



Consideration of Heavy Metals Contamination in Turkish Foodstuffs: Çemen (Fenugreek Paste) and Hot Spicy Tomato Dip and Human Health Risk Assessment

Kuddusi KARABODUK^{1,*}, Erdoğan HASDEMİR², Mehmet Levent AKSU³

¹Gazi University, Life Sciences Application and Research Center, Ankara/Turkey

²Gazi University, Faculty of Sciences, Department of Chemistry, Ankara/Turkey

³Gazi University, Faculty of Education, Department of Chemistry, Ankara/Turkey

Article Info

Received: 09/12/2016

Revised: 16/01/2017

Accepted: 19/01/2017

Keywords

Fenugreek paste
Hot spicy tomato dip
Heavy metal
ICP-OES
Health risk index

Abstract

In this study the heavy metal contents such as Fe, Co, Ni, Cu, Zn, Cr, Al, Mn, Pb, Cd in three different fenugreek pastes and hot spicy tomato dips purchased from three different markets in Ankara were investigated by the use of ICP-OES equipment. Metal contamination may come from the foodstuff materials and the equipment in fabricated. The metals present in the samples were found to be Fe (3.27-32.74 ppb), Co (16.54-18.86 ppb), Ni (57.38-59.76 ppb), Cu (14.37-16.90 ppb), Zn (58.18-63.38 ppb), Cr (85.88-97.00 ppb), Al (105.40-253.10 ppb), Mn (26.95-34.42 ppb), and Pb (102.40-114.20 ppb), Cd (55.97-56.87 ppb). The weekly intake values and health risk of the toxic metals Cd and Pb in Health risk index of FAO/WHO were separately evaluated. The HRI values of fenugreek paste and hot spicy tomato dip are below 1, so these foodstuffs are quite safe and healthy.

1. INTRODUCTION

Fenugreek paste (FP) (semi-solid paste) has a prominent place in Turkish cuisine. It is served as an aperitif in breakfast and in supper with the main dish due to its biter and spicy taste. It is also used to make beef bacon by cutting the connection of meat from the outside medium and stops its deterioration by its low pH value (4.83) and induces a spicy aroma to it. The fenugreek paste is made from finally ground fenugreek, garlic and red hot pepper [1,2].

Fenugreek is a leguminous plant, which grows North Africa, Mediterranean countries, Europe, western Asia, and northern India. Fenugreek plant has been used in alternative medicine and food for so many years. It contains phospholipids, glycolipids, oleic acid, linolenic acid, linoleic acid, choline, vitamins A, B1, B2, C, nicotinic acid, niacin, and many other functional elements [3].

Hot spicy tomato dip (HSTD) is an appetizer, which contains largely tomato. Although the contents of hot spicy tomato dip changes according to the region it also contains pepper pure, garlic, onions, salt and spices. Also it may contain olive oil or sunflower oil depending upon the choice and taste. As fenugreek paste, hot spicy tomato dip is a popular dish throughout the country.

The heavy metals are not biologically degradable and constantly accumulate in the environment [4,5]. The mind boggling pace of urbanization and industrialization and ever increasing anthropogenic pollution cause the increase of the metals in an uncontrolled manner in air, terrain and aqueous media which has a very destructive effect upon the environment [6]. The accumulation of these metals in plants causes a prolonged effect upon the health of humans. The extension of the limits of these metals cause acute and chronic intoxication, cancer, teratogenesis and mutation [7,8]. These metals are particularly accumulated in brain, liver and kidneys causing a permanent damage in these organs [9]. The metals such as Cr, Cd and Pb interact with the enzymes in the structure of the plants effecting their physiological growth even if at very small concentrations [10]. The order of harmful and intoxicative effects of the heavy metals upon animals and humans are as follows: Hg > Cu > Zn > Ni > Pb > Cd > Cr > Sn > Fe > Mn > Al [11].

*Corresponding author, e-mail: kuddusi@gazi.edu.tr

However, some of them such as Cu, Zn, Mn, and Fe are essential for the organism. They provide micronutrients and activate some of the enzymes in human body [12]. The insufficient or the excessive intake of these metals causes various complications [13].

