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Investigation of chromium content in foodstuffs and nutrition supplements by GFAAS and determination of changing Cr(III) to Cr(VI) during baking and toasting bread

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Abstract

In our work the chromium content of foodstuffs, spices, beverages and nutrition supplements was determined. We set out to determine in what quantity these satisfy the organism's daily chromium requirement. We wanted to get an answer about to the question if a sportsman wants to plan his diet from the chromium consumption point of view, does he believe that the data given satisfy the necessary essential amount of chromium content. The results obtained were compared to data published by other authors and data can be found in the Internet. These data do not only differ significantly from the results obtained by us, but from each other as well. At present there is no available literature data to us demonstrating whether toxic chromium compounds can occur from the natural Cr(III) content of cereal milling products used when baking and toasting bread, that is why we considered examining it.

Keywords: Foodstuff; Bread; Chromium; GFAAS

1. Introduction

Cr(III) is an essential form of chromium as a trace element in the human body. There is no generally accepted and stated amount of essential chromium requirement for the body. The US National Academy of Sciences established that the adequate daily dietary intake range of Cr(III) is 20–120 μg/day for children (between 1 and 3 years: 20–80 μg/day, between 4 and 6 years: 30–120 μg/day) and it is 50–200 μg/day for children 7 plus and for adults uniformly. These values refer to the consumption of mainly foodstuffs (NAS/NRC, 1980; The webpage of the Healthy Eating Club, URL). In Hungary the recommended daily value of Cr(III) intake is 120 μg/day for children and for adults as well (Hungarian XC law, 1995).

For meeting the daily chromium requirements there are a lot of various products on the market such as medicines containing various chromium(III) complexes and medicinal products (for example "Chromium Picolinate tabs", "Centrum Multivitamin" and other tabs containing minerals, "Béres-Drops", etc.). The values published about food-products on different web pages and in some scientific journals differ from each other in some cases. Earlier studies about the thermal transformations of chromium at our department have demonstrated that some of the chromium compounds in tobacco are transformed to Cr(VI) during burning (Sógor, Gáspár, & Posta, 1998). That is why we considered the examination of chromium compounds in bread and cereal milling products and their possible transformations to a toxic Cr(VI) state during baking and toasting.

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2. Materials and methods

2.1. Reagents and apparatus

To prepare sample solutions ultra pure water was used, which was made by a Millipore Milli-Q RG apparatus. We used 65% nitric acid and 30% hydrogen-peroxide (made by Spektrum 3D Co.) for the wet digestion of the samples. For the microwave digestions a MILESTONE-MLS-1200 Mega MDR apparatus was used. For the calibration of the AAS instrument 1000 mg/L Cr(III)-nitric MERCK standard was applied. For the thermal investigations solid chromium compounds which were made by MERCK. All the reagents were analytical grade. For the chromium analysis a graphite furnace atomic absorption spectrometer (Perkin Elmer AAnalyst type 600 apparatus with Zeemann background correction) was used. The injected volume of the samples was 20–40 μl. The temperature program of the furnace was made by the manufacturer. We performed the flame atomic absorption spectrometric determinations by UNICAM SP 1900 Spectrometer. The thermal experiments were carried out with a Paulik–Paulik–Erdey thermogravimetric analyzer made by MOM.

2.2. Sample preparation

The wet digestion of the samples under atmospheric pressure was not complete. The microwave assisted digestion was complete and fast in any case. During this operation 0.2–0.8 g of solid samples, 5 cm^3 concentrated nitric acid and 0.25–0.5 cm^3 hydrogen-peroxide were put into the teflon vessels. The sample solutions were filled up with ultra pure water after the digestion.

2.3. Sample analysis

The digested sample solutions were subsequently analyzed by GFAAS. Graphite furnace heating program was used according to the manufacturer's recommendations. Three replications for all sample analysis were performed.

For method validation the analytical procedure was checked against reference material NIST Corn Bran reference 00458433 with certified chromium content of 0.11 mg kg^{-1}. The found chromium concentration was 0.106 ± 0.003 mg kg^{-1} (for three replicates of five determinations), which is within 95% confidence interval for reference material.

3. Results and discussion

3.1. Chromium content of foodstuffs and beverages

All foodstuffs and wines used during our measurements were of Hungarian origin (excluding the egg-yolk obtained from German hen), while beers were products of Hungary, Slovak and Czech Republic.

