

Quality control of milk and dairy products

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Abstract: The aim of this study was to investigate the quality of raw milk samples (cow, goat and sheep) and dairy products samples (yoghurt, cream) collected from private manufacturers and commercial pasteurized cow milk and dairy products samples. To assess the quality control of these samples was determined the total acidity, the pH, the proteins content and other specific parameters. Also, in this purpose were identified the antiseptic preservatives. The Cd, Cu, Cr, Fe, Mn, Mg, Pb, Zn levels were measured in milk and dairy products samples by flame atomic absorption spectrometry (FAAS). This study demonstrates that, in the analyzed milk and dairy products samples, among toxic metals only lead has been found in high concentration. At present, the CE Regulation no. 1881/2006 establishes a limit for Pb in raw milk of 0.02 mg/kg w.w. and 0.1 mg/kg w.w. for fats and fat milk. The Pb concentrations found in raw milk were below MRLs. In pasteurized milk and dairy products Pb concentrations were higher than MRLs only in two samples: one of pasteurized milk (0.05 mg/kg), respectively one of yoghurt (0.2 mg/kg).

Keywords: milk, dairy products, quality control, FAAS

1. Introduction

In recent decades an increasingly important role in the human diet has been attached to milk and dairy products (yoghurt, cream).

The heat treatment of milk is considered the most crucial process in the dairy industry. The quality of milk is affected by these heating treatments as a consequence of the interaction between carbohydrates and proteins or Maillard reaction [1].

Quality control is required at each step in the production of milk and dairy products to ensure safety of food and to show compliance with regulatory and customer requirements [2].

Inorganic contaminants, such as metals arise from various environmental sources. Some of them are nutritionally essential at lower levels (copper, zinc, iron, chromium, manganese etc.) and others are significant food contaminants (cadmium and lead) [3-4]. Measurements of essential and/or potential toxic elements are also very helpful in assessment of quality of milk during its manufacturing treatment and production.

Typically, for total concentration measurements of metals in milk by means of

different spectrometric detection techniques [5, 6], samples are digested prior analysis. The most frequently used digestion procedures have been the traditional dry ashing and wet digestion that allow destruction of organic matter of the sample [7].

The goal of this study was to investigate the quality of raw milk samples (cow, goat and sheep) and dairy products samples (yoghurt, cream) collected from private manufacturers and commercial pasteurized cow milk and dairy products samples. To assess the quality control of these samples was determined the pH for milk samples, total acidity and the proteins content for all milk and dairy products samples analyzed in this study. Also, in this purpose were identified the antiseptic preservatives. To reveal the presence of antiseptic preservatives: salicylic acid, formaldehyde, sodium hydrogen carbonate and gelatin were used identification reactions. The presence of starch and egg powder was followed because usually these common forgeries are introduced in cream.

Flame atomic absorption spectrometry (FAAS) due to its relatively low cost and excellent analytical performances is probably the most widely used technique for analyzing a variety of

metals in food. In this study, samples of milk and dairy products were analyzed to determine their content in Cd, Cu, Cr, Fe, Mn, Mg, Pb, Zn.

2. Experimental

The nitric acid (65%) and hydrogen peroxide solutions used were of ultrapure grade, purchased from Merck.

The stock standard solutions of Cd, Cu, Cr, Fe, Mn, Mg, Pb, Zn at concentration of 1000 μ g/mL and all the other chemicals were obtained from Merck (Germany). Deionized water was used for the preparation of all solutions.

All glassware was initially washed with detergent and water, then the glassware was rinsed several times with deionized water and dried.

2.1. Sampling

The raw milk samples (cow, goat and sheep) and dairy products samples (yoghurt, cream) were collected from private manufacturers and commercial pasteurized cow milk and dairy products samples were collected from local market in Constantza, Romania.

Basic information about the milk and dairy products samples are presented in **Table 1**.