The analyses of heavy metals were carried out with induced coupled plasma atomic emission (ICP-AES) [14-16], inductively coupled plasma mass spectrometry (ICP-MS [17,18], flame atomic absorption spectrometry (FAAS) [19-21], graphite furnace atomic absorption spectrometry (GFAAS) [22,23], and inductively coupled plasma optical emission spectrometry (ICP-OES) [24,25].

FP and HSTD dishes are very rich in nutritional value. In addition, they have a very pleasant taste. Within our knowledge there are no study related to their heavy metal contents in these foodstuffs. This study involved the investigation of the heavy metal contents fenugreek paste and hot spicy tomato dip of different brands with different compositions according to the region purchased from different markets in Ankara, by wet burning process using ICP-OES equipment. The data obtained was evaluated according to Turkish Nutrient Codex and World Food Organization stipulations. Health risk index of FAO/WHO evaluations for Cd and Pb were separately carried out.

2. MATERIALS AND METHODS

2.1. Analytical methods

1 g of sample were kept in 5 mL HNO₃ for six hours and heated in a water bath until the emission of a brown fumes ceased. Then 2 mL H₂O₂ added to it. The resulting solution was evaporated till its volume remains 1mL and it was made to 25 mL with de-ionized water and each sample was filtered off from 0.45 µm filter paper. The stock solutions were prepared from 1000 ppm standard calibration (Merck) solutions. The analyses were carried out by the use of with a Perkin-Elmer 5300 DV brand ICP-OES.

There were 5 ppb, 10 ppb, 25 ppb, 50 ppb, 100 ppb and 200 ppb solution samples were prepared in water (2% HNO₃) of 10 different metals prepared and their percentage recoveries were calculated. The r² values of the standard solution were within 0.9960 and 0.9990.

2.2. Data analysis

2.2.1. Daily intake of metals (DIM)

DIM values of the metals were computed by the use of the following formula:

$$DIM = \frac{C \times D}{B}$$

The C, D and B values correspond to the heavy metal concentration of the sample (mg/kg), daily intake of fenugreek paste/ hot spicy tomato dip and average body weight of the person respectively [26]. The calculation of the daily intake of fenugreek paste/ hot spicy tomato dip was based upon the data obtained by the survey carried out upon 40 male and female participants. The average body weight of the participants was 50 kg.

2.2.2. Health risk index (HRI)

In order to evaluate the risk posed by the heavy metals upon human health one needs to find the exposure level of the human body to these metals. The HRI value is calculated by the use of the following formula:

$$HRI = \frac{DIM}{Rf_D} \quad [27]$$

Here Rf_D is the oral reference dose or the daily intake of a human with (mg/kg). This value were found to be 0.004 and 0,001 (mg/kg) for Pb and Cd.

3. RESULTS AND DISCUSSION

3.1. Concentrations of heavy metals in fenugreek paste and hot spicy tomato dip

The system was validated by taking the ICP-OES data of mixture of standard metals solution samples. The data obtained with these samples with known concentrations are tabulated in Table 1.

Table 1. The percentage recoveries of the mixture of standard metal solution samples with known concentrations.

Metal	Percentage Recovery					
	5 ppb	10 ppb	25 ppb	50 ppb	100 ppb	200 ppb
Fe	92	97	94	95	96	102
Co	96	89	93	104	98	105
Ni	85	92	107	102	110	98
Cu	105	95	97	98	92	108
Zn	87	91	95	95	98	109
Cr	93	88	96	105	104	108
Al	85	91	107	101	105	109
Mn	108	97	99	96	102	106
Pb	118	114	105	106	95	94
Cd	106	109	104	97	105	96

The amounts of Fe, Co, Ni, Cu, Zn, Cr, Al, Mn, Pb and Cd simultaneously determined in the local fenugreek pastes and hot spicy tomato dips with ICP-OES were tabulated in Table 2.

