Review article

Chromium in food products

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Abstract: *Chromium plays an important role in human and animal bodies. According to the oxidation state chromium can be advantageous for human health and, simultaneously possesses toxic properties. In this work the studies concerning the chromium content in the total and Cr (VI) forms in selected and frequently used during breakfast food products were presented. The largest quantities of the metal occur in raw cereal products (non-roasted buckwheat or brown rice bread) and herbs such as garlic or mint. The lowest chromium contents were observed in raw and UHT milk samples.*

Keywords: *speciation, chromium, atomic absorption spectrometry, bread, cereals, herbs, milk.*

Introduction

Particular attention to the content of chromium in the environment has been paid because of the significant health effects caused by ion forms of the metal discharged from industrial sources. As a result of the industrial activities, chromium compounds are discharged into the environment in liquid, solid and gaseous forms and they may adversely affect it.

Chromium is a controversial element because its trivalent forms are necessary for the proper functioning of the organism. On the other hand, hexavalent chromium compounds are toxic and carcinogenic for him. In industry hexavalent chromium is popular, therefore it pollutes soil and water in a significant way, following accumulates in plant tissues.

Chromium gets into human body as a result of breathing, the consumption of water and food products.

Determination of total chromium contents cannot affect the food assessment. Nowadays, evaluation of potential toxicity of elemental forms is required. Thus, the analysis of a sample with respect to hexavalent chromium is needed.

Chromium in bread

From several thousands of years bread, an excellent source of energy, is one of the main ingredients of human diet. The bread consists of minerals, proteins and B complex group of vitamins necessary for organism. The cereals used in production of bread are sources of important mineral ingredients such as phosphorus, calcium, potassium, iron, zinc or sodium. Many other components, including chromium, occur in trace amounts. Nevertheless, in order to assure the appropriate bread quality monitoring should be carried out in respect of assessment of contamination contents. These contaminants may originate from both the technological procedures and the ingredients used in flour and then in bread production. Cereals of which flour is produced, have the ability to extract minerals from soils and water, and accumulate them in their tissues, especially in grains. Some studies, concerning chromium [1], carried out with several wheat cultivars demonstrated the uptake of the element from the soils. Other study [2] performed with several vegetables and grains grown in area irrigated with tannery effluent, demonstrated that wheat and rice exhibit the most ability to bioaccumulation more chromium, just after a tomato.

Soraes et al. [3] performed chromium speciation analysis in white and whole bread samples by electrothermal atomization atomic absorption spectrometry (ETAAS). The method was applied to determine the total and hexavalent chromium in 152 bread samples, 76 white bread and 76 whole bread samples, were randomly acquired in 20 bakeries of the local market of Porto (Portugal).

The aim of the above study was the selective quantification of the expected low levels of hexavalent chromium in the presence of relatively high levels of trivalent chromium, the predominant species of the metal. Thus, the attention was focused on the prevention of the alteration of the oxidation state of hexavalent chromium. In this order, the alkaline extraction of chromium (VI) was applied. The method is often used to determine the connections with soils, nevertheless during the study of bread samples in respect of chromium (VI) presence the procedure has proved to be very affective.

The mean values for total chromium were 47.3±20.0 and 50.9±22.2 μg/kg of dry weight for white bread and whole bread samples, respectively (Table 1). The mean values found for hexavalent chromium were 5.65±5.44 and 6.82±4.88 μg/kg of dry weight for white bread and whole bread samples, respectively, which were slightly above 10% of the total chromium contents. They recognized that pH value does not affect the extraction procedure of chromium (VI) both in white and whole bread samples.

It is known that flour as the component of bread is obtained from whole cereal grain, and chromium content is higher in the cereal outer parts [4]. Therefore, Soraes et al. expected that the value for chromium for whole bread will be higher. The study has not confirmed the hypothesis. Total and hexavalent chromium content has proved to be similar both in white and whole bread samples.