Table 1. Studied milk and dairy products

Label	Samples	Production
RM1	Raw cow milk	Private manufacturer
RM2	Raw goat milk	Private manufacturer
RM3	Raw sheep milk	Private manufacturer
PM1-5	Pasteurized cow milk	Commercial
Y1	Yoghurt	Private manufacturer
Y2	Yoghurt with fruits	Commercial
Y3-Y7	Yoghurt	Commercial
C1	Cream	Private manufacturer
C2-C3	Cream	Commercial

2.2. Analysis of sample

The pH measurement of milk samples was conducted using pH/ISE meter, Model Consort 530.

The antiseptic preservatives (acetone, salicylic acid, formaldehyde, sodium hydrogen carbonate,

and gelatin) were revealed by the identification reactions. These antiseptic preservatives were identified in all samples, except acetone which was identified only in milk samples.

The presence of acetone in milk samples was indicated by reaction with sodium nitroprusside in ammonia medium, when a violet complex occurs.

The salicylic acid was identified by reaction with diluted solution of FeCl₃ when is observed a violet coloration.

To identify formaldehyde, the samples were treated with sulfuric acid to precipitate proteins. Then the mixture was subjected to distillation and in the distillate was identified the formaldehyde by reaction with phenol, which led to the formation of a red ring on the surface.

The sodium hydrogen carbonate compound was identified by reaction with bromothymol blue when the coloration varies from green-yellow to blue.

Using the reaction with picric acid it can be identified the gelatin. When gelatin is found in large quantities it appears a precipitate and when gelatin is found in small quantities it appears a opalescent yellow coloration.

The presence of hydrogen peroxide in dairy products samples was evidenced by the reaction with potassium dichromate in acid medium when at the contact area appears a blue green ring.

The identification of peroxidase in milk samples was made by high pasteurization control test based by the reaction with phenol or aromatic amines. A dark blue coloration indicates the improper pasteurization of the sample containing raw milk.

Starch from the cream samples was identified by the blue coloration given in the reaction with iodine in potassium iodide. The adding of egg in cream samples can be highlighted by the reaction of the sample with acetic acid when the sample coagulates.

The measurements of total acidity, proteins content, hydrogen peroxide content and metallic ions (Cd, Cu, Cr, Fe, Mn, Mg, Pb, Zn) were realized by the following techniques:

- titrimetric method with NaOH as titrant for determining the total acidity;

- titrimetric method with $\text{Na}_2\text{S}_2\text{O}_3$ as titrant for determining hydrogen peroxide content of milk samples;
- Kjeldahl method for proteins content;
- the flame atomic absorption spectrometry for determining metals, after a mineralization step.

To obtain a finally solution suitable for the introduction in the spectrometer is necessary a mineralization step. In this context milk and dairy products samples were submitted digestion with 8 mL HNO_3 and 10 mL H_2O_2 at 150°C in a Digesdhal device provided by Hach Company. After the complete digestion, the samples solution was filtered, transferred quantitatively to 50 mL volumetric flasks and brought to volume with deionized water. Then Fe, Mn, Mg and Zn were determined by FAAS in air/acetylene flame using standard calibration curve. Analyses were made in triplicate and the mean values are reported.

For the determination of eight essential elements (Cd, Cu, Cr, Fe, Mn, Mg, Pb, Zn) the flame atomic absorption spectrometer Shimadzu AA6500 was used. Monoelement hollow cathode lamps were employed to measure the elements, except the copper which was measured using multi element hollow cathode lamp. The acetylene was 99.999% purity at a flow rate 1.8-2.0 L/min. The characteristics of metal calibration curves are presented in **Table 2**.

