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Levels of Toxic Elements in Green Coffee and Their Infusions Commercialized in Argentina

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Abstract

Green coffee is the grain that is extracted from the fruit of the coffee plant and that wasn't roasted; therefore it conserves its organoleptic properties and active principles. The benefits of the consumption of their infusions are mainly related to the presence of chlorogenic acids that have antioxidant activity. However, the content of essential, non-essential and toxic elements began to be studied to improve their quality, nutritional value and certain sensory properties. The objective of this work is to