Table 2. The metal contents fenugreek paste (FP) and hot spicy tomato dips (HSTD)

Metals (ppb)	Samples					
	FP1	FP2	FP3	HSTD 1	HSTD 2	HSTD 3
Fe	30.74±1.42	10.50±1.69	3.27±0.60	32.47±2.17	9.52±0.44	15.31±1.02
Co	16.85±1.69	18.86±1.20	16.69±0.38	18.23±0.92	16.54±5.12	18.05±1.79
Ni	58.04±3.44	59.76±3.47	57.38±0.77	58.44±2.05	58.92±0.24	58.85±0.61
Cu	15.92±0.68	16.90±0.97	15.85±0.55	16.10±1.58	15.17±1.26	14.37±1.38
Zn	60.63±0.48	61.75±0.75	63.38±0.18	58.53±0.47	58.18±0.17	55.38±0.14
Cr	96.37±2.25	93.28±0.82	94.56±2.39	95.95±2.68	97.00±2.18	85.88±3.01
Al	191.30±1.01	201.20±1.10	105.40±1.76	208.70±2.98	211.40±6.86	253.10±1.36

Mn	31.27±0.09	30.71±0.17	34.42±0.33	29.16±0.28	29.38±0.25	26.95±0.34
Pb	113.70±5.68	114.20±3.30	107.50±1.44	104.20±7.84	102.40±6.44	112.70±6.33
Cd	55.97±0.20	56.10±0.34	56.49±0.39	56.56±0.50	55.98±0.75	56.87±0.43

The rheological characterization of fenugreek paste have been carried out and the pathological bacteria which may form in it have been investigated in detail [1,2]. The data present in the literature do not allow us to make any comparison of the heavy metal contents of FP and HSTD foodstuff. However, the Pb and Cd levels of ketchup were found to be 25.0 and 14.1 ppb respectively [28].

Cd and Pb are particularly toxic. They may come from the food chain or the production process and they may cause a great harm human health even taken in trace amounts. That is why these to metals need special attention. Although there are no limits for heavy metals set for either fenugreek paste or hot spicy tomato dip in the circular of the maximum limits of pollutants in the Turkish food Codex stipulated were taken to be the maximum acceptable levels in food stuff. The average Pb levels found in this study was higher from the lower level given by the codex however it remains lower than the higher limit (0.02-1.5 mg/kg).

3.2. Health risk assessment

The Joint FAO/WHO Expert Committee on Food Additives (JEF-CA) recommends that provisional tolerable intakes of Cd and Pb are 7.00, 25.00 $\mu\text{g kg}^{-1} \text{week}^{-1}$ respectively. A body weight of 50 kg and an intake quantity of fenugreek paste or hot spicy tomato dip per day of 50 g were presumed. The weekly intake value of these metals according to these data are listed in Table 3.

Table 3. The weekly intake and HRI values Cd and Pb

Sample	Weekly intake ($\mu\text{g/kg}$ body weight)		Health Risk Index (HRI)	
	Cd	Pb	Cd	Pb
FP 1	0.39	0.80	0.056	0.028
FP 2	0.39	0.79	0.056	0.029
FP 3	0.40	0.75	0.056	0.027
HSTD 1	0.40	0.73	0.057	0.026
HSTD 2	0.38	0.72	0.056	0.025
HSTD 3	0.39	0.78	0.057	0.028

Based upon the weekly intake values listed in Table 3 one has to consume 18 kg and 30 kg of fenugreek paste or hot spicy tomato dip in order to exceed the tolerable amounts stipulated for Cd and Pb. Since this is in proportionate beyond any extend there is no situation posing any threat against the health of human. The HRI values indicate a similar situation. The fact that HRI values are below 1 shows that the foodstuff are quite safe and healthy [29]. This value has been very much below 1 for the fenugreek pastes and hot spicy tomato dip investigated in this study.

4. CONCLUSIONS

In this study, the metal content of fenugreek paste and hot spicy tomato dip as regard to 10 different metals. Pb and Cd were separately investigated due their toxic effects. The data were valuated according to both Turkish Food Codex and the Joint FAO/WHO Expert Committee on Food Additives (JEFCA). The studies carried out revealed that there was no unhygienic situation for both foodstuff.