We determined the total chromium content in cereal milling products, in bread, in spices (e.g., black pepper, cinnamon, thyme), in eggs and in alcoholic beverages (wines, beers) originating from various sources. It can be seen from the results that the chromium content of the analyzed foodstuffs can differ by an order of magnitude from literature data published by other authors or on the Internet. These data date back to the nineties.

It can be seen in Fig. 1 that the chromium content of the analyzed Hungarian wines (different brands: 4 red and 8 white wines) is in the interval of 1 and 2.8 μg/100 g. One of the analyzed wines called "Mátraaljai Kékfrankos" has the highest chromium content (5.3 μg/100 g). The average of these results was compared to the literature data.

It can be seen in Fig. 2 that the literature data differ a lot from one another. The reason for this could probably be the origin of the wines according to the geographical area of the production. The methods, the tools, the utensils and the equipment used for their production and the storage have an influence on the chromium content (Kumpulainen, 1992; Medina & Sudraud, 1980; Stoewsand et al., 1979; Van Schoor, Claes, & Deelstra, 1986; George Mateljan Foundation, URL). Moreover, the pH and the temperature of the stored product are important too. The "Healthy Eating Club" does not distinguish between white and red wine, furthermore they publish the highest chromium content in wines.

We analyzed the chromium content of quail's egg-yolk from Hungary, and also German (D) and Hungarian (H)

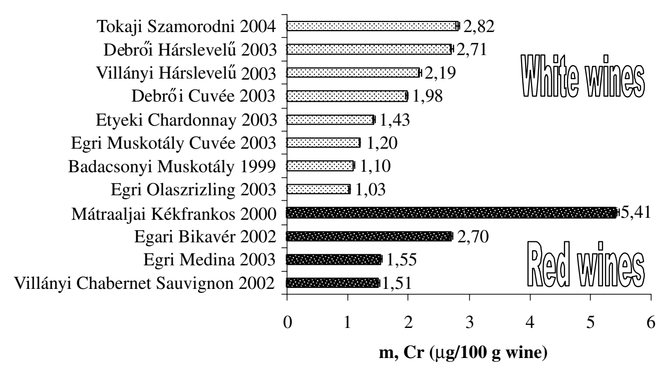

Fig. 1. Chromium content of Hungarian white and red wines.

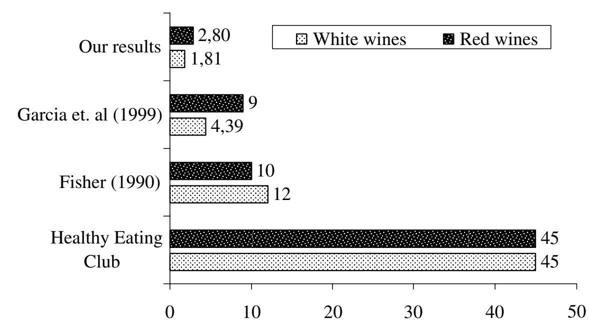

Fig. 2. Our data and the literature data of the chromium content of wines.

hen's egg-yolks (Fig. 3). There is not any significant difference between the chromium content of various types of egg-yolks. However, there is big difference between our results and the literature results as to the chromium content in egg-yolks. This can be seen in Fig. 4.

The chromium content of various Hungarian (Soproni Ászok, Arany Ászok, Borsodi Beer), Slovak (Topvar, Zlatý Bažant, Corgoň) and Czech (Velkopopovický Kozel, Pilsner Urquell) beers was investigated. Beers (from every brand) stored in cans and in glasses were compared. There were no significant differences in their chromium content.

The webpage "Healthy Eating Club" presents 3–30 μg Cr/100 g value in beers, but the chromium content of the 8 analyzed beers is much less (0.06–1.36 μg Cr/100 g beer).

It can be seen in Table 1 that there are differences between our results and the literature data too in case of the chromium content of spices. The literature data in Table 1 do not represent the real chromium content of certain Hungarian products.

The chromium content of the thyme (Thymi vulgaris herba, Bionit Ltd., Kistarcsa, Hungary) is 1205 μg/100 g. The value published by Fischer (1990) is 1000 μg/100 g but another value reported by others (Garcia, Cabrera, Sanchez, Lorenzo, & Lopez, 1999) is only 85 μg/100 g. However, the mineral content of thyme depends mainly on the growing location because it can accumulate large quantities of minerals. The other examined spices are Hungarian products too (made by "Horváth Rozi" Ltd., Hungary).

