LEVELS OF LEAD AND CADMIUM ON WHEAT FLOURS ON THE ROMANIAN MARKET: AN ATOMIC ABSORPTION SPECTROMETRY ANALYSIS

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ABSTRACT

Cereal industry and its derived products, especially wheat flour, have a big economic and social importance in Romania and worldwide. Therefore, as wheat flour is the main ingredient for obtaining bread, the most consumed product among Romanian people, its safety is of real wide interest.

The present work aims to determine the concentrations of Lead and Cadmium in 33 different wheat flour samples, available on the Romanian market. Analysis was performed by atomic absorption spectrometry with graphite furnace (GF-AAS), after dry digestion. Lead content ranged between 0.002 and 0.137 mg/kg while cadmium content ranged between 0.0002 and 0.024 mg/kg. All samples were within the accepted limits, imposed by the legislation in force.

INTRODUCTION

Wheat is one of the most used cereals in the world, because it is used to obtain flour, the main ingredient in making bread and bakery products, pastries and cakes (Doe et al, 2013, Gordana et al, 2014). Besides the high content in nutrients, wheat also contains certain minerals, such as Cu, Fe, Zn, Mn, Ni, used for the proper functioning of vital processes (Gordana et al, 2014). Also, it was observed that, high consumption of whole grains, have been associated with decreased risk of developing several chronic diseases. However, these whole grains may also contain contaminants, microbiological, such as mycotoxins or infectious agents, or chemicals, such as heavy metals or acrylamide during processing (Thielecke and Nugent, 2018). Heavy metals include lead, cadmium, arsenic or mercury. The main source of heavy metals comes from mineral fertilizers or pesticides based on toxic metals (Gordana et al, 2014). Another important source of grain contamination is through the use of wastewater for crop irrigation, which can contain significant amounts of heavy metals that remain in the soil. Other sources may be represented by industrial or traffic emissions, the harvesting and / or storage process (Khan et al, 2016). These heavy metals, bio-accumulate, are persistent, are not biodegradable and have a long half-life (Tegegne, 2015). These metals can cause serious harmful disease on human health, such as renal tubular damage, osteoporosis, cancer (Lei et al, 2015) and a good monitoring of heavy metals from food and environment is very important (Khan et al, 2016).

For this reason, the aim of this study was to evaluate the concentrations of lead and cadmium of 33 samples of wheat flour, with different ash content, purchased from various stores and from some producers. Also, these results will be compared with other results from the literature, to see if there are significant differences between the results.

MATERIAL AND METHOD

Sample collection

In this study, a total of 33 samples of wheat flour, whit different ash content, from different producers were used. The samples, presented in Table 1, were bought from different stores in Romania and kept at room temperature until the time of analysis.

Reagents

All the reagents were of analytical grade. Nitric acid (HNO_3) was purchased from Merck. Lead standard solution 1000 mg/L Pb for AA ($Pb(NO3)_2$ in HNO_3 2%) and cadmium standard solution 1000 mg/L Cd for AA ($Cd(NO_3)_2$ in HNO_3 2%) were used to obtain the calibration curves. These standard solutions were purchased from Scharlau. Ammonium phosphate monobasic ($NH_4H_2PO_4$) from Sigma-Aldrich was used as chemical modifier. Ultrapure water (resistivity 18.2 MΩ.cm) was used to obtain solutions, dilutions and to prepare samples. All glassware was previously cleaned and decontaminated with 10% HNO_3 and rinsed with deionised water before use.

Equipment

Heavy metals analysis was performed using an AAnalyst 600 graphite furnace atomic absorption spectrometer system from Perkin Elmer. For Pb and Cd, measurements were made using the hollow cathode lamps at 283.31 nm respectively 228.86 nm. This equipment is provided with Transversely Heated Graphite Atomizer (THGA) furnace assembly and longitudinal Zeeman-effect for background correction. For dry ashing method, a L1206 Caloris furnace, was used to disintegrate the samples, with a temperature range between room temperature and 1150°C. An OHAUS Adventurer Pro analytical balance, Model AV 264, with an accuracy of 0.0001 g was used for weighing the samples.

Sample preparation

For heavy metals content analysis, samples were prepared by dry ashing method, taking in work 5 grams of each type of wheat flour. Initially, the sample was well homogenized, weighed, transferred to a clean crucible which is labelled according to the sample number and subjected to slowly increasing heating in muffle furnace from room temperature to 550°C, for 6 h, to obtain white ash residue. The ash was left to cool, rinsed with 2.5 mL of 50% (v/v) HNO_3, heated on a water bath for 10 min, filtered through filter paper and then diluted with deionized water in a 50 mL volumetric flask and made up to the mark. For the heavy metals' determination, three solutions were prepared for each sample and three separate readings were made for each solution.

Calibration

Calibration curve for each element was performed using reagents described above. For both metals, a 5-points calibration curve was made. For Pb, the analytical working solutions are the following: 10 μg/L, 20 μg/L, 30 μg/L, 40 μg/L and 50 μg/L, while for Cd are the following: 1 μg/L, 2 μg/L, 3 μg/L, 4 μg/L and 5 μg/L. The calibration curves reveal a good linearity over the whole range of concentrations. The detection and quantification limits of Pb was 2.0 μg/L, respectively 6.0 μg/L, and for Cd was 0.2 μg/L, respectively 0,6 μg/L. For both metals a regression coefficient higher than 0.995 was obtained. The recovery of lead and cadmium was between 95 % and 98%.