However, the effect of the ever increasing population of the world causes the accumulation of the heavy metals in the environment with an alarming pace. These accumulated environmental metal concentrations are administered by the humans in various ways. Therefore, the preparation and keeping of fenugreek paste or hot spicy tomato dip should be standardized. In addition to these, the equipment used during this process must be made off with inert material and transportation of these foodstuffs must comply with the existing norms.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors

REFERENCES

- [1] Işıklı, N. D. and Karababa, E., “Rheological characterization of fenugreek paste (çemen)”, *Journal of Food Engineering*, 69:185–190 (2005).
- [2] Yetim, H., Sagdic, O., Dogan, M. and Ockerman, H. W., “Sensitivity of three pathogenic bacteria to Turkish cemen paste and its ingredients”, *Meat Science*, 74:354–358 (2006).
- [3] Ahmad, A., Alghamdi, S. S., Mahmood, K. and Afzal, M., “Fenugreek a multipurpose crop: Potentialities and improvements”, *Saudi Journal of Biological Sciences*, 23:300–310 (2016).
- [4] Gómez-Sagasti, M. T., Alkorta, I., Becerril, J. M., Epelde, L., Anza, M. and Garbisu, C., “Microbial Monitoring of the Recovery of Soil Quality During Heavy Metal Phytoremediation”, *Water Air Soil Pollution*, 223:3249–3262 (2012).
- [5] Chung, S. G., Ryu, J. C., Song, M. K., An, B., Kim, S. B., Lee, S. H. and Choi, J. W., “Modified composites based on mesostructured iron oxyhydroxide and synthetic minerals: A potential material for the treatment of various toxic heavy metals and its toxicity”, *Journal of Hazardous Materials*, 267:161–168 (2014).
- [6] Demirezen, D. and Uruç, K., “Comparative study of trace elements in certain fish, meat and meat products”, *Meat Science*, 74:255–260 (2006).
- [7] Zhang, Y., Zhou, J., Gao, F. J., Zhang, B. J., Ma, B. and Li, L. G., “Comprehensive ecological risk assessment for heavy metal pollutions in three phases in rivers”, *Transactions of Nonferrous Metals Society of China*, 25:3436–3441 (2015).
- [8] Dziubanek, G., Piekut, A., Rusin, M., Baranowska, R. and Hajok, I., “Contamination of food crops grown on soils with elevated heavy metals content”, *Ecotoxicology and Environmental Safety*, 118:183–189 (2015).
- [9] Mcmanamon, C., Burke, A. M., Holmes, J. D. and Morris, M. A., “Amine-functionalised SBA-15 of tailored pore size for heavy metal adsorption”, *Journal of Colloid and Interface Science*, 369:330–337 (2012).
- [10] Hansch, R. and Mendel, R. R., “Physiological functions of mineral micronutrients (Cu, Zn, Mn, Fe, Ni, Mo, B, Cl)”, *Current Opinion in Plant Biology*, 12:259–266 (2009).