Bread is an important fraction of the daily diet and contributes to the intake of a great part of chromium. From the data obtained in the described study come that, in terms of mean values, 10% of the total chromium present in bread is in the toxic hexavalent form. Accordingly, on the basis of a mean daily ingestion of three bread units, the daily intake of total and hexavalent chromium were calculated. Namely, for total chromium was up to 12.7 μg/day and for hexavalent chromium – 1.98 μg/day. Referring to total chromium, bread can contribute to 120 μg/day [3].

Table 1. Contents of total chromium and hexavalent chromium in bread samples (mean values, micrograms per kilogram of dry weight) [3]

Sample	total Cr [μg/kg]	Cr (VI) [μg/kg]	Cr(VI)/total Cr
white bread n=76	47,3 ± 20,0 (5,0-111,0)* median: 45,5 Cv (%): 42,4	5,65 ± 5,44 (<5,60-18,80) median: 5,60 Cv (%): 96,0	0,15 ± 0,21 (0,01-1,34)
whole bread n=76	50,8 ± 22,2 (15,1-126) median: 44 Cv (%): 43,6	6,82 ± 4,88 (<5,60-19,70) median: 6,60 Cv (%): 72,0	0,16 ± 0,14 (0,01-0,60)
white and whole bread n=152	49,1 ± 21,1 (5,0-126) median: 44,6 Cv (%): 43,0	6,24 ± 5,19 (<5,60-19,70) median: 6,5 Cv (%): 83,0	0,16 ± 0,18 (0,01-1,34)

n – number of samples, Cv – coefficient of variation, * – minimum and maximum values are indicated in parentheses

Chromium in cereal products

Most of daily intake originates from food and has a form of trivalent compounds. Cereals products, rice, groats, breakfast flakes and dietetic crisp bread samples are a group representing significant part of the whole of the daily diet (27-35%) [5]. Based on it, the determination of total chromium in the products collected in Lublin (Poland) was performed [6]. The analysis was performed using flame AAS after dry mineralization in quartz ovens at 400°C.

The authors observed that the content of chromium in roasted buckwheat ranged within 0.19-0.21 mg/kg. Much higher chromium contents were noticed in non-roasted buckwheat, 0.82 mg/kg, about four times as many than in roasted one. Barley groats contained less chromium (from 0.04 mg/kg to 0.22 mg/kg).

The chromium contents in couscous groats ranged from 0.10 mg/kg to 0.25 mg/kg. Less presence of chromium in semolina was observed, mean 0.10-0.13 mg/kg. Millet was distinguished by relatively large content of chromium – mean 0.68 mg/kg.

With regard to dietetic crisp bread samples, the most of chromium was in brown rice bread (0.86 mg/kg), and the lowest in wheat one (0.19 mg/kg). Relatively high level of chromium was observed in white rice bread (0.50 mg/kg).

Kot et al. studying different species of rice noticed that the highest mean of chromium content is found in white long-grain rice (0.41 mg/kg), afterwards long-grain rice with an average of total chromium 0.30 mg/kg, natural brown rice – 0.35 mg/kg, and rice with vegetables and mushrooms – 0.20 mg/kg. Relatively low amount of chromium was determined in jasmine rice – mean 0.12 mg/kg.

Analyzing of presence of chromium in breakfast rice, the highest amounts of the metal was found in wheat flakes and wheat-corn flakes, 0.61 and 0.66 mg/kg, respectively. The lowest ones were monitored in barley flakes and corn flakes, 0.20 and 0.19 mg/kg, respectively.

The similar results as above, concerning the study of chromium in cereals, were obtained by Mateos et al. [7, 8] and Lendinez et al. [9]. Their study has shown that the cereal grain used to make the breakfast cereal had a considerable influence on the Cr content.

Chromium in herbs

Chromium often occurs in several food and beverages that affect its common appearance in the daily diet and medical therapy as well. Additionally, data on Cr content in certain aromatic herbs shows that the plants accumulate chromium and could contribute to dietary intake of this element [10, 11].

