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Effect of processing on contents and relationships of mineral elements of milk

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The effects of pasteurization, sterilization and, drying of milk on the contents of Cu, Fe, Zn, Mn, Ca, Mg, Na, and K at different stages of these processes were studied. Determinations were made by atomic-absorption spectrophotometry with flame and emission. The existence of statistically significant differences ($p < 0.001$) for Cu and Fe is observed with a tendency to decrease slightly during pasteurization and sterilization. In the drying process, statistically significant differences were observed ($p < 0.001$) for all the elements. By a Scheffé multiple-range analysis, the formation of a single homogeneous group composed of raw and homogenized milk was observed for all the mineral elements. For Fe, Ca, Na, and K, two homogeneous groups were formed, one of concentrated skimmed milk and the other of powdered milk. The relationships between the mineral elements investigated in the different processes were studied by multivariate-factor analysis.

INTRODUCTION

The mineral content of milk may vary greatly and is influenced by numerous factors involved in its secretion from the mammary gland, such as the breed of animal and time of year (Tiscornia, 1977; Moreno-Rojas *et al.*, 1993). The mineral content may also vary because of its handling by humans (Moreno-Rojas *et al.*, 1991). Among these factors, the technological processes to which the milk is subjected to obtain a more prolonged shelf life could cause alterations in the concentrations of minerals present in that milk. The effects produced by the processes of sterilization, pasteurization, and drying on the contents in milk of copper (Cu), iron (Fe), zinc (Zn), manganese (Mn), calcium, (Ca), magnesium (Mg), sodium (Na), and potassium (K) are now studied.

MATERIALS AND METHODS

Samples

Samples of fresh, pasteurized, and sterilized milk (250 ml) were taken from the central milk depot, Lactaria Andaluza SA (Seville), and samples in the process of drying (100 g) from Uniasa (Granada) during routine production. All the samples from each process corresponded to the same storage tank and the following procedures were undertaken.

(a) Milk-pasteurization process
In order to verify the technological effect of pasteurization on the mineral content in milk, ten samples of raw milk, ten of pre-heated milk, and ten after pasteurization were taken.

(b) Milk-sterilization process
As previously, ten samples of raw milk, ten of pre-heated milk, and ten after sterilization were taken in order to verify the effect on the mineral content.

(c) Manufacturing process of powdered milk
In order to study the effect of the drying of the milk on its mineral content, ten samples of natural milk, ten of pasteurized milk, ten of concentrated-skimmed milk and ten of powdered milk were taken.

Sample analysis

The samples were analyzed by the method of Gabrielli Favretto (1990), with certain modifications. samples (50 g of fluid milk or 10 g of concentrated milk or 5 g of powdered milk) were weighed into crucibles, dried and incinerated in a furnace at 450°C for 16 h. After cooling, 2N nitric acid (2 ml) was added, and the sample was dried on a thermostatic plate and again placed in the furnace at 450°C for 1 h. The ash was recovered in 5 ml 2N $HN0_3$, diluted to volume in a 25-ml volumetric flak with 0·1N HNO_3, and stored in polypropylene flasks under refrigeration. For Ca, the solution was diluted, 1:100, and lanthanum chloride ($LaCl_3.7H_20$) was added to give a 0·27% final solution.

Analyses were performed by using a Perkin–Elmer Model 2380 atomic-absorption spectrophotometer, with an air–acetylene flame. Single-element hollow-cathode lamps were used for all elements except for Na and K, which were determined by emission by using the same instrument. Deuterium background correction were used for Mn determination. For each element being determined, the analysis included duplicate analysis 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 the calculation of the detection limit (3SD), the definition and criteria of the IUPAC were followed (Long & Winefordner, 1983; Analytical Methods Committee, 1987).

The sensitivities (in μg/ml) obtained for each element were 0·044, 0·072, 0·370, 1·375, 0·089, 0·034, 6·42, and 6·70 for Cu, Fe, Zn, Ca, Mg, Mn, Na, and K, respectively. In terms of minimum concentrations detectable in fluid milk at fresh weight, the concentration limits obtained corresponded to (μg/g): 0·003, 0·015, 0·050, 0·002, 9·4, 1·22, 100, and 50·0 for Cu, Fe, Zn, Mn, Ca, Mg, Na, and K, respectively. Mean recoveries (ten replicates) in Non-fat Milk Powder (NBS 1549) were Cu, 97·1%; Fe, 101·1%; Zn, 100·3%; Mn, 98·5%; Ca, 102·0%; Mg, 101·4%; Mn, 98·5%; Na, 104·1%, and K, 96·3%.

Statistical analysis

Data obtained from the chemical analysis of the samples were evaluated statistically by using a two-factor analysis of variance with a Scheffé multiple-range test, correlation, and multifactorial analysis (Snedecor & Cochran, 1971; Chatfield & Collins, 1980; Piggott, 1986; Molina-Alcala *et al.*, 1992).

