Food Chemistry 254 (2018) 78–79

Contents lists available at ScienceDirect

Food Chemistry

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

Letter to the Editor

Comment on recent article speciation of Cr in bread and breakfast cereals, published in *Food Chemistry,* (2017) *129*, 1839–1843 by Mathebula, M. W., Mandiwana, K., & Panichev, N.

The main sources of chromium (Cr) in human diet consist of meat, dairy products, potatoes, bread and tea (Alberti-Fidanza, Burini, & Perriello, 2002; Karak & Bhagat, 2010; Lendinez, Lorenzo, Cabrera, & López, 2002; Novotnik, Zuliani, Ščančar, & Milačič, 2013). The concentrations of total Cr in these foodstuffs range in general from about 0.2 to 0.3 mg kg^{-1} (dry mass), while in tea infusions between 0.04 up to 0.42 mg L^{-1}. The consumption of foodstuffs of animal or plant origin is considered to be safe, since Cr, even if animals or plants were exposed to Cr(VI), is present in the trivalent oxidation state, as Cr(VI) has been reduced in these organisms (Langård & Costa, 2007). Despite this accepted fact, several authors recently reported the presence of Cr(VI) in plants (Panichev, Mandiwana, Kataeva, & Siebert, 2005; Elci et al., 2010), bread samples (Soares, Vieira, & Bastos, 2010) and teas (Mandiwana, Panichev, & Panicheva, 2011). In these studies, the alkaline extraction of Cr(VI) with 0.1 mol L^{-1} Na_2CO_3 (Panichev et al., 2005; Elci et al., 2010; Mandiwana et al., 2011) or 0.01 mol L^{-1} NaOH + 0.1 mol L^{-1} NH_4NO_3 (Soares et al., 2010) was applied. The applicability of different alkaline extraction procedures for the determination of total Cr(VI) in soil and soil water-soluble Cr(VI) was first evaluated by James and co-workers in 1995. It is of key importance to stress that in this work, Cr(VI) in soil extracts was quantified by speciation analysis using the 1,5 diphenylcarbazide spectrophotometric method (James, Petura, Vitale, & Mussoline, 1995). On the contrary, the authors who applied similar alkaline extractions for the determination of Cr(VI) in plants, bread and teas (Panichev et al., 2005; Elci et al., 2010; Soares et al., 2010; Mandiwana et al., 2011) or hot water extraction to obtain tea infusions (Mandiwana et al., 2011), did not use speciation analysis for quantification of Cr(VI) in the alkaline or hot water extracts, but determined the total Cr content by electrothermal atomic absorption spectrometry (ETAAS). The Cr concentrations determined by ETAAS were stated to be those of Cr(VI).

In their recent paper, Mathebula, Mandiwana, and Panichev (2017) determined the total Cr content in alkaline 0.10 mol L^{-1} Na_2CO_3 extracts of bread and breakfast cereals samples by ETAAS and although speciation analysis was not applied, they defined their analytical method as speciation. More, the extracting agent used is not novel (Panichev et al., 2005; Elci et al., 2010; Mandiwana et al., 2011) as Na_2CO_3 is one of the reagents commonly used for the extraction of total Cr(VI) from solid matrices (James et al., 1995). Na_2CO_3 enables extraction of total Cr(VI) and soluble Cr (VI) from samples, but is not selective enough and some Cr(III) is also co-extracted. In addition, during the extraction at highly alkaline conditions, the Cr(III) co-extracted, may be partially oxidised to its hexavalent form, leading to overestimation of the content of Cr(VI). To prevent such analytical artefacts, $MgCl_2$ is commonly added to precipitate the dissolved $Cr(OH)_3$ (Novotnik, Zuliani, Ščančar, & Milačič, 2012) and the speciation analysis is mandatory to obtain the true data on Cr(VI) content in alkaline extract (James et al., 1995; Novotnik et al., 2012; Ščančar & Milačič, 2014).

We would also like to make a comment on the interpretation of Mathebula et al. (2017) about the Cr(III) oxidation during the toasting of bread. They presumed that after adding baking powder ($NaHCO_3$) to dough as a leavening agent, it decomposed to Na_2CO_3 during baking. The authors stated that Cr(III) present in bread was, at elevated temperature of toasting, oxidised to its toxic Cr(VI) form due to the presence of Na_2CO_3 and oxygen. Up to 87% of total Cr in bread was reported to be oxidised. This explanation was not supported by the experimental results presented in Table 3 for the pH of aqueous extracts of untoasted and toasted bread. These data showed that the pH of toasted bread extracts did not increase in comparison to those of untoasted bread (pH of samples analysed were acidic, ranging from 5.4 to 5.8). Clearly, the amount of baking powder added to bread did not cause any increase in pH of bread during toasting. It should be pointed out that the oxidation of Cr(III) with oxygen at elevated temperatures (100–200 °C) is possible only at highly alkaline pH's (Ščančar & Milačič, 2014). Conclusion that Cr(III) was oxidised during bread toasting at pH below 5.8, which is not favourable for oxidation of Cr(III) is most probably wrong, not based on the current knowledge from the field. With the analytical methodology applied, the authors determined the total Cr content extractable in 0.10 mol L^{-1} Na_2CO_3, and not Cr(VI).

Based on the determination of total extractable Cr, without any speciation analysis, the authors concluded that bread and breakfast cereals contain Cr(VI). The authors even recommended the "safe dose" of consumption of bread and breakfast cereals that would not exceed maximum acceptable concentration (MAC) of 0.003 mg Cr(VI) kg^{-1} per bw per day (half a bowl (65 g) of breakfast cereal and four slices of toasted (122 g) or untoasted bread (160 g)). Such recommendations are inadmissible and alarming. Alarming since due to the high toxicity of Cr(VI), consumption of these basic dietary items would represent a long-term chronic exposure and health threat to the majority of the human population.

