Determination of Some Heavy Metals Level in Kashar Cheese Produced in Thrace Region*

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In this research, 50 samples of kashar cheese produced and sold in Trakya (Thrace) region, were studied for analysis of heavy metals as Lead (Pb), tin (Sn), copper (Cu) and mercury (Hg). Heavy metal contents of samples were determined by Atomic Absorption Spectrophotometer (AAS) after having been burned in a microwave oven. As a result of this study, average heavy metal contents of 50 samples found as; lead (Pb):0.0600 ppm, tin (Sn): 0.0366 ppm, copper (Cu): 0.5036 ppm, mercury (Hg): 0.0214 ppm. The obtained results show that mean concentrarions of copper and tin in samples are below average levels whereas some results in lead and mercury are above the average levels.

Keywords: Kashar cheese, lead, tin, cupper, mercury

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Trakya Bölgesinde Üretilen Kaşar Peynirlerinin Bazı Ağır Metal Düzeylerinin Belirlenmesi*

Bu çalışmada Trakya Bölgesinde üretilen kaşar peynirlerinin kurşun (Pb), kalay (Sn), bakır (Cu) ve civa (Hg) içeriklerinin belirlenmesi amaçlanmıştır. Bu amaçla bölgeden 50 adet kaşar peyniri örneği toplanmıştır. Örnekler mikrodalga fırında yakıldıktan sonra ağır metal içerikleri Atomic Absorption Spectrophotometer (AAS) cihazı kullanılarak belirlenmiştir. Analiz sonuçlarına göre kaşar peyniri örneklerinde ortalama olarak Pb:0.0600 ppm, Sn: 0.0366 ppm, Cu: 0.5036 ppm ve Hg: 0.0214 ppm düzeylerinde belirlenmiştir. Yapılan analizler sonucunda elde edilen değerler örneklerin ortalama Cu ve Sn içerikleri belirlenen limit değerlerin altında, Pb ve Hg içeriklerinin ise limit değerlerin üstünde olduğu göstermektedir.

Anahtar kelimeler: Kaşar peyniri, kurşun, kalay, bakır, civa

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Introduction

Because of their long term toxicological effects, inorganic or aggregated forms of chemical substances represent a severe risk in food and hence feeding . Heavy metals are widespread in environment and it is reported that heavy metal levels in milk and milk products in industrially developed areas is much higher than those in rural areas since metal contamination in food increases rapidly with the increase of environmental pollution due to industrial waste products. Even if the concentration of heavy metals in a living organism is low, it is proved to be more toxic or poisonous than any other metal (John & Howard, 1996). Heavy metals have no beneficial effects, they can cause health problems even in very low concentrations; furthermore toxic effects can be seen when the limit of heavy metals are exceeded (FAO/WHO, 1993). Because of this fact, the maximum legal concentrations of heavy metals in food and beverages consumed on regular base have been determined and are checked regularly by the legal entities (Şimşek et al., 2000).

Especially, milk and its products are contaminated with heavy metals such as lead, cadmium, antimony, arsenic, copper, mercury, manganese, zinc and tin. Due to the contamination, the metal concentration of consumptive?(consumed) cheese depends on the type of cheese, the way, place, tools and equipment of production.(Feeley et al., 1972, Moreno-Rojas et al., 1994). Although Kashar is one of the most popular cheeses in Turkey, there is no valid data about the heavy metal contents of Kashar cheese produced in industrially developed Thrace region.

The purpose of the present study is to determine the concentration of some heavy metals in Kashar cheese samples consumed in Thrace region, besides if the legal tolerance levels are exceeded or not.

Material and Method

The collection of samples

A total of fifty Kashar cheese samples were collected from the retail markets in Thrace region of Turkey (approximately 250 g samples in their original packages). The samples, taken to the laboratory, were homogenized and stored at -20 ºC before analysed.

Reagents and chemical standarts

During the experiment, nitric acid (HNO_3 65%), hydrogen peroxide (H_2O_2 30%), and multi-element calibration standard-2A (10g/ml, Agilent, Palo Alto, CA) were used. Aqueous standards were prepared with appropriate dilution of a 10 mg/l multi-element solution with ultra pure water and stored at refrigerator.