RESULTS AND DISCUSSION

Table 1 shows basic statistics of the mineral content of milk at different stages of its pasteurization process. Table 2 lists statistics for the sterilization process and Table 3 those for the drying process.

In a study made by Galeno (1985), although the technological processes of milk conservation were not specifically investigated, data for whole, raw, pasteurized, and sterilized milk were reported in which small differences in the mineral contents of the different types of milk were observed. Slightly lower concentrations of Fe and Cu were found in the pasteurized and sterilized milk than in the raw milk. The concentrations of Zn were also seen to be lower in the sterilized milk, although, they were rather higher in the pasteurized milk than in the raw milk.

Partly coinciding with Galeno's results, in this work, somewhat lower mean concentrations in pasteurized and sterilized milk than in raw milk for these three mineral elements were obtained except for Cu in sterilized milk and Zn in pasteurized milk, which showed the same concentrations as in raw milk. In the drying process the percentage of fatless dry matter increased between zero and eleven times depending on the degree of desiccation and on the initial and final percentages of fat in the milk. This is the proportion found both in our data and in the majority of those consulted in the literature (Wong *et al.*, 1978; Varo *et al.*, 1980), for all the mineral elements investigated.

One-factor variance analyses were carried out on the mineral contents of the milk throughout the pasteurization process, and statistically significant differences were found ($p < 0.001$) for Cu and Fe and with a lower degree of significance ($p < 0.05$), for Mn owing to a slight decrease in the concentrations during the process. The one-factor variance analyses made in the sterilization process showed statistically significant differences ($p < 0.001$) for Cu, Fe, and Zn, which were also due to a slight diminution in the concentrations throughout the proccess.

Scheffé multiple-range analyses ($p < 0.05$) were carried out on the elements that had been seen to have statistically significant differences throughout any of the processes, in order to establish homogeneous groups. In all the elements in which differences in the

Table 1. Mineral contents of milk (mean ± SD) expressed in mg/kg fresh weight throughout the pasteurizing process

Milk	Cu	Fe	Zn	Mn	Ca	Mg	Na	K
Raw (n = 10)								
Mean	0·16^{b}	0·46^{c}	3·70^{a}	0·020^{b}	1 251^{a}	116^{a}	592^{a}	1 709^{a}
S.D.	0·02	0·10	0·22	0·004	48	3	18	57
Pre-heated (n = 10)								
Mean	0·12^{a}	0·41^{b}	3·74^{a}	0·020^{b}	1 241^{a}	115^{a}	598^{a}	1 686^{a}
S.D.	0·01	0·03	0·03	0·003	39	2	19	40
Pasteurized (n = 10)								
Mean	0·12^{a}	0·30^{a}	3·63^{a}	0·017^{a}	1 289^{a}	115^{a}	609^{a}	1 685^{a}
S.D.	0·01	0·03	0·06	0·003	60	5	19	34
Total (n = 30)								
Mean	0·14	0·39	3·69	0·019	1 260	115	600	1 693
S.D.	0·02	0·08	0·14	0·003	52	3	19	44

^{a,b,c} Scheffé homogeneous groups ($p < 0.05$) for each element (fresh weight).

Table 2. Mineral contents of milk (mean ± SD) expressed in mg/kg fresh weight throughout the sterilizing process

Milk	Cu	Fe	Zn	Mn	Ca	Mg	Na	K
Raw (n = 10)								
Mean	$0{\cdot}11^{a}$	$0{\cdot}40^{c}$	$3{\cdot}61^{b}$	$0{\cdot}025^{a}$	$1\,283^{a}$	113^{a}	601^{a}	$1\,746^{a}$
S.D.	0·01	0·03	0·19	0·005	67	6	16	66
Pre-heated (n = 10)								
Mean	$0{\cdot}11^{a}$	$0{\cdot}33^{b}$	$3{\cdot}57^{b}$	$0{\cdot}023^{a}$	$1\,281^{a}$	113^{a}	607^{a}	$1\,694^{a}$
S.D.	0·02	0·04	0·10	0·003	39	4	16	67
Sterilized (n = 10)								
Mean	$0{\cdot}10^{a}$	$0{\cdot}30^{a}$	$3{\cdot}26^{a}$	$0{\cdot}024^{a}$	$1\,283^{a}$	114^{a}	603^{a}	$1\,693^{a}$
S.D.	0·01	0·03	0·12	0·004	54	6	17	24
Total (n = 30)								
Mean	0·11	0·34	3·48	0·024	1 282	113	604	1 711
S.D.	0·05	0·05	0·21	0·004	52	5	16	59

^{a,b,c} Scheffé homogeneous groups ($p < 0{\cdot}05$) for each element (fresh weight).

pasteurization or sterilization process were determined, it was verified that the mineral content in raw and treated milk formed different homogeneous groups and that the pre-heated milk belonged, depending on the circumstances, to one or other of the groups or, in the case of Fe, formed an intermediate group.

