AAS DETECTION OF HEAVY METAL IN SHEEP CHEESE (THE BANAT AREA, ROMANIA)

Gogoaşă I1, I.Gergen1, Maria Rada3, D.Pârvu1, Camelia Ciobanu1, Despina Bordean1, C. Măruţoiu2, Diana Moigrădean1

1Faculty of Food Products Technology, University of Agricultural Sciences and Veterinary Medicine, Calea Aradului, Nr. 119, Timisoara, Romania. Email: ionelgogoasa@yahoo.com.
2”Lucian Blaga” University, Sibiu, Romania.
3”Victor Babes” University of Medicine and Pharmacy, Timisoara, Romania.

Key words: heavy metals, atomic absorption spectrometry, cheese, Banat area

Abstract. In this paper we present results of the measurement of some heavy metals in sheep cheese samples from three hill and alpine areas in the Banat area. We analysed, using flame and graphite furnace atomic absorption spectrometry, the following heavy metals: Fe, Mn, Zn, Cu, Co, Ni, Cr, Pb, and Cd. The concentration ranges in the cheese samples were: 7.22-8.85, 1.36-1.83, 17.39-23.17, 0.691-0.886, 0.020-0.102, 0.002-0.010, 0.214-0.225, 0.193-0.314 and 0.001-0.003 mg/kg for iron, manganese, zinc, cooper, cobalt, nickel, chromium, lead and cadmium, respectively. Analysing experimental data shows that the specific soil and climate factors in the area favour cheese assortments with normal heavy metal contents under the form of essential elements and of low concentrations of heavy metals potentially toxic or toxic much below admitted toxicity levels.

INTRODUCTION

Milk and milk products are foods with major implications in man’s health. Such foods can ensure optimal vital functions, including working, thinking, and creating capacities. This is why doctors recommend a daily ratio of at least 400 ml of milk or its equivalent in dairy products. The importance of milk products in the feeding of the Romanians under the form of milk products results from the total consumption of milk and milk products. Thus, in 2004, in Romania they produced 1,577,000 hl of milk, 2,708,000 hl of fresh milk products (3.5% fat), and 7,000 t of butter and 53,000 t of cheese [9]. This is to show that we have a good level of good quality of milk and milk product consumption due to the nutritious factors they supply, i.e. proteins, sugars, fats, mineral salts, and vitamins [2, 8].

Due to their role in the human body, mineral salts are basic elements that define the quality and nutritious value of milk products. Under the form of macro- and micro-elements, heavy metals fulfil a series of functions of extreme importance: maintaining osmotic pressure and electrolytic balance in the muscle tissue and in blood, play a buffer role in the muscles, support muscle contraction, act as activators of inhibitors of enzymes, are involved in the metabolism of carbon hydrates, fats, and proteins, make up some fats, proteins, vitamins, or enzymes, and play a plastic role in the structure of some tissues [6, 7]. There is no biological phenomenon without direct or indirect involvement of these elements.

From a nutritional point of view, metal elements in the composition of milk products can be grouped in essential metals (Fe, Mn, Cu, Zn, Co, Cr, etc.) and in non-essential metals (represented mainly by Hg, Cd, Pb, etc.). The presence of the latter, even in low concentrations, leads to metabolic disorders with extremely serious consequences. It is very important to mention that for both heavy metal categories the increase of their concentration above admitted limits considered optimal has toxic effects on consumers of milk and milk...
products. This is why concentration levels for some heavy metals in milk and milk products are ruled by every country’s sanitary regulations.

All the above mentioned shows that milk products should be assessed both as energetic, plastic, and bio-stimulating nutrient sources and as a source of contaminating mineral elements with a less or more serious impact on the vital body functions. This asks for research in the field of concentration levels of metals in milk products as a fundament for preventing and avoiding the marketing of contaminated products. Romania’s accession in the EU asks for food products, including milk products that have a proper quality level that fits European standards in the field.

MATERIAL AND METHOD

In order to carry out our experiment we sampled 10 types of sheep cheese in three mountain and hill areas in the Banat area: the Godeanu Mountain area (the Godeanu cheese), the Țarcu Mountain area (the Țarcu cheese), and the Rugi locality area (the Rugi cheese), which after homogenising and mineralising were tested for heavy metals. In order to measure cheese content, we sampled 10 g of each fresh cheese type, we dried them, we calcinated them for 6 hours at 550°C. The ashes was recuperated in 10 ml of HNO₃ 20%. After evaporation we led the contents on water to dry bath to 50 ml with the help of HNO₃ 2%.

From the extracts above we measured, by flame atomic absorption spectrometry, Fe, Mn, Zn, and Cu. The other heavy metals Co, Ni, Cr, Pb, and Cd were measured by graphite furnace atomic absorption spectrometry.

To make the measurements, we used a Varian air-acetylene Spectr AA-110 flame atomic absorption spectrometer and a Varian GTA-110 with deuterium background corrector atomic absorption spectrometer. Working conditions were those recommended by the machine supplier. All reactants we used had high purity (Merck).