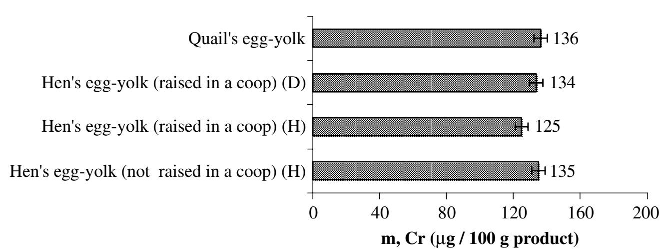

Fig. 3. Chromium content of egg-yolks.

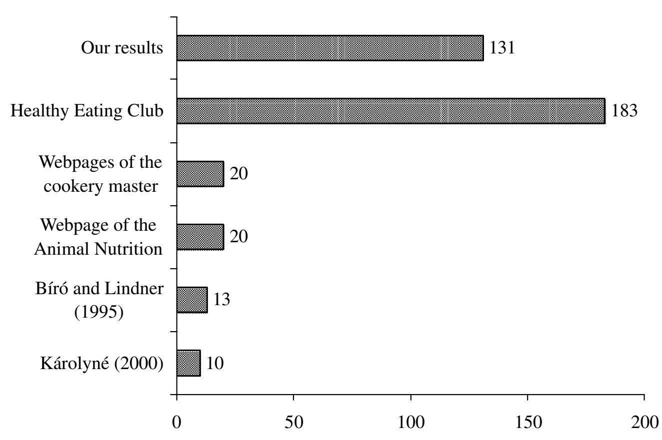

Fig. 4. Literature data about the chromium content of egg-yolks. (See above-mentioned references for further information).

Table 1
Chromium content of certain spices

Sample	m, Cr (μg/100 g)	Literature data m, Cr (μg/100 g)
Thyme (Hungarian product)	1205	1000;[a] 85[b]
Black pepper (Hungarian product)	144	370;[a] 21[b]; 74[c]
Cinnamon (Hungarian product)	57.5	36[b]
Mace (Hungarian product)	37.7	57[b]; 39[c]
Oregano (Hungarian product)	337	52[b]

[a] Fischer (1990).
[b] Garcia and Cabrera (2000).
[c] All About Natural Herbs and Spices webpage.

The obtained chromium content of broccoli purchased from a local farm (Debrecen, Hungary) is 11.9 μg/100 g. The literature data is 3–22 μg Cr/100 g (Chromium information webpage, URL; Anderson, Bryden, & Polansky, 1992; Bíró & Lindner, 1995). The chromium content of various Hungarian cereal milling products (wheat flour, semolina, wheat bran, corn flour, durum flour) was established too. The obtained results were 0.89–9.22 μg Cr/100 g.

3.2. Chromium content of nutrition supplements

From our examinations it turned out that all the investigated nutrition supplements contained similar or in some cases more (about 10–20 μg Cr/tablet) chromium, than certified by the manufacturer, which data can be found on the container. These are Cr(III) compounds, which are free from danger for human health. The analyzed nutrition supplements were the followings: Béres-chromium (Béres Rt., Hungary), Chromium-carnitine (Vireco Kft., Hungary), Dietet-In (Selenium Pharma, Hungary), Bio-chromium (Pharma Nord, Belgium), Chromium-picolinate (Universal Nutrition, USA).

According to our investigation only one tablet of the Béres-chromium product satisfy the recommended daily value (RDV) of chromium (according to the RDV in Hungary) in case of its total absorption in the human body. The chromium content obtained for Béres-chromium product was 121 μg Cr/tablet and the values for the other nutrition supplements were between 23.8 and 72.2 μg Cr/tablet.

We determined the chromium content in a Hungarian brewer's yeast product (Fig. 5), which corresponded with the data from two different sources in the literature but it did not agree with the data published by Fischer (1990) because that is nearly five times larger than our results.

