentrations in cheese at 6 months for the three elements analysed, the daily intake estimates are: 5·94 μg/day for copper, 31·1 μg/day for iron and 223·1 μg/day for zinc. The contributions of nutrients presented by the three minerals studied in fresh cheese for a male adult, with an energy intake of 1800 kcal/day (NRC, 1989) is from 19 to 28% of requirement for copper, 30% for iron and 141% for zinc. These figures indicate that this type of cheese is a poor source of iron and copper whilst it is an excellent source of zinc.

ACKNOWLEDGEMENT

Research work supported by Ministry of Education and Science of Spain, CICYT ALI88-0660.

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