RESULTS AND DISCUSSIONS

The content of lead and cadmium from the wheat flour is reported in Table 2. Results are presented as mean ± SD of the 3 replicated. Of the 35 samples, Pb was detected in 15 samples, while Cd was detected in 31 samples. Lead and cadmium content in the analysed samples ranged between < 0.002 and 0.137 mg/kg, respectively between < 0.0002 and 0.024 mg/kg.

Presence of cadmium was reported in much more samples compared to lead, but the concentrations were much lower. Specifically, for lead and cadmium content in wheat flour there are no maximum allowed limits. According to EU Regulation no. 1881/2006 the maximum allowed limits for the content of Pb and Cd in wheat are 0.2 mg/kg wet weight. Analysing the obtained results, no contamination with heavy metals was found. Wheat flour samples can be consumed safely by consumers.

In Table 3, a comparison was made between the study results and the results from the specialized literature. The differences between the concentrations of Pb and Cd may be due to several factors, among which the presence in a high concentration of these metals in the soil and in the irrigation water, as a result of the pollution from the highway traffics. Among other factors number annual variation, cultivar differences, genetic, regional variations (Hammed et al, 2016). Studies have also shown that by processing, the levels of these metals decrease linearly from the raw material to the final product obtained. Different absorption capacity for heavy metals depending on the wheat species could be also a factor.

CONCLUSIONS

In this study, we successfully determined the amount of heavy metals in different wheat flour samples using graphite furnace atomic absorption spectrometry (GF – AAS). The levels found are lower than the limits imposed for lead and cadmium in wheat. As general conclusion, regarding potentially toxic heavy metals (Pb and Cd) content, the flour is safe for consumption.

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Table 1

Samples description

Sample code	Wheat flour type
WF 1	Superior white wheat flour 000
WF 2	White wheat flour type 480
WF 3	White wheat flour type 480
WF 4	White wheat flour type 550
WF 5	White wheat flour type 550
WF 6	White wheat flour type 550
WF 7	White wheat flour type 550
WF 8	White wheat flour type 550
WF 9	White wheat flour type 650
WF 10	White wheat flour type 650
WF 11	White wheat flour type 650
WF 12	White wheat flour type 650
WF 13	White wheat flour type 650
WF 14	White wheat flour type 650
WF 15	White wheat flour type 650
WF 16	White wheat flour type 650
WF 17	White wheat flour type 650
WF 18	White wheat flour type 650
WF 19	White wheat flour type 650
WF 20	White wheat flour type 650
WF 21	White wheat flour type 650
WF 22	White wheat flour type 650
WF 23	White wheat flour type 650
WF 24	Black flour type 1350 1350
WF 25	Black flour type 1350 1350
WF 26	Black flour type 1350 1350

WF 27	Graham flour
WF 28	Graham flour
WF 29	Graham flour
WF 30	Dietary wheat flour
WF 31	Whole grain flour
WF 32	Whole grain flour
WF 33	Whole grain flour

Table 2

Summary of Lead and Cadmium concentration in analysed wheat flour

Sample code	Heavy metal content (mg/kg)	
	Pb ± SD	**Cd ± SD**
WF 1	< 0.002	0.008 ± 0.003
WF 2	< 0.002	0.010 ± 0.003
WF 3	< 0.002	0.003 ± 0.001
WF 4	0.006 ± 0.001	0.008 ± 0.002
WF 5	0.103 ± 0.010	0.002 ± 0.001
WF 6	< 0.002	0.007 ± 0.001
WF 7	0.016 ± 0.005	0.005 ± 0.002
WF 8	0.013 ± 0.003	0.005 ± 0.001
WF 9	0.015 ± 0.003	0.008 ± 0.003
WF 10	0.007 ± 0.003	0.007 ± 0.003
WF 11	0.013 ± 0.004	0.008 ± 0.002
WF 12	0.087 ± 0.012	0.006 ± 0.002
WF 13	< 0.002	0.008 ± 0.001
WF 14	0.024 ± 0.006	0.006 ± 0.002
WF 15	< 0.002	0.008 ± 0.003
WF 16	< 0.002	0.005 ± 0.001
WF 17	< 0.002	0.010 ± 0.003
WF 18	< 0.002	0.007 ± 0.002
WF 19	0.016 ± 0.005	0.003 ± 0.001
WF 20	0.012 ± 0.005	0.004 ± 0.001
WF 21	0.012 ± 0.004	0.010 ± 0.003
WF 22	< 0.002	< 0,0002
WF 23	< 0.002	0.004 ± 0.001
WF 24	< 0.002	0.011 ± 0.003
WF 25	< 0.002	< 0,0002
WF 26	0.137 ± 0.014	0.007 ± 0.002
WF 27	< 0.002	0.008 ± 0.002

WF 28	0.038 ± 0.005	0.024 ± 0.002
WF 29	< 0.002	0.013 ± 0.003
WF 30	< 0.002	0.014 ± 0.004
WF 31	< 0.002	0.015 ± 0.003
WF 32	< 0.002	0.011 ± 0.003
WF 33	0.017 ± 0.005	0.007 ± 0.002

Table 3

Comparative study on Pb and Cd levels in wheat flour

Reference	Pb (mg/kg)	Cd (mg/kg)
This study	< 0,002 – 0.137	0.008 – 0.024
Ghanati et al, 2019	0.049 – 0.083	0.477 – 0.821
Hammed and Koki, 2016	0.100 – 0.250	< 0.005
Doe et al, 2013	0.220 – 0.340	0.250 – 0.600
Nejabat et al, 2017	0.013 – 0.140	0.008 – 0.031
Tejera et al, 2013	0.037 – 0.056	0.023 – 0.027