Table 2. Characteristics of metal calibration curves

Metal	λ , nm	Concentration range (ppm)	Correlation coefficient
Cd	228.8	0.008 - 1.600	0.9999
Cu	324.7	0.010 - 1.200	0.9990
Cr	357.9	0.020 - 3.000	0.9874
Fe	248.3	0.020 - 4.000	0.9976
Mn	279.5	0.008 - 1.600	0.9984
Mg	289.2	0 - 15.000	0.9748
Pb	282.3	0.002 - 6.000	0.9950
Zn	213.9	0.016 - 0.510	0.9932

3. Results and discussions

Immediately after the collection of milk samples, the pHs of each sample were determined. The pH varies in the range 6.2-7.0. These values are comparable with those encountered in other milk samples in literature [8]

One objective of this study was to investigate the presence of antiseptic preservatives of the analyzed milk and dairy products samples. Following the identification reactions it was observed that acetone and salicylic acid weren't present in any samples. Also, starch and egg powder weren't identified in any cream samples.

Formaldehyde was present in one pasteurized milk sample (PM3) and in four yoghurt samples (Y2, Y4, Y6 and Y7).

In four pasteurized milk samples (PM1-PM4) and in two yoghurt samples (Y2 and Y6) it was observed the appearance of an opalescent yellow coloration, which demonstrates the presence of gelatin in small quantities in these samples.

The milk samples with high acidity cannot be pasteurized. In this case the NaHCO_3 compound is usually added to neutralize the lactic acid. This compound was identified by reaction with bromothymol blue. The coloration varies from green-yellow to blue depending on quantity of NaHCO_3 in milk sample according to the **Table 3**. As it can be seen from the **Table 4** the presence of NaHCO_3 was detected only in two pasteurized milk samples, in small quantities.

Table 3. Relationship between the amount of NaHCO_3 in milk samples and the coloration formed

Quantity of NaHCO_3 (%)	Coloration
-	yellow
0.03	greenish
0.05	dark green
0.07	blue - green
0.30	greenish blue

Table 4. The quantity of NaHCO_3 in milk samples

Sample	Amount of NaHCO_3 (%)
RM1	-
RM2	-
RM3	-
PM1	0.03
PM2	-
PM3	-
PM4	-
PM5	0.03

The presence of peroxidase in milk shows if these samples are improper pasteurized or if the samples contain raw milk. The identification

reaction was positive for the raw milk samples, which was expected and for only one pasteurized milk sample (PM3).

Hydrogen peroxide was identified in three yoghurt samples (Y3, Y4, Y7) and wasn't found in any cream samples. In case of milk samples, the hydrogen peroxide was found in only one pasteurized milk sample (PM3 – 0.054 mg/Kg).

In **Table 5** the amount of proteins found in the all analyzed samples is reported. The amount of proteins in the milk and dairy products samples revealed that the analyzed samples of the present study contained lower amounts than those values reported in commercial goat milk products (2.92% in fluid milk and 3.99% in yoghurt) [9].

Table 5. The amount of proteins in milk and dairy product samples

Sample	Amount of proteins (%)
RM1	0.313
RM2	0.047
RM3	0.031
PM1	0.011
PM2	0.025
PM3	0.031
PM4	0.025
PM5	0.027
Y1	0.035
Y2	0.035
Y3	0.037
Y4	0.040
Y5	0.028
Y6	0.017
Y7	0.042
C1	0.043
C2	0.027
C3	0.023

From **Table 6** it can be observed that the highest values of total acidity there were registered for raw milk samples. The total acidity is expressed in Torner grade which represents the volume of NaOH necessary to neutralize 100 mL of milk.

The concentrations (mg/kg) of essential and/or potential toxic elements in the milk and dairy product samples are reported in **Tables 7** and **8**: the values below detection limits are shown with a less than (<) sign before the detection limit.

The precision (expressed as standard deviation SD) of the results was determined from three replicates of homogenized samples, giving a good standard and precision for the analytical results of essential elements obtained by FAAS.

