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Heavy Metal Content of Potato and Corn Chips from Turkey

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Because of negative and/or positive important roles of traces heavy metals ions in the body functions, the determinations of the traces heavy metal ions in environmental samples including natural waters and foods are the important part of the analytical chemistry and public health studies around the world (Abduli and Safari E, 2003; Taher *et al.*, 2003; Cesur, 2004; Krishna *et al.*, 2004; Kadioglu *et al.*, 2005). While the consumption of the food in the diets, the traces metal contents of foods are directly taken to the body (Tuzen *et al.*, 2003; Soylak *et al.*, 2004; Ferreira *et al.*, 2004; Mendil *et al.*, 2005). Potato and corn chips are an important place in our daily diet (Pedersen and Olsson, 2003; Sandhu *et al.*, 2002; Sivakesava and Irudayaraj, 2000). Especially, children also consume corn and potato chips at big amounts. Consequently, the contents of the chips including traces heavy metal ions are important. In the determination of the traces heavy metal ions in food samples, atomic absorption spectrometry (AAS) is the main instrument. For AAS determinations, the physical state of the sample analyzed should be liquid. Because of this, prior to AAS determinations of metals in food samples, a digestion procedure is necessary. Wet digestion is important methodology for the digestion of the traces heavy metals in solid samples. Because of high sample-processing time, costs and hazards, instead of these methodologies, the researchers have preferred microwave digestion procedures. Also wet digestion processing uses large volumes of concentrated acid in open beakers over heat. Microwave techniques are widely applied for the decomposition of various foods such as mushroom (Tuzen *et al.*, 2003), vegetables (Araújo *et al.*, 2002; Tuzen, 2003), corn and potato (Dolan and Capar, 2002).

In the present work, the levels of copper, zinc, manganese and iron in some corn and potato and corn chips produced in Turkey were determined by FAAS after microwave digestion.

MATERIALS AND METHODS

All reagents used present work, were of analytical reagent grade unless otherwise stated. Double deionised water (Milli-Q Millipore 18.2 MΩ/cm resistivity) was used for all dilutions. H_2SO_4, HNO_3 and H_2O_2 were of suprapur quality (E.

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Merck). All the plastic and glassware were cleaned by soaking in dilute nitric acid (1+9) and were rinsed with distilled water prior to use. The standard solutions of investigated metal ions for calibration procedure were produced by diluting a stock solution of 1000 mg/L of the all the investigated element supplied by Sigma and Aldrich.

A Perkin Elmer AAnalyst 700 model flame atomic absorption spectrometer with deuterium background corrector was used in the present study. All AAS measurements were carried out in an air/acetylene flame. The operating parameters for the investigated elements were set as recommended by the manufacturer.

Milestone Ethos D closed vessel microwave digestion system (maximum pressure 1450 psi, maximum temperature 300 °C) was used. Teflon reaction vessels were used all the digestion procedures. The reaction vessels were cleaned using 5 ml of concentrated nitric acid before each digestion.

Wet digestion of potato and corn chips samples was performed using a mixture of HNO_3: H_2O_2 (8:4) (12 mL for a 1.0 g sample). This mixture was heated up to 130 °C for 3 h. After cooling, 5 ml of distilled water was added to the sample and mixed. The residue was filtered through blue band filter paper. Then the sample was diluted to 10 ml with distilled water. Blank digestions were also carried out in the same way. The levels of analytes in the final solutions were determined by FAAS.

Apple Leaves (SRM 1515) standard reference material (SRM) and chip samples were accurately weighed around 100 mg and 1000 mg, respectively. The chip samples were transferred to Teflon vessels. Then related acid mixtures were added to samples. The microwave digestion programs were applied to the samples. After microwave digestion program completed, the residue was filtered through blue band filter paper. Then the sample was diluted to 10 ml with distilled water. The metal determinations were performed by flame atomic absorption spectrometry. A blank digest was carried out in the same way for each digestion. All sample solutions were clear.

RESULTS AND DISCUSSION

Three different microwave programs given in Table 1 were applied to a reference material (Apple Leaves (SRM 1515)) with HNO_3:H_2O_2 (4:2) mixture. Total digestion times of the programs are: 31 minutes for Program 1, 33 minutes for Program 2, and 36 minutes for Program 3. Program 1 was preferred. Program 1 was provided to the minimum digestion time and highest recovery values for the reference standard material.

The mixture of HNO_3:H_2O_2 (4:2), HNO_3:H_2SO_4 (4:2) and HNO_3:HCl (4:2) were applied to reference material by using program 1. The reference material was also digested with wet digestion. The results for this work were given in Table 2. All

Table 1. Operating conditions for microwave digestion system for the chip samples

	Program 1		Program 2		Program 3	
Steps	Time (min)	Power (W)	Time (min)	Power (W)	Time (min)	Power (W)
1	2	250	4	250	5	250
2	2	0	2	0	2	0
3	6	250	5	500	6	550
4	5	400	6	400	7	400
5	8	550	8	550	8	550
6	8	Vent	8	Vent	8	Vent

Table 2. The digestion performance of the various microwave digestion program for the trace heavy metal contents of Apple Leaves (SRM 1515) reference material, n=4

	Fe	Cu	Mn	Zn
Certified Value (μg/g)	83	5.64	54	12.5
Program 1a	82.9±4.7	5.48±0.36	52.7±3.5	12.8±0.9
Recovery, %	99	97	98	103
Program 1b	79.5±5.9	5.32±0.45	50.1±4.3	11.9±0.7
Recovery, %	96	94	93	95
Program 1c	80.2±6.1	5.26±0.50	51.6±3.9	12.2±1.1
Recovery, %	97	93	96	98
Wet digestion, a	78.6±7.4	5.29±0.52	51.8±0.5	12.1±1.2
Recovery, %	95	94	96	97

a: HNO_3:H_2O_2; 4:2, b: HNO_3:H_2SO_4; 4:2, c: HNO_3:HCl; 4:2

analytical results for analyte ions in reference material were within or near the certified values for different acid mixtures for microwave digestion and wet digestion with some exceptions.