Wet burning of Samples

The burning processes, which are necessary to eliminate organic compounds and transfer the inorganic elements into soluble phase, were accomplished by using a Mars-5 microwave wet ashing system (CEM Corp., Matthews, NC, USA) and its accessories (Ellen and Van Loon 1990, Fuente et al. 1997, CEM corporation, Nordic Committee on Food Analysis (Anonymous, 1998). Approximately 2 g of sample was weighed into 100 ml teflon vessels. Samples were digested with 5 ml HNO_3 and 2 ml of H_2O_2 in a microwave digestion system. The resulting extracts were cooled and diluted to 10 ml with deionized water (Milli-Q Millipore 18.2 MΩ/cm conductivity). A blank digest was carried out in the same way. All sample solutions were clear. The samples were digested according to the following temperature programme as follows: 2 min. for 400 w, 2 min. for 400 w, 6 min. for 400 w, 5 min. for 400 w, 8 min. for 800 w, 8 min. for vent. After this, the clear solutions were analysed by AAS.

Determination of lead, tin, copper, and mercury

Measurements are made for every single element by using different cathode lamps (Varian 280 Z Atomic Absorption) in spectrophotometer. Experiments for Pb, Sn and Cu elements are carried at wavelengths of 283.3 nm, 286.3 nm and 324.7 nm, respectively (Anonymous 1988) and the experiment for mercury is carried at wavelength of 253.7 nm (Anonymous 1989).

Statistical Analyses

All data is statistically analysed by using SPSS 10.0 professional Statistics 1999. The experimental data is tested by ANOVA (One way ANOVA randomized complete blocks) and the differences between means are achieved by using the Duncan multiple range test.

Results and Discussion

The data about the heavy metal content of Kashar cheese samples produced and sold in Thrace region, is given in Table 1.

Although the content of Pb was between the range of 0.06-0.04 ppm for 21 samples, it was not at a detectable level for 29 samples (Table 1). According to the Turkish Food Codex, the maximum Pb level in Kashar cheese should be at 0.30 ppm (Anonymous 2002) but according to the results, 3 samples of Kashar cheese had higher Pb content than standard level. The difference in Pb content for all Kashar cheese samples is considered to be significant ($p<0.01$). The reason for high Pb content might be attributed to unsuitable galvanized or tin-coated metal containers used for milking and transportation of milk. The obtained results indicate that using similar equipment during the production of cheese might affect the Pb content of cheese. More researches about that should be done to reveal the source of this contamination. According to a study done in Italy, the average value of Pb content was determined to be 0.60 pp. and according to another study, the amount of Pb in the cheese samples collected from different regions in Romania was between the range of 0,03 and 0.24 ppm, (Hura, 2002). At a study in Turkey, the avarage values were found to be 0.14 ppm (for Çecil cheese) and 1.20 ppm (for Çömlek cheese) (Mendil, 2006).

Table 1. The contents of lead, copper, tin and mercury in Kashar cheese samples (ppm)

Samples Number	Pb	Cu	Sn	Hg	Samples Number	Pb	Cu	Sn	Hg
1	0.02^{a}	0.67^{k}	nd	nd	26	0.40^{g}	0.55^{h}	nd	nd
2	nd	0.43^{e}	nd	nd	27	0.10^{c}	0.45^{e}	nd	nd
3	nd	0.62^{j}	0.32^{d}	nd	28	0.05b	0.44^{e}	nd	nd
4	0.30^{f}	0.40^{d}	nd	nd	29	nd	0.45^{e}	nd	0.12^{f}
5	nd	0.51^{g}	nd	nd	30	0.13^{d}	0.50^{g}	0.14^{b}	nd
6	nd	0.32^{b}	nd	0.06^{bc}	31	0.02^{a}	0.67^{k}	nd	nd
7	nd	0.48^{f}	0.25^{c}	nd	32	nd	0.43^{e}	nd	nd
8	0.11^{c}	0.60^{i}	nd	0.10^{e}	33	nd	0.62^{j}	nd	0.10^{e}
9	nd	0.66^{k}	nd	nd	34	nd	0.40^{d}	0.14^{b}	nd
10	nd	0.45^{e}	nd	nd	35	nd	0.51^{g}	nd	nd
11	0.40^{g}	0.55^{h}	nd	nd	36	nd	0.26^{a}	nd	0.05^{b}
12	0.10^{c}	0.45^{e}	nd	nd	37	nd	0.48^{f}	nd	nd
13	0.05^{b}	0.44^{e}	nd	nd	38	0.11^{c}	0.60^{i}	nd	0.10^{e}
14	nd	0.45^{e}	nd	0.12^{f}	39	nd	0.66^{k}	nd	nd
15	0.13^{d}	0.50^{g}	0.14^{b}	nd	40	nd	0.45^{e}	nd	nd
16	0.02^{a}	0.67^{k}	nd	nd	41	0.40^{g}	0.55^{h}	nd	0.08^{d}
17	nd	0.43^{e}	nd	nd	42	0.10^{c}	0.45^{e}	nd	nd
18	nd	0.62^{j}	nd	nd	43	0.05^{b}	0.44^{e}	nd	nd
19	nd	0.40^{d}	nd	nd	44	nd	0.45^{e}	nd	0.12^{f}
20	nd	0.51^{g}	nd	nd	45	0.13^{d}	0.50^{g}	0.14^{b}	nd
21	nd	0.34^{c}	nd	0.07^{cd}	46	0.02	0.67^{k}	nd	nd
22	nd	0.48^{f}	0.14^{b}	nd	47	nd	0.43^{e}	nd	nd
23	0.11^{c}	0.60^{i}	nd	0.10^{e}	48	0.21^{e}	0.62^{j}	0.56^{e}	0.15^{g}
24	nd	0.66^{k}	nd	nd	49	nd	0.40^{d}	nd	nd
25	nd	0.45^{e}	nd	nd	50	nd	0.51^{g}	nd	nd
			Min.value			nd	0.26	nd	nd
			Max.value			0.40	0.67	0.56	0.15
			Average value			0.06	0.5036	0.0366	0.0214
			Limit value			0.30	1.00	250.00	0.03