Our comments are supported also by experimental work performed in our group (Novotnik et al., 2013) in which the reliability of data reporting the existence of Cr(VI) in tea infusions and bread was checked by speciation analysis. We have repeated the experiments of Mandiwana et al. (2011) and Soares et al. (2010) and applied speciation analysis of Cr by high performance liquid chromatography coupled to inductively coupled plasma mass spectrometry (HPLC-ICP-MS), using Cr stable isotopes to follow species interconversions during the extraction procedures. For this purpose, extracting solutions were doubly spiked with enriched stable isotopes of ^{50}Cr(VI) and ^{53}Cr(III) and the elution profiles of Cr obtained by HPLC, recorded at m/z 50, 52 and 53. Speciation analysis data confirmed that Cr(VI) was not present nor in the samples of alkaline extracts, neither in tea infusion extracts due to the presence of antioxidants and organic matter which prevent any existence of Cr(VI) in tea infusions or bread samples. In these sample matrices, even the added enriched ^{50}Cr(VI) spike was reduced. With similar experiments, Novotnik, Zuliani, Ščančar, and Milačič (2015) confirmed also that Cr(VI) cannot exist in Neem tea leaves and Neem tea infusion. Ščančar and Milačič (2014) critically overviewed Cr

https://doi.org/10.1016/j.foodchem.2018.01.191
Received 11 October 2017; Accepted 31 January 2018
Available online 02 February 2018
0308-8146/

speciation analysis based on liquid chromatography and spectrometric techniques and discussed the advantages of the use of stable isotopes as tracers to follow species transformation during sample preparation and quantification of Cr species by HPLC-ID-ICP-MS. They pointed out that isotopically enriched Cr(VI) and Cr(III) spike solutions, which are used as tracers, importantly contribute to the trueness of the results obtained. In this critical review, the significance of the use of adequate analytical methodologies and speciation analysis in the determination of Cr(VI) was emphasized, in order to prevent erroneous conclusions made on the basis of artefacts of the wrongly applied analytical methodologies.

With this letter to the Editor, we want to warn Food Chemistry readers against wrongly interpreted data on Cr speciation in foodstuffs, which were based on total Cr determination without performing adequate speciation analysis.

References

Alberti-Fidanza, A., Burini, G., & Perriello, G. (2002). Trace elements in foods and meals consumed by students attending the faculty cafeteria. *Science of the Total Environment, 287*, 133–140.

Elci, L., Divrikli, U., Akdogan, A., Hol, A., Cetin, A., & Soylak, M. (2010). Selective extraction of Cr(VI) using a leaching procedure with sodium carbonate from some plant leaves, soil and sediment samples. *Jornal of Hazardous Materials, 173*, 778–782.

James, B. R., Petura, J. C., Vitale, R. J., & Mussoline, G. R. (1995). Hexavalent Cr extraction from soils: A comparison of five methods. *Environmental Science and Technology, 29*, 2377–2381.

Karak, T., & Bhagat, R. M. (2010). Trace elements in tea leaves, made tea and tea infusion: A review. *Food Research International, 43*, 2234–2252.

Langård, S., & Costa, M. (2007). Chromium. In G. F. Nordberg, B. A. Fowler, & M. Nordberg (Eds.). *Handbook on the toxicology of metals* (pp. 487–510). (3rd ed.). Academic Press, Inc.

Lendinez, E., Lorenzo, M. L., Cabrera, C., & López, C. M. (2002). Cr levels in spices and aromatic herbs. *Science of the Total Environment, 278*, 183–189.

Mandiwana, K. L., Panichev, N., & Panicheva, S. (2011). Determination of Cr(VI) in black, green and herbal teas. *Food Chemistry, 129*, 1839–1843.

Mathebula, M. W., Mandiwana, K., & Panichev, N. (2017). Speciation of Cr in bread and breakfast cereals. *Food Chemistry, 217*, 655–659.

Novotnik, B., Zuliani, T., Ščančar, J., & Milačič, R. (2012). The determination of Cr(VI) in corrosion protection coatings by speciated isotope dilution ICP-MS. *Journal of Analytical Atomic Spectrometry, 27*, 1484–1493.

Novotnik, B., Zuliani, T., Ščančar, J., & Milačič, R. (2013). Chromate in food samples: An artefact of wrongly applied analytical methodology? *Journal of Analytical Atomic Spectrometry, 28*, 558–566.

Novotnik, B., Zuliani, T., Ščančar, J., & Milačič, R. (2015). Content of trace elements and Cr speciation in Neem powder and tea infusions. *Journal of Trace Elements in Medicine and Biology, 31*, 98–106.

Panichev, N., Mandiwana, K., Kataeva, M., & Siebert, S. (2005). Determination of Cr(VI) in plants by electrothermal atomic absorption spectrometry after leaching with sodium carbonate. *Spectrochimica Acta Part B, 60*, 699–703.

Soares, M. E., Vieira, E., & Bastos, M.d. L. (2010). Cr Speciation analysis in bread samples. *Journal of Agricultural and Food Chemistry, 58*, 1366–1370.

Ščančar, J., & Milačič, R. (2014). A critical overview of Cr speciation analysis based on high performance liquid chromatography and spectrometric techniques. *Journal of Analytical Atomic Spectrometry, 29*, 427–443.

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