RESULTS AND DISCUSSION

Experimental results in the assessment of heavy metals in the three cheese types are shown in Table 1.

Table 1 Heavy metal content (average values) in some cheese types

<table>
<thead>
<tr>
<th>Cheese type</th>
<th>Metal content (mg/kg fresh edible product)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>The Godeanu cheese</td>
<td>8.85</td>
</tr>
<tr>
<td>The Țarcu cheese</td>
<td>7.22</td>
</tr>
<tr>
<td>The Rugi cheese</td>
<td>8.00</td>
</tr>
</tbody>
</table>

As one can see in Table 1 and Figures 1-3, the distribution of the metal elements we analysed in the three cheese assortments is different.

This can be explained not only by the nature of each metal, but also by the existence of a correlation between the different geographical location, sheep breeds, and processing type [1]. On the other hand, heavy metal concentration in cheese also depends on pollution sources (geogenic or man-induced).

It is well-known that Banat soils are characterised by a supplementary charge of heavy metals; their physical and chemical features and climate conditions substantially diminish the changing of these heavy metals into forms accessible to plants and then to animals [4]. On the other hand, there were no cases of obvious man-made pollution. As a result, the only source
of contamination with heavy metals could be the processing of milk in improper sanitary conditions.

The best represented of these elements is zinc, an element essential to the human body. It was measured in close concentrations between 17.39 and 23.17 mg/kg, with higher concentrations in the alpine areas (Figure 1).

Iron, an extremely important element for the human body functioning and not only was measured in much lower amounts, close within the three areas (between 7.22 and 8.25 mg/kg). As zinc, slightly higher concentrations of iron were detected in cheese from alpine areas (Figure 1).

![Figure 1 Concentrations of Zn, Fe, Mn, and Cu in different types of cheese](image)

Manganese and copper were detected in much lower amounts compared to Zn and lower than Fe.

The distribution of the two elements is almost even, their concentration varying between 1.36 and 1.83 mg/kg in Mn and 0.691 and 0.886 mg/kg in Cu. The lowest amounts of these two elements were in products from the hill areas.

The other heavy metals we analysed were detected in low amounts (Cr and Pb) and very low amounts (Co, Ni, and Cd).

Chromium, a microelement essential for the human body, was detected in low and close concentrations between 0.214 and 0.225 mg/kg (Figure 2).

Lead, a heavy metal with a strong toxic character, was detected in lower concentrations between 0.193 and 0.314 mg/kg. The lowest contents were in the Godeanu cheese (Figure 2).

Cobalt, nickel, and cadmium were detected in extremely low concentrations between 0.02 and 0.05 mg/kg in Co, 0.002 and 0.010 mg/kg in Ni, 0.001 and 0.003 mg/kg in Cd. As the concentration of these heavy metals in all samples we analysed is extremely low, we cannot detect them clearly per type of cheese (Figure 3).
As for the distribution of toxic heavy metals (Cd and Pb) or potentially toxic heavy metals (Cu and Zn) whose maximum admitted concentration in Romania is as shown in Figures 4 and 5, their concentrations is below maximum limits (MAL) [10].

Moreover, in all types of cheese, extremely toxic heavy metals Pb and Cd were detected much below toxicity levels.
Comparing experimental data with data in literature concerning the distribution of metal elements in different milk products, we can see that they are within admitted limits characteristic for this type of foods [3, 5].

As a consequence, as there are no major pollutants, the specific soil and climate conditions in the three areas under study favour the manufacturing of cheese with normal contents of heavy metals under the form of essential micro-elements and of low and very low concentrations of potentially toxic and toxic heavy metals much below admitted toxicity levels.
CONCLUSIONS

Milk products, foods with major implications for man’s health should be assessed both as a source of energetic, plastic, and bio-stimulating nutrient source and as a source of contaminating minerals with a more or less serious impact on the vital physiological functions of the human body.

This is the main reason why we carried out the assessment of heavy metal content in sheep cheese from three different areas of the Banat area: the Godeanu Mountain area (the Godeanu cheese), the Țarcu Mountain area (the Țarcu cheese), and the Rugi locality area (the Rugi cheese), areas famous for their traditions in cheese making.

We analysed, using flame and graphite furnace atomic absorption spectrometry, the following heavy metals: Fe, Mn, Zn, Cu, Co, Ni, Cr, Pb, and Cd.

Experimental results in assessing heavy metals are within normal limits characteristic for this kind of food.

Experimental data confirm the fact that, in the absence of pollutants, soil and climate factors specific to the area favour the manufacturing of cheese assortments with normal contents of heavy metals, under the form of essential microelements and of very low concentrations of potentially toxic or toxic heavy metals much below admitted toxicity levels.

BIBLIOGRAPHY

4. Gogoașă I., 2005, Teză doctorat: Cercetări privind poluarea (contaminarea) cu metale grele a unor legume și fructe din zona de vest a României, Universitatea de Științe Agricole și medicină Veterinară a Banatului Timișoara.
5. Mendil D., 2006, Mineral and trace metal level in some cheese collected from Turkey, Food Chemistry, 96, 532-537.