Food Chemistry 217 (2017) 655–659

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Speciation of chromium in bread and breakfast cereals

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ARTICLE INFO

Article history:
Received 9 September 2015
Received in revised form 2 September 2016
Accepted 5 September 2016
Available online 7 September 2016

Keywords:
Bread
Cereals
Chromium
High-Resolution Continuum Source Atomic Absorption Spectrometer
Speciation

ABSTRACT

Bread and breakfast cereals are a major constituents of the human diet, yet their Cr(VI) content is not known. Chromium(VI) was determined in these products by high resolution continuum source atomic absorption spectrometer (HR-CS AAS) after leaching Cr(VI) with 0.10 mol L^{-1} Na_2CO_3.

The results showed that 33–73% of total Cr (58.17 ± 5.12 μg kg^{-1}–156.1 ± 6.66 μg kg^{-1}) in bread exist as Cr(VI) and the highest total Cr content was found in brown bread. It was shown that Cr(III) is oxidized to Cr(VI) during toasting of bread.

Chromium(VI) content in breakfast cereals ranged between 20.4 ± 4 μg kg^{-1} and 470.4 ± 68 μg kg^{-1}. Therefore, it can be concluded that bread and breakfast cereals contains Cr(VI) which does not exceed maximum acceptable concentration (MAC) of 0.003 mg $kg^{-1}bw^{-1}$ day^{-1} through daily consumption of half a bowl (65 g) of breakfast cereal and four slices of toasted (122 g) or untoasted bread (160 g).

1. Introduction

Bread and breakfast cereals are a major constituents in the human diet (Dewettinck et al., 2008). Grains (wheat, rice, corn, oats and ryes) are the main raw materials used in the baking of bread and preparation of breakfast cereals. They are processed in various ways to obtain the desired products. Cereal products preparation process involves mixing the grain ingredients and flavoring agents in a large rotating cooker to form a smooth paste. The product is passed through a drying oven where the moisture is removed. The cooled grain product is then flattened between two metal rollers to form the final raw material which can be used in the making of breakfast cereals and flour for making bread (Fast & Caldwell, 2000).

The main source of Cr into the grain is the soil in which the grain grows (Cubadda, Raggi, & Marconi, 2005). Stainless steel equipment is widely used during food-processing and therefore it is possible that some amount of Cr can be transferred to grain mixtures during processing. The amount transferred depends on the length of contact time between the food and the metal and the processing temperature (Reilly, 2004).

Chromium exists in solid matrices in two oxidation states with conflicting biological properties, viz., Cr(III) and Cr(VI) valence states. Trivalent chromium, Cr(III), is necessary for the proper functioning of living organism whereas hexavalent chromium, Cr(VI), is carcinogenic to humans (Costa & Klein, 2006). Over-exposure to Cr (VI) through consumption of Cr(VI) contaminated food could result in gastrointestinal and neurological effects, cancer, abdominal pains, vomiting and hemorrhage (ATSDR, 1998).

Chromium(III) plays a number of important physiological functions in human bodies through its involvement in carbohydrates, lipids and protein metabolisms (Guerrero-Romero & Rodriguez-Moran, 2005; Jomova & Valko, 2011). The effects of Cr(III) on insulin action are illustrated in Fig. 1. The inactive form of the insulin receptor is converted to the active form by binding insulin (step 1). Once the insulin is bound to the receptor, it triggers a movement of chromium from the blood into the insulin-dependent cells (step 2) to bind with a peptide known as Apo-Lower molecular weight Cr (Apo-LMWCr) binding substance (step 3). Apo-LMWCr binds to the insulin receptor and enhances its activity to keep the blood sugar level from getting too high or too low (step 4) (Vincent, 2000).

The safety of bread and breakfast cereals consumption can therefore be evaluated through assessment of their Cr(VI) content. Although a number of studies have been carried out to determine total Cr in bread and breakfast cereals (Akinyele & Shokunbi, 2015; Bratakos, Lazos, & Bratakos, 2002; Cabrera, Teissedre, Cabanis, & Cabanis, 1997; Gallo, Serpe, & Brambilla, 1997; Gonzalez, Gallego, & Valcarcel, 1999; Grijalva, Ballesteros, & Cabrera 2001; Lamsal & Beauchemin, 2015; Lendinez, Lorenzo, Cabrera, & Lopez, 2001), there is currently only one publication about Cr(VI) determination in bread (Soares, Viera, & Bastos, 2010) and none in breakfast cereals.