The one-factor variance analyses carried out on the drying process by using the mineral concentration at fresh weight indicated (as was to be expected) statistically significant differences for all the elements ($p < 0{\cdot}001$), and, by Scheffé multiple-range analyses ($p < 0{\cdot}05$), three homogeneous groups were formed for all the elements (Table 3), one by the raw and homogenized pre-heated milk, another by skimmed-concentrated milk and other by the dried milk. These results were mainly due to the differences in moisture between the products so it was decided to carry out a new study of variance analyses ($p < 0{\cdot}05$) on a dry-weight basis, which demonstrated the formation of a single homogeneous group for all the elements (Table 3) in raw and homogenized milk. For Cu, Zn, Mn, and Mg, concentrated-skimmed and dried milk formed a single homogeneous group, and two groups in the rest of the elements. The differentiation between the liquid milks and the other two may be due to the skimming produced before the concentration rather than to the drying process itself.

Study of the relationship between the mineral elements

In order to determine the relationship between the different mineral elements investigated throughout the processes studied, two types of successive statistical studies were carried out. In the first place, the degree of linear correlation between the elements investigated was estimated. In order to obtain a more simplified view of the relationship between the elements, multivariate factor analyses were carried out.

A correlation study of both the pasteurization process and the sterilization process showed a large number of non-significant coefficients. In the pasteurization process, the elements that showed high, positive correlation coefficients with each other were Cu, Fe, Zn, Mn, and K (with the exception of Fe with K), but the relationship between the remaining elements was not clear, as between the elements in the sterilization process.

The multifactorial analysis done on the pasteurization process indicated that only the first two factors possessed eigen values higher than 1 (78·9% variability). The first factor gives a result of two groups of elements,

Table 3. Moisture and mineral contents of milk (mean ± SD) expressed in mg/kg fresh weight throughout the drying process

Milk	Moisture	Cu	Fe	Zn	Mn	Ca	Mg	Na	K
Raw (n = 10)									
Mean	89·2	$0{\cdot}13^{aX}$	$0{\cdot}35^{aX}$	$3{\cdot}90^{aX}$	$0{\cdot}026^{aX}$	$1\,293^{aX}$	110^{aX}	541^{aX}	$1\,617^{aX}$
S.D.	0·1	0·01	0·01	0·11	0·003	61	7	5	24
Homogenized-heated (n = 10)									
Mean	89·2	$0{\cdot}12^{aX}$	$0{\cdot}35^{aX}$	$4{\cdot}11^{aX}$	$0{\cdot}027^{aX}$	$1\,332^{aX}$	111^{aX}	548^{aX}	$1\,687^{aX}$
S.D.	0·1	0·01	0·02	0·12	0·003	29	5	4	36
Skimmed-concentrated (n = 10)									
Mean	53·5	$0{\cdot}63^{bY}$	$1{\cdot}62^{bY}$	$21{\cdot}6^{bY}$	$0{\cdot}140^{bY}$	$6\,631^{bY}$	613^{bY}	$2\,800^{bZ}$	$9\,436^{bZ}$
S.D.	0·01	0·07	0·06	0·40	0·016	194	33	25	251
Milk powder (n = 10)									
Mean	4·5	$1{\cdot}28^{cY}$	$3{\cdot}44^{cZ}$	$44{\cdot}5^{cY}$	$0{\cdot}308^{cY}$	14329^{cZ}	$1\,256^{cY}$	$5\,600^{cY}$	$18\,764^{cY}$
S.D.	0·3	0·06	0·12	0·6	0·024	249	39	50	414

^{a,b,c} Scheffé homogeneous groups ($p < 0{\cdot}05$) for each element (fresh weight).
^{X,Y,Z} Scheffé homogeneous groups ($p < 0{\cdot}05$) for each element (dry weight).

one with high values formed by Zn, Mn, Fe, Cu, and K, and the other group (with values close to zero) formed by Na, Ca, and Mg. On introducing the second factor, a disintegration of the groups occurred; the Fe clearly broke away from the first group and so, to a certain degree, did the Cu.

A multifactorial analysis on the sterilization process showed that only the first factor had a value itself of over 1. This first factor caused proximity between the Fe, K, and Zn but the remaining elements disintegrated. The action of the second factor only increased the disintegration by separating the Zn from the first group formed and separating the others even more.

In the studies of relationships between elements in the drying process, moisture was also introduced as a variable since it was assumed that there was a possible interaction of the moisture with the elements investigated in this process and, indeed, in the correlation matrix, it was verified that there were negative coefficients of over 0·9 ($p < 0{\cdot}001$) between the moisture and all the elements. At the same time, correlation coefficients of over 0·9 ($p < 0{\cdot}001$) were also found between all the elements, but these were positive. This fact showed that the process affected all the elements, in the same way, i.e. opposite to the effect on the moisture content, this being quite logical in view of the sharp reduction in the water content that had been produced. A multifactorial analysis showed a single factor as causing, 99·9% variability, and the distribution with respect to this factor of the variables situated all the elements on the positive side and the moisture on the opposite side. This single-factor distribution made a graph unnecessary.

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