The chromium content in foods is relatively low and most foods have a content below 0.1 μg/g [12,13]. However, proteinaceous foods such as meats, fish, seafood, pulses and nuts are rich sources of chromium (>0.100 μg/g) [14]. It is caused by Cr (III) that has a strong tendency to form coordinate and chelate compounds and it interacts with protein molecules to form strong and stable crosslinks. Spices, cacao and cacao products, and whole meal products also contain higher contents.

The presence of chromium in the soil has an essential influence on its content in plant tissues. Cary and Kubota noticed that plant samples taken from plants growing on high-Cr soils contained higher Cr concentrations than similar plants growing on low-Cr soils [15].

Garcia et al. [16] in order to determine chromium in spices and herbs used electrothermal atomization atomic absorption spectrometry (ETA-AAS). Generally, 72 samples from 17 different species of flavors available on market and the most popular in Spain were analyzed. Before determination, the sample was mineralized by NH_3 and V_2O_5.

A wide variability of results was observed not only between the different types of spices and aromatic herbs, but also for the same type of sample (Table 2). In the study mentioned, the chromium levels ranged from the not detectable to 1.42 μg/g (expressed in dry wt.). The presence of Cr has been detected in 95% of the analyzed samples. The most elevated Cr concentrations were in dried garlic (0.99 μg/g) and mint (1.11 μg/g) samples, while the lowest content of chromium was observed in aniseed (0,01 μg/g), and then in white and black pepper, 0,11 and 0,12 μg/g, respectively. The capacity of Cr accumulation in certain aromatic plants such as oregano and Alexandrian laurel creates them as potential sources of Cr for the correction of Cr deficiency in humans. The obtained data show that the concentration of chromium in spices and herbs is higher than other foods and beverages, and additional studies are necessary to estimate its contribution to the dietary intake of chromium.

Table 2. Concentration of chromium in spices and aromatic herbs used in preparation of salads and meat [16]

Levels of chromium (dry wt.) in spices and aromatic herbs				
Sample	**Systematic name**	**n**	**Chromium [µg/g]**	
			Mean	**Range**
Aniseed	*Pimpinella ansium*	3	0,01	0,02-0,03
Basil	*Calamintha acions*	3	0,54	0,54-0,61
Cinnamon	*Cinnamonum casia*	6	0,36	n.d.*-0,76
Garlic	*Allium sativum*	4	0,99	0,80-1,42
Laurel	*Laurus nobilis*	5	0,60	0,41-0,68
Mint	*Menta piperita*	4	1,11	1,06-1,14
Mustard	*Brassica juncea*	4	0,30	0,29-0,31
Nutmeg	*Myristica fragans*	4	0,57	0,57-0,60
Onion	*Allium cepa*	3	0,85	0,80-0,91
Oregano	*Origanum vulgare*	3	0,52	0,41-0,63
Parsley	*Petroselinum sativum*	3	0,02	0,01-0,02
Paprika	*Capsicum annum*	6	0,33	0,19-0,65
Pepper (black)	*Piper nigrum*	5	0,21	n.d.*-0,73
Pepper (white)	*Piper nigrum*	3	0,11	n.d.*-0,31
Saffron	*Crocus sativus*	4	0,12	0,11-0,14
Thyme	*Thymus vulgaris*	3	0,83	0,83-0,91
Vanilla	*Vanilla planifolia*	3	0,35	0,32-0,37
Mixture (for salad)	-	3	0,22	0,22-0,23
Mixture (for meat)	-	3	0,41	0,41-0,41

*not detectable

Chromium in pausterised cow's and UHT milk

Due to the nutritive values of milk and milk products and the role that play in nutrition of the newborn makes speciation of chromium important, as their rapid growth makes them more susceptible to its toxic effects. Therefore, Abayneh et. al. [17] determined the concentration of total chromium and chromium (VI) in eight different brands of pasteurised cow's milk purchased from supermarkets in Tshwane, South Africa. ICP-MS method used in the analysis enabled to determine selective and accurate low concentrations of chromium (VI) in the presence of total chromium.