Table 6. The values of total acidity in milk samples

Sample	Total acidity (Torner grade)
RM1	19.9
RM2	20.0
RM3	21.0
PM1	17.0
PM2	17.0
PM3	18.0
PM4	19.5
PM5	21.0

Table 7. Cd, Cu, Cr and Pb in milk and dairy product samples (mg/Kg)

Sample	Cd	Cu	Cr	Pb
RM1	0.001	0.096	0.085	0.020
RM2	0.005	0.172	0.093	<0.0049
RM3	0.002	0.137	0.079	<0.0049
PM1	0.007	0.187	0.089	<0.0049
PM2	0.011	0.209	0.062	<0.0049
PM3	0.005	0.210	0.073	<0.0049
PM4	0.004	0.141	0.057	0.054
PM5	0.010	0.092	0.067	<0.0049
Y1	0.093	2.057	0.417	<0.0049
Y2	0.259	3.001	0.423	<0.0049
Y3	0.161	2.040	0.170	0.200
Y4	0.159	1.061	0.457	<0.0049
Y5	0.052	1.610	0.279	<0.0049
Y6	0.110	2.870	0.375	0.100
Y7	0.152	0.894	0.425	<0.0049
C1	0.234	1.459	0.253	<0.0049
C2	0.203	2.577	0.357	<0.0049
C3	0.302	0.650	0.279	<0.0049

This study demonstrates that, in the analyzed milk and dairy products samples, only lead, among toxic metals, has been found in high concentrations. At present, the CE Regulation no. 1881/2006 establishes a limit for Pb in raw milk of 0.02 mg/kg w.w. and 0.1 mg/kg w.w. for fats and fat milk [10]. The Pb concentrations found in raw milk were below MRLs. In pasteurized milk and dairy products Pb concentrations were higher than MRLs

only in two samples: one of pasteurized milk (PM4 - 0.05 mg/kg), respectively one of yoghurt (Y3 - 0.2 mg/kg).

Table 8. Fe, Mn, Mg and Zn in milk and dairy product samples (mg/Kg)

Sample	Fe	Mn	Mg	Zn
RM1	1.003	0.014	41.460	1.425
RM2	0.835	0.057	72.596	2.457
RM3	1.013	0.042	64.473	2.358
PM1	0.678	0.012	70.478	3.063
PM2	1.247	0.060	62.830	1.126
PM3	0.973	0.043	59.753	2.135
PM4	0.825	0.020	68.247	2.919
PM5	0.837	0.036	61.732	2.047
Y1	8.732	1.625	235.340	5.835
Y2	19.948	4.888	239.730	7.350
Y3	11.760	1.373	178.940	3.680
Y4	7.320	1.548	173.770	3.889
Y5	7.777	1.015	158.29	1.356
Y6	9.926	1.278	246.130	6.630
Y7	6.689	0.730	189.600	4.514
C1	5.557	0.443	153.750	0.253
C2	7.956	0.541	186.510	0.357
C3	3.972	0.121	138.970	0.279

Cd and Cu concentrations detected in raw milk samples were lower than those detected in raw bovine milk reported in literature (0.001 - 0.022 Cd mg/Kg and <0.136 - 0.737 Cu mg/Kg) [3].

There were no indications of abnormal levels of Fe and Cr in the analyzed samples. The obtained concentrations in this study were lower than MRLs established in total diet study by Ministry of Agriculture, Fisheries and Food since 1999 [11]. According to this MRL the concentration value for Fe in milk is 4.1 mg/Kg, in dairy products is 12.0 mg/Kg and for Cr is 0.3 mg/Kg in milk and 0.9 mg/Kg in dairy products. An exception is for the Fe concentration in fruit yoghurt sample. The fruit yoghurt showed greater concentrations of all studied elements due to the addition of the fruit to the product.

The Zn concentrations in the milk samples are in the range of 1.126-3.063 ppm. These concentrations were lower than those determined in commercial goat milk by Parker (3.10 ppm) [9].

4. Conclusions

The study was conducted to assess the quality of milk and dairy products samples.

The results obtained in this study indicate few chemical or microbiological differences between the studied samples. This fact may be due to the differences in sources of original milk used for processing the products and to the action of different enzymes.

This study showed that the studied milk and dairy products samples are rich in nutrients, without health risks.

5. References

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