The determination of Cr(VI) can be carried out by many analytical techniques only after the separation of Cr(VI) from Cr(III) spe-

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http://dx.doi.org/10.1016/j.foodchem.2016.09.020
0308-8146/

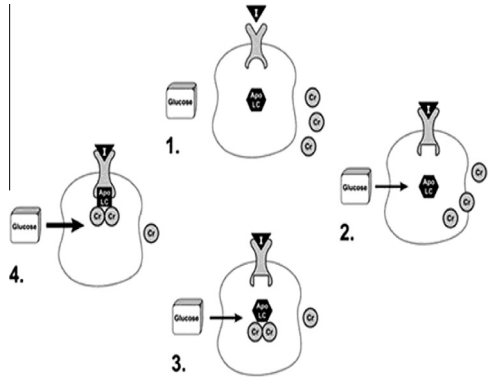

Fig. 1. A proposed model for the potential effects of chromium on insulin action.

cies. In one publication devoted to the determination of Cr(VI) in bread, separation was achieved through the treatment of samples with 0.01 mol L^{-1} NaOH by shaking the sample mixture for 17 h, further addition of 1 mol L^{-1} NH_4NO_3 and shaking for further 30 min (Soares et al., 2010). Though the applied method is scientifically sound, the sample pre-treatment method is too long and thus increases the possibility of elements losses and contamination. This drawback can be circumvented by treatment of samples with Na_2CO_3. Therefore, the aim of this study is to develop a rapid reliable analytical method of the determination of Cr(VI) in bread and breakfast cereals using Na_2CO_3 as the leaching agent.

2. Materials and methods

2.1. Instrumentation

An Analytikjena high resolution continuum source atomic absorption spectrometer (HR-CS AAS), contrAA 600 (Thuringia, Germany) was used in all measurements. It makes use of xenon lamp as a continuous source of light instead of traditional hollow cathode lamp. The slit width was 0.7 nm and argon (Ar) was used as the purge gas. The spectrometer is equipped with autosampler AS-GF and the entire system was controlled by means of Aspect CS English software running under Microsoft windows. PIN platform graphite tubes (Analytikjena, Germany) were used for atomization of Cr at 357.87 nm. The temperature program used during this study is summarized in Table 1. The optimum pyrolysis and atomization temperatures were set at 1200 °C and 2450 °C, respectively.

2.2. Reagents and solutions

Standard stock solution containing 1000 mg L^{-1} Cr (Merck, South Africa) was used to prepare the working calibration standard solutions through appropriate dilution with ultra-pure water. Na_2CO_3 (0.10 mol L^{-1}) was used to leach Cr(VI) in the samples prior its determination. Suprapure nitric acid (65% v/v), HNO_3 (Merck, Germany), and suprapure hydrochloric acid (32% v/v), HCl (Merck, Germany) were used to dissolve the ashed samples prior the determination of the total chromium content. All dilutions were carried out by adding ultra-pure water (18.2 MΩ cm^{-1}) obtained from Direct Q-5 Milli-Q system (Millipore, USA). Buffer solutions (pH 4 and pH 7) were used to calibrate the pH meter (Hanna instrument model H13519N) prior the measurements of pH.

2.3. Samples

Different brands of breakfast cereal and bread samples were purchased from retail stores in Pretoria, Gauteng province, South Africa. Small portions of bread samples were placed on a clean paper and dried in an oven at 120 °C for 1 h. Breakfast cereal samples were stored in polypropylene sample tubes. The samples were ground to particle size of less than 200 μm by IKA A11 milling system (Staufen, Germany) prior sample pretreatment.

2.4. Leaching of Cr(VI) in breakfast cereals and untoasted bread

Approximately 0.25 g of samples were transferred into 100 mL glass beakers, 25.0 mL of 0.10 mol L^{-1} Na_2CO_3 was added and the contents were boiled up to 20 min. The samples were allowed to cool to room temperature, transferred into 50 mL polypropylene tubes and diluted to 25.00 mL with deionized water. The samples were filtered through hydrophilic Millipore PVDF 0.45 μm filter prior analysis by HR-CS AAS

2.5. Leaching of Cr(VI) in toasted bread

Bread samples were toasted for 3 min on an Essential 900 W bread toaster, allowed to cool to room temperature and ground to grain size of less than 200 μm diameters. Approximately 0.25 g of samples were treated with 0.10 mol L^{-1} Na_2CO_3 as described in Section 2.4.

2.6. Sample preparation for total Cr determination in breakfast cereals and bread

Approximately 0.5 g powdered samples were transferred into porcelain crucibles and ashed at 600 °C for 3 h in a muffle furnace. To dissolve the sample, the ash was allowed to cool, then two drops of ultrapure water and 0.50 mL concentrated HNO_3 and 0.50 mL concentrated HCl were added and the content was mixed thoroughly to dissolve the ash. The solutions were filtered through Whatman No. 1 filter paper and diluted to 25 mL in 50 mL polypropylene test tubes prior analysis by HR-CS AAS.

2.7. pH measurements in bread

Approximately 5 g bread sample was suspended in 50 mL of ultra pure water, mixed well and the suspension was allowed to stand for an hour prior the pH measurement in the supernatant solution.

Table 1
Temperature program for the atomization of Cr in bread and breakfast cereals.

Step	Temp (°C)	Ramp (°C/s)	Hold(s)	Gas purge (mL min^{-1})
Drying	80	6	20	250
Drying	90	3	20	250
Drying	110	5	10	250
Pyrolysis	350	50	20	250
Pyrolysis	1200	300	10	250
Gas adaption	1200	0	5	0
Atomization	2450	1500	5	0