3.3. Thermal experiments

Thermal investigations were performed in order to establish whether the natural Cr(III) content of the wheat flour and the bread changes to Cr(VI) considerably during baking and toasting bread. Firstly, we determined the chromium content of bread and wheat flour by using GFAAS method. In the flour (wheat, corn) and in the bread that was made from flour the chromium content is nearly the

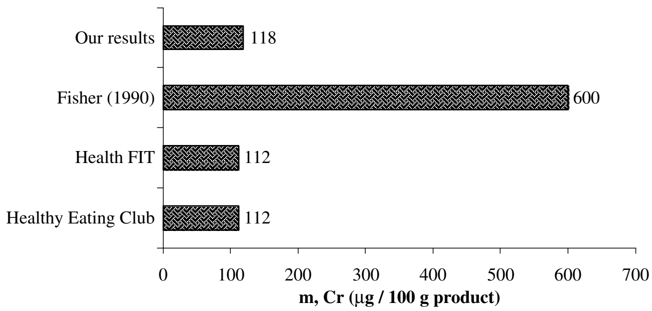

Fig. 5. Literature data about the chromium content in brewer's yeast.

same. Our results have proved that the flour provides the chromium content of the bread. Various types of flour were used for our additional examinations.

We put 0.5 g durum flour and 0; 0.5; 1; 5 cm^3 5 μg/L Cr(III)-solution in order into the melting pots. After that we put these samples into a temperature controlled melting furnace. We gradually increased the temperature up to 900 °C by using 50 °C/30 min heating steps. After the heating program we found greenish solid residue at the bottom of the melting pots. We added 10 cm^3 ultra pure water to the solid samples and then they were put into a microwave oven for 5 min. After the heating and dissolving the residue of the solution was completed up to 5 cm^3 and their chromium content was measured by GFAAS method. Even though the solubility of the Cr(VI) compounds is very good in hot water, we did not get chromium in a detectable quantity in the solution. We found that the Cr(III) compounds had not changed to Cr(VI) at all.

These results indicate that flour does not favour the Cr(III) to change to Cr(VI) during the heating process. The greenish substance that emerged is probably Cr_2O_3. Thermogravimetric experiments were performed for the verification of this assumption. We heated 0.5 g sample smoothly to 900 °C. In the case of the wheat flour after heating, the melting pots were absolutely empty because all the organic substances had left from the system. We performed thermogravimetric experiments with $Cr(CH_3COO)_3$ and $K_2Cr_2O_7$ compounds, of which derivatograms corresponded with the data in the literature (Liptay, 1976). The ratio 1:1 mixture of $Cr(CH_3COO)_3$ and $K_2Cr_2O_7$ compounds behaved similar to the two compounds separately. By the derivatogram, the ratio of the Cr(III) and Cr(VI) compounds did not change. For this reason, we heated the chromium compounds and the flour ratio 1:1 mixture. In the case of the chromium compounds we found some greenish substance in the melting pot, which is not soluble in water alike the greenish product, which was made from the Cr(VI) and the flour mixture. We added 250 cm^3 ultra pure water to the products in which the precipitate settled and chromium was not proved by FAAS method in the solution phase. This is explained by the fact that the flour ensures reductive medium for the Cr(VI) and it reduces it to Cr(III).

4. Conclusion

The Cr(III) in considerable quantity does not change to Cr(VI) during the heating process (at the temperature of baking and toasting bread) because the organic substances of the flour ensure reductive medium. Moreover, if there were Cr(VI) compounds in the bread they would reduce to Cr(III) as well at high temperature (at toasting temperature). So our examinations have proved that no toxic chromium compounds originate during baking and toasting bread.

If we want to plan our diet with regard to intake of chromium, on the basis of the Internet or any other literature data, then we can make mistakes of an order of magnitude. In every case the chromium content of a given foodstuff can only be decided on the basis of concrete samples and concrete analysis, and, unfortunately, this prevents people from compiling the right diet themselves, with the help of which they could provide their bodies in known and required quantities.

The methods and circumstances of producing the foodstuffs, the utensils, the equipment utilised for their production and storage (with particular regard to stainless steel utensils and cans), the origin of the foodstuffs (according to geographical area of production) have great influence on chromium content (Kumpulainen, URL) and exact mass (e.g., half-a cup of broccoli) of the given foodstuff cannot be found. It can be said that smaller measures of deviation are also displayed in relation to foodstuffs of identical type (e.g., egg-yolk) but originating from different sources, therefore when planning diets serving for supplementing chromium intake, it is questionable which source is to be regarded as definitive. The use of diet supplement preparations containing chromium could offer assistance in solving this problem.

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