- [11] Shubina, N. A. and Kolesov, G. M., "Determination of Heavy Metals as Environmental Pollutants: Use of Instrumental Neutron Activation Analysis", *Journal of Analytical Chemistry*, 57(10):912–919 (2002).
- [12] Yadav, A., Ram, A., Majithiya, D., Salvi, S., Sonavane, S., Kamble, A., Ghadigaonkar, S., Jaiswar, J. R. M. and Gajbhiye, S. N., "Effect of heavy metals on the carbon and nitrogen ratio in *Avicennia marina* from polluted and unpolluted regions", *Marine Pollution Bulletin* 101:359–365 (2015).
- [13] Lewis, S., Donkin, M. E. and Depledge, M. H., "Hsp70 expression in *Enteromorpha intestinalis* (Chlorophyta) exposed to environmental stressors", *Aquatic Toxicology*, 51:277–291 (2001).
- [14] Zachariadis, G. A. and Sahanidou, E., "Multi-element method for determination of trace elements in sunscreens by ICP-AES", *Journal of Pharmaceutical and Biomedical Analysis*, 50:342–348 (2009).
- [15] Xie, J. H., Shen, M. Y., Nie, S. P., Liua, X., Yina, J. Y., Huang, D. F., Zhanga, H. and Xie, M. Y., "Simultaneous analysis of 18 mineral elements in *Cyclocarya paliurus* polysaccharide by ICP-AES", *Carbohydrate Polymers*, 94:216–220 (2013).
- [16] Gong S., Luo, L., Gong, W., Gao, Y. and Xie, M., "Multivariate analyses of element concentrations revealed the groupings of propolis from different regions in China", *Food Chemistry*, 134:583–588 (2012).
- [17] Dai, B., Cao, M., Fang, G., Liu, B., Dong, X., Pan, M. and Wang, S., "Schiff base-chitosan grafted multiwalled carbon nanotubes as a novel solid-phase extraction adsorbent for determination of heavy metal by ICP-MS", *Journal of Hazardous Materials*, 219-220:103–110 (2012).
- [18] Filipiak-Szok, A., Kurzawa, M. and Szłyk, E., "Determination of toxic metals by ICP-MS in Asiatic and European medicinal plants and dietary supplements", *Journal of Trace Elements in Medicine and Biology*, 30:54–58 (2015).
- [19] Zhao, X., Song, N., Jia, Q. and Zhou, W., "Determination of Cu, Zn, Mn, and Pb by microcolumn packed with multiwalled carbon nanotubes on-line coupled with flame atomic absorption spectrometry", *Microchimica Acta*, 166:329–335 (2009).
- [20] Mortada, W. I., Kenawy, I. M. M., Abdelghany, A. M., Ismail, A. M., Donia, A. F. and Nabieh, K. A., "Determination of Cu^{2+} , Zn^{2+} and Pb^{2+} in biological and food samples by FAAS after preconcentration with hydroxyapatite nanorods originated from eggshell", *Materials Science and Engineering C*, 52:288–296 (2015).
- [21] Yıldız, E., Saçmacı, Ş., Kartal, Ş. and Saçmacı, M., "A new chelating reagent and application for coprecipitation of some metals in food samples by FAAS", *Food Chemistry*, 194:143–148 (2016).
- [22] Li, J., Jia, C., Lua, Y., Tang, S. and Shim, H., "Multivariate analysis of heavy metal leaching from urban soils following simulated acid rain", *Microchemical Journal*, 122:89–95 (2015).
- [23] Ali, M. M., Ali, M. L., Islam, Md. and Rahman, Md. Z., "Preliminary assessment of heavy metals in water and sediment of Karnaphuli River, Bangladesh", *Environmental Nanotechnology Monitoring & Management*, 5:27–35 (2016).
- [24] Chand, V. and Prasad, S., "ICP-OES assessment of heavy metal contamination in tropical marine sediments: A comparative study of two digestion techniques", *Microchemical Journal*, 111:53–61 (2013).
- [25] Orecchio, S., Amorello, D. and Barreca, S., "Wood pellets for home heating can be considered environmentally friendly fuels? Heavy metals determination by inductively coupled plasma-optical emission spectrometry (ICP-OES) in their ashes and the health risk assessment for the operators", *Microchemical Journal*, 127:178–183 (2016).

- [26] Liu, B., Huang, Q., Cai, H., Guo, X., Wang, T. and Gui, M., “Study of heavy metal concentrations in wild edible mushrooms in Yunnan Province, China”, *Food Chemistry*, 188:294–300 (2015).
- [27] Mahmood, A. and Malik, R. N., “Human Health Risk Assessment Of Heavy Metals Via Consumption Of Contaminated Vegetables Collected From Different Irrigation Sources In Lahore, Pakistan”, *Arabian Journal of Chemistry*, 7:91–99 (2014).
- [28] Hadiani, M. R., Farhangi, R., Soleimani, H., Rastegar, H. and Cheraghali, A. M., “Evaluation of heavy metals contamination in Iranian foodstuffs: canned tomato paste and tomato sauce (ketchup)”, *Food Additives & Contaminants: Part B*, 7 (1):74–78 (2014).
- [29] Fang, Y., Sun, X., Yang, W., Ma, N., Xin, Z., Fu, J., Liu, X., Liu, M., Mariga, A. M., Zhu, X. and Hu, Q., (2014) Concentrations and health risks of lead, cadmium, arsenic, and mercury in rice and edible mushrooms in China”, *Food Chemistry*. 147:147–151 (2014).