Relative standard deviations of total chromium and Cr(VI) in milk samples were contained in the ranges of 2.67 to 6.47% and 2.54 to 3.67%, respectively. These low deviations indicated a high accuracy of the method. The content of total chromium in the raw milk was situated in the range of 33.2 to 57.1 µg/L. On the basis of these results, milk samples contained 1.31 to 3.28% Cr(VI). This indicates the presence of Cr(VI) in relatively low concentrations with reference to the total Cr. Consequently, there is a low risk to the consumers.

Table 3. Concentrations of Cr(VI) and total Cr in milk samples [17]

	Cr (VI) concentration (μg/L) ± SD	**Total Cr concentration (μg/L) ± SD**
Brand 1	1,39 ± 0,09	54,0 ± 1,7
Brand 2	1,25 ± 0,05	42,5 ± 1,6
Brand 3	1,44 ± 0,07	43,9 ± 1,3
Brand 4	0,61 ± 0,03	33,2 ± 0,90
Brand 5	0,87 ± 0,04	35,8 ± 1,1
Brand 6	0,75 ± 0,02	57,1 ± 1,8
Brand 7	1,01 ± 0,05	39,8 ± 1,0
Brand 8	0,81 ± 0,03	51,6 ± 1,4

The contents of total chromium found for a large majority of milk samples (Table 3) were within the same range with the results reported in 2008 by Ataro et al [18]. Ambusha et al. [17] in their work claim that the higher concentrations of total Cr in these commercial brands could be influenced by environmental conditions such as proximity to mines, or the equipment processing milk. Chromium can be present in milk, although stainless steel is commonly used for manufacturing the equipment used in pasteurising, clarifying and processing milk as it is easily cleaned and considered relatively inert.

The other research team [19] also focused on the quantitative determination of total chromium and Cr (VI) but in 60 UHT (Ultra High Treatment) milk samples of different commercial brands acquired at random in the local market in Porto (Portugal). Total chromium was determined directly in milk with the addition of a surfactant and a mixture of Pd and Mg as a chemical modifier. For the selective separation of hexavalent chromium, the sample pre-treatment consisted in precipitation of proteins and elution of the supernatant through a Chromabond NH_2 column. The chromium was eluted by nitric acid. Atomic absorption spectrometry with electrothermal atomization (ET-AAS) was used in the determination of the metal. The detection limits were 0.2 and 0.15 μg/l for total chromium and hexavalent chromium, respectively. The validation of both procedures was performed by the standard additions method and the recoveries were higher than 93% in all cases.

In the cited paper the mean total chromium values were 0.95 μg/l in skim, half-fat (simple and supplemented together) and whole milk, respectively (Table 4). Lameiras et al. were not able to state whether the relationship exists between the decrease in total chromium level and the decrease in the level of fat in milk. The Cr (VI) values found (< 0.15–1.20 μg/l) were, in terms of mean values (< 0.15–0.68 μg/l), about 2–4 times lower than those for total chromium. As hexavalent chromium is well absorbed through the gastrointestinal tract and is a genotoxic species, a risk from such levels in milk is not observed.

Table 4. Total chromium and hexavalent chromium contents (µg/l) (range and mean values) in 60 milk samples obtained in the local market in Porto (Portugal) [19]

Species	Skim milk	Simple half-fat milk	Supplemented half-fat milk	Whole milk
Total chromium	0,95 (<0,63-1,77)	1,33 (0,65-2,74)	0,95 (0,65-1,36)	2,70 (1,42-5,70)
Chromium (VI)	<0,15 (<0,15-0,15)	0,48 (0,15-0,74)	0,40 (0,24-0,60)	0,68 (0,20-1,20)

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