In order to compare wet and microwave digestion procedures for chip samples, a potato chip sample was digested. For microwave digestion of potato chips, Program 1 was used by using with mixture of HNO_3:H_2O_2. For wet digestion, HNO_3:H_2O_2 mixture was used. Approximately, total time for the wet digestion is 4 hour for a sample. For microwave digestion for a sample, total time was one hour.

The recovery values for the wet and microwave digestions were quantitative (> 95%). The relative standard deviations were less than 10 % for all the investigated elements. T-test was used in this study ($p<0.05$). The comparison of wet and microwave digestion methods showed no statistically significant differences in results (Table 3).

The detection limit based on 3σ of the reagent blank and quantitation limit based on 10σ of the reagent blank for flame atomic absorption spectrometry (FAAS) are calculated for each investigated analyte ions. The results are given in Table 4. The

Table 3. Comparison of trace metal contents in a chip sample using wet and microwave digestion methods (as μg/g), n=5

Element	Wet digestion	Microwave digestion[b]
Cu	2.43±0.21	2.58±0.12
Zn	10.8±1.1	11.4±0.5
Mn	3.75±0.29	3.62±0.10
Fe	15.9±1.4	16.3±0.9

[b]Program 1a

contamination was not a problem in the determinations, because of the level of the each analyte ions in the blank digest were close to detection limits given in Table 4.

Table 4. Detection and quantitation limit as mg/l for investigated analyte ions by FAAS

Metal	Limit of detection (3σ)	Limit of quantitation (10σ)
Fe	0.21	0.70
Zn	0.10	0.33
Mn	0.15	0.50
Cu	0.12	0.40

The levels of copper, zinc, manganese and iron in thirteen potato and corn chip samples were determined after application of microwave digestion with Program 1 by the aid of the mixture of HNO_3:H_2O_2 (4:2). In the metal determinations were performed by flame AAS. The results were given in Table 5. The investigated elements concentration ranges in the analysed samples for microwave digestion were <1-3.6 μg/g for copper, 4.5-14.4 μg/g for zinc, 1.1-6.3 μg/g for manganese and 9.4-22.4 μg/g for iron (Table 5).

The lowest and highest iron contents were found in Cheetos Chip and Lays Chip samples. Minimum and maximum manganese levels were determined in Migros Chip and Ruffles Chips samples. The lowest and highest zinc contents were found in Migros Cips and Doritos Alaturca Chips. The highest copper content was determined in Kar Cipso. In general, copper concentrations were found to be <1 μg/g in the chip samples. The metal contents of corn and potato samples have been reported as 0.28-1.26 μg/g for copper, 2.4-3.55 μg/g for iron, 3.50-2.52 μg/g for zinc and 0.884-8.40 μg/g for manganese, respectively (Dolan and Capar, 2002).

Metals like iron, copper, zinc and manganese are essential metals for human, since they play an important role in biological systems. But the essential heavy metals can produce toxic effects when the metal intake is excessively elevated (Schroeder, 1973; Mendil *et al.*, 2005). The order of accumulation of trace metals in potato and corn chip samples from Turkey was determined as iron > zinc > manganese > copper, respectively. The order of given above for trace metals can be explained by their affinities to the protein molecules in potato and corn chip samples.

Table 5. The levels of investigated ions in the corn and potato chip samples produced and marketed in Turkey

			Concentration (μg/g)			
No	Sample	Properties	Cu	Zn	Mn	Fe
1	Lays	Spicely aroma	3.1±0.3	9.6±0.7	3.4±0.3	22.4±2.1
2	Ruffles	Potato chips	2.4±0.2	6.1±0.5	6.3±0.5	11.3±1.0
3	Migros cips	Potato chips	1.5±0.1	7.1±0.6	2.0±0.1	12.2±1.1
4	Cheetos	Corn appetizers	<1	6.0±0.5	1.1±0.1	10.7±0.9
5	Mini cheetos	Natural corn semolina	<1	5.2±0.5	1.2±0.1	13.5±1.3
6	Doritos alaturca	Corn chips with sesame and cheese	1.8±0.2	14.4±1.2	4.7±0.4	20.4±1.8
7	Kar (Cerezos)	Corn appetizers with pistachio nut	2.5±0.2	13.3±1.1	5.0±0.4	16.1±1.5
8	Cheetos (Fritolay)	Corn appetizers	<1	5.6±0.4	1.5±0.1	9.4±0.8
9	Migros cips	Potato chips with cheese and herb	<1	5.1±0.5	2.4±0.2	12.9±1.1
10	Doritos	Potato chips with spices	<1	11.6±1.0	3.6±0.3	15.9±1. 4
11	Migros cips	Chips with wheat, beef and onion	<1	4.6±0.4	3.4±0.3	15.5±0.9
12	Kar cipso	Potato chips	3.6±0.3	9.2±0.8	3.0±0.3	10.4±0.7
13	Migros cips	Corn chips with cream cheese	<1	4.5±0.3	1.1±0.1	11.3±1.1

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