Different lover case indicate significant differences among themselves of Kaşar cheese (P<0.01)

[nd] Not Detectable

Pb values, which we have both identified within the specified limits and the values in general, are under the average literature values. If 100 g cheese is considered to be consumed every day, Pb concentration level in body varies between 0.06 ppm and 1 ppm. For an avarage adult (60 kg body weight), the provisional tolerable daily intake (PTDI) for lead is 214 mg (FAO/WHO 1999) and in our study, the lead level was not exceed the limit. To minimize excessive Pb intake, a maximum tolerance level is important. This can easily be achieved with good production processes and with the prohibition of the sales of contaminated products (Schwartz, 1994, Debake et al., 2002).

In this study, Cu contents of Kashar cheese were determined as follows: minimum 0.26 ppm, maximum 0.67 ppm, and the average was found to be 0.5036 ppm (Table 1). According to the Turkish Food Codex, the acceptable limit value for Cu content is 1.0 ppm (Anonymous, 2002). The obtained results from all of the samples are below this limit. In terms of Cu content, Kashar cheeses have significant differences ($p<0.01$). Concerning the amount of Cu that can be found in hard cheeses, such as cheddar, the nutritional risk is even greater when the cheese is exposed to lipid oxidation which is technologically important in terms of discoloration (Jime'nez et al. 1984). In some studies, ranging limits of the Cu were reported 0.1-1.3 ppm in Mozarella cheese (Basile et al., 1978), 1.0 ppm in Manchego cheese (Moreno-Rojas et al. 1994) and 0.2-0.4 ppm in Gouda cheese (IDF, 1992). In this study, the Cu values determined in the samples were similar to the hard cheeses' and are also close to the value, described in the Turkish Food Codex, they are below the limit.

Concerning the Sn content, in the analysis of the kashar cheese samples collected from different markets, the maximum level was 0,56 ppm whereas the minimum levels could not be found and the average level was found to be as 0.0366 ppm (Tablo. 1). The differences among the values were significant ($p<0.01$). According to the Turkish Food Codex, the Sn content in Kashar cheese must be 250 ppm as maximum and all samples were found to be acceptable (Anonymous 2002). Food poisoning due to Sn occurs very rarely and just occurs due to the environmental pollution. Yet, some other complications may occur such as, acute eye and skin irritations, headaches, abdominal pain; nausea and dizziness, severe sweating, shortness of breath, long-term depression, liver damage, immune system impairment, chromosomal anomalies, red blood cell deficiency, brain damage, nervousness, sleep disorders, amnesia (Shills et al., 1994).

The average Hg content in Kashar cheese was found to be as 0.0214 ppm (Table 1). The minimum level of Hg content could not be found wheras the maximum value was found to be 0.15 ppm. The differences in the specified amounts of Hg in cheese samples were found to be significant ($p<0.01$). According to the Turkish Food Codex, the acceptable amount of Hg in cheese must be as maximum 0.03 ppm (Anonymous 2002). In this study, Hg contents of the 12 samples were above the acceptable limit value.

Conclusion

In this study, Pb, Cu, Sn and Hg contents of Kashar cheese were determined in terms of food safety. While Cu and Sn contents of all cheese samples are under the maximum acceptable limit which has been determined by Turkish Food Codex, Pb and Hg contents of these samples were found to be above this limit. The high levels of Pb and Hg contents in cheese samples may be an important risk factor for the human body and may cause serious health problems. Therefore, the containers used in the production process of cheese must not contain heavy metals. The manufacturers must be informed about this issue so the government has an important role for preventing the environmental pollution. Our results showed that some contaminations occurred depending on the equipment used during the production of the milk and/or production process of the cheese. Further researches are necessary to find out the exact source of contamination.

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