# Changes in the Mineral Content in Cheeses of Different Compositions during 6 Months of Ripening

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**Abstract**: The mineral content of cheese depends on the origin of the milk (cow, ewe, goat) and its ripening. In this work the effect of different factors on the mineral composition and the correlation between minerals (Ca, Fe, Mg, K, Na, and Zn) and the type of milk used are studied. The One-Way ANOVA procedure revealed that the effect of cow's milk was statistically significant on Fe, K, P, and Zn; goat's milk was statistically significant for Fe and Mg, and ewe's milk was statistically significant for K. The effect of the ripening time was statistically significant in all cases, except for Zn; the effect of the season was statistically significant for K, Mg and P and the effect of the year was statistically significant in the case of K, Na, P, and Zn. The percentage of cow's cheese was positively correlated with K and P; the percentage of ewe's cheese was negatively correlated with K, Mg, Na, and P and the percentage of goat's cheese was negatively correlated with Na, and P.

**Keywords**: mineral composition, cows, ewes, goats, ripening, cheese

## INTRODUCTION

The consumption of cheese is of great nutritional interest, due in particular to its composition of micronutrients and especially minerals (LUCAS *et al.* 2008). The mineral content of milk depends on numerous factors, such as: genetic characteristics, the stage of lactation, environmental conditions, the type of pasture, soil contamination etc. (ANGUITA 1996; GAMBELLI *et al.* 1999; PARK 2000; CICHOSCKI *et al.* 2002; PATIÑO *et al.* 2005). The heavy metal content of cheese is variable due to factors such as differences between species, geographical area, characteristics of the manufacturing practices and possible contamination from the equipment during the process (MORENO-ROJAS *et al.* 1994; MENDIL 2006).

The mineral compounds participate in the coagulation; influence the draining of the whey and the texture of the curd and on them properties such as stability to heat and the capacity of coagulation depend (PATIÑO *et al.* 2005).

Particularly, during cheese ripening some of the mineral salts may migrate from the central part towards the external layer of the cheese block or *vice versa* (GAMBELLI *et al.* 1999). Furthermore, changes in the composition and in physical-chemical parameters throughout the manufacture and ripening of cheese are of great importance since they determine not only the nutritional value, but also the organoleptic characteristics and quality (PRIETO *et al.* 2002).

The aim of this study is to determine the effect of different factors – milk composition (cow's, ewe's and goat's), seasonality, month of ripening, year on the content of Ca, Fe, K, Mg, Na, P, and Zn in samples of cheeses of 16 different compositions with known percentages of cow's, ewe's and goat's milk made and monitored over a 6-month ripening period. The milk used was from two years and was collected in winter and summer.

## MATERIAL AND METHODS

***Samples and cheese-making procedure***. To perform the present study a total of 227 cheeses of known composition were elaborated and controlled (Gonzalez *et al.* 2007). Bovine, ovine and caprine raw milk were obtained directly from the producers in Zamora (Spain). Cheeses with different compositions were elaborated, prepared with known, varying amounts of milk from cows, ewes and goats with percentages ranging between 0% and 100%. These were cylindrical, with an initial diameter of 10 cm and a thickness of 5 cm and they were monitored over 6 months (at 0.2, 1, 2, 3, 4, 5, and 6 months), using one of the pieces at each time.

***Analytical methods***. The samples of ground cheese are submitted to desiccation with a heater at 105°C for 24 hours. Once dry, they are ground and submitted to mineralisation in a microwave system measuring the composition in the resulting solution by plasma ICP-optical spectroscopy.

The mineralisation is carried out weighing 0.5 g of dry ground sample, later introducing it into a high pressure capsule. In a first phase 5 ml of $HNO_3$ (c) are added and a potential of 300 watts is applied for 5 minutes. Once the sample is cold another 5 ml of $HNO_3$ (c) and 1 ml of $H_2O_2$ 30% are added applying a potential of 300 watts for 7 minutes. The sample is cooled to room temperature and made up to 100 ml with distilled water and conserved at 4°C until its analysis with ICP. The process is carried out in the Servicio de Análisis Químico de la Universidad de Salamanca (Spain).

***Statistical analysis***. One-Way ANOVA procedure and Pearson's correlation study were carried out with the SPSS 13.0 for Windows software package (SPSS, Inc., Chicago, IL). The effects of year, month of ripening, season, cow's, ewe's and goat's milk were evaluated. Pearson's correlation coefficient is a measure of linear association. This method with a significance test (two-tailed) was used to evaluate the correlations between elements.

## RESULTS AND DISCUSSION

### Chemical composition – Changes in mineral content

Table 1 presents the minimum, maximum, mean and standard deviation for calcium, iron, phosphorus, magnesium, potassium, sodium and zinc found in the chemical analysis. The levels of calcium and phosphorus were more abundant in the cheeses of cow's milk, results which do not coincide with other bibliographical data which show that these two elements are found in similar quantities in milk from goat and cow and are more abundant in ewe's milk (Raynal-Ljutovac *et al.* 2008).

The ratio Ca:P was 2.15; an elevated value compared with those obtained by Park (2000) for goat cheeses and for cow cheeses (Prieto *et al*. 2002); the ratio being close to 1.2 considered normal by Jenness (1980).

The concentration of magnesium does not present variations during the process of ripening and its average levels of concentration (402.3 ppm) are in agreement with those found by Moreno-Rojas *et al.* (1994), Cichoscki *et al.* (2002) and Herrera *et al.*( 2006).

The average concentrations of zinc (57.5 ppm) and iron (201.5 ppm) are above the average de-

Table 1. Chemical composition

| Analyte | N° of samples | Minimum | Maximum | Mean | SD |
|---|---|---|---|---|---|
| Ca (g/kg) | 227 | 4.49 | 40.38 | 8.06 | 3.39 |
| P (g/kg) | 227 | 2.35 | 6.03 | 3.75 | 0.66 |
| K (g/kg) | 227 | 0.62 | 2.17 | 1.25 | 0.34 |
| Na (g/kg) | 227 | 2.76 | 13.92 | 7.93 | 2.52 |
| Fe (ppm) | 227 | 8.18 | 2706.6 | 201.5 | 362.1 |
| Mg (ppm) | 227 | 258 | 687 | 402 | 65 |
| Zn (ppm) | 227 | 18.9 | 401.8 | 57.5 | 40.5 |

scribed by Park (2000) for goat's cheeses. This could be related to the caseinic fraction (95% zinc and 50% iron) as reported by Anguita (1996) and/or with a possible contamination by the utensils and recipients used in the manufacture (Park 2000; Cichoscki *et al.* 2002), which could increase the concentration of Fe and Zn.

The amount of K shows great variability with the breed of the animal, with highest values in cow's cheeses and lowest in ewe's cheeses. The decrease of K with the ripening could be due to the process of draining of the whey (94% according to Cichoscki *et al.* (2002)) and acidification (Almenara *et al.* 2007). The average content of potassium 1.25 g/kg coincides with those described by Herrera *et al.* (2006).

The elevated concentration of sodium throughout the ripening process with an average value of 7.93 g/kg is principally due to the addition of salt during the process and throughout ripening, coinciding with that observed by Gambelli *et al.* (1999). With regard to the seasonal variability, the cow's cheeses elaborated in winter present lower concentrations of sodium than the cheeses elaborated with goat's milk. In contrast to what occurs with cheeses elaborated in summer, the highest concentrations of sodium are present in cow's cheeses and the lowest are present in goat's cheeses.

### Statistical analysis of the data

Table 2 shows the effects of the factors studied by One-Way ANOVA procedure for the different minerals at a level of significance of 95%. The factor year shows a significant effect in the concentrations of potassium, sodium, phosphorus and zinc. The factor month of ripening has significant effects in the concentrations of all the studied minerals with the exception of Zn, a phenomenon which

Table 2. ANOVA

| Effect | Ca | P | Fe | Mg | K | Na | Zn |
|---|---|---|---|---|---|---|---|
| Year | 0.809 | 0.000* | 0.332 | 0.548 | 0.000* | 0.000* | 0.008* |
| Month | 0.026* | 0.000* | 0.012* | 0.000* | 0.000* | 0.000* | 0.324 |
| Season | 0.099 | 0.000* | 0.766 | 0.003* | 0.000* | 0.053 | 0.639 |
| Cow | 0.095 | 0.000* | 0.015* | 0.247 | 0.000* | 0.534 | 0.045* |
| Ewe | 0.454 | 0.313 | 0.074 | 0.236 | 0.000* | 0.360 | 0.467 |
| Goat | 0.075 | 0.086 | 0.046* | 0.000* | 0.916 | 0.101 | 0.355 |

*significant effect at 95%

Table 3. Correlations between the mineral components

| Calcium | | Phosphorus | | Magnesium | | Potassium | | Sodium | | Zinc | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Level of significance | | | | | | | | | | | |
| 99% | 95% | 99% | 95% | 99% | 95% | 99% | 95% | 99% | 95% | 99% | 95% |
| P | Mg | Ca | | K | Ca | Mg | | K | Zn | | Ca |
| 0.296 | 0.167 | 0.296 | | 0.384 | 0.167 | 0.384 | | 0.445 | –0.168 | | 0.142 |
| | Zn | K | | P | | Na | | P | | | Na |
| | 0.142 | 0.622 | | 0.582 | | 0.445 | | 0.203 | | | –0.168 |
| | | Mg | | | | P | | | | | |
| | | 0.582 | | | | 0.622 | | | | | |
| | | Na | | | | | | | | | |
| | | 0.203 | | | | | | | | | |

Pearson Correlation Coefficient

could be due to the different degrees of mobility of the different elements.

The seasonality (winter/summer) has a significant influence on the concentration of potassium, magnesium and phosphorus. The seasonal variation in the composition of the milk, as is known, is due to changes in the bio-availability and quality of the pastures throughout the year and to an increase in the proteolytic activity associated to the age of lactation of the animal.

The results show that in the cheeses elaborated the percentage of cow's milk has a significant effect on the concentrations of iron, potassium, phosphorus and zinc. The percentage of ewe's milk has a significant effect on the concentration of potassium and finally the percentage of goat's milk originates a significant effect on the concentrations of iron and magnesium.

### Relationships between elements the type of milk and mineral concentration

The correlations between elements were studied and the results are shown in Table 3. The concentration of Ca was positively correlated at the 0.01 level (2-tailed) with P and at the 0.05 level (2-tailed) with Mg and Zn, which is in agreement with Moreno-Rojas *et al.* (1994) and Gambelli *et al.* (1999). The K was positively correlated at the 0.01 level (2-tailed) with Mg, Na and P, similar data were obtained by Gambelli *et al.* (1999); Mg was positively correlated at the 0.01 level (2-tailed) with P and Na was positively correlated at the 0.01 level (2-tailed) with P and negatively correlated at the 0.05 level (2-tailed) with Zn. Iron was the only mineral not correlated with other minerals in the study.

The correlations between the type of milk and mineral concentration were evaluated and the results are shown in Table 4. The results revealed that the percentage of cow's cheese was positively correlated at the 0.01 level (2-tailed) with K and P; the percentage of ewe's cheese was negatively correlated at the 0.01 level (2-tailed) with K and at the 0.05 level (2-tailed) with Mg, Na and P, and the percentage of goat's cheese was negatively correlated at the 0.01 level (2-tailed) with Na and at the 0.05 (2-tailed) level with P.

Table 4. Correlation between the type of milk and mineral concentration

| Cow's milk | | Ewe's milk | | Goat's milk | |
|---|---|---|---|---|---|
| Level of significance | | | | | |
| 99% | 95% | 99% | 95% | 99% | 95% |
| K | | K | Mg | Na | P |
| 0.318 | – | –0.327 | –0.136 | –0.192 | –0.137 |
| P | – | | Na | | |
| 0.192 | | | –0.157 | | |
| | | | P | | |
| | | | –0.152 | | |

Pearson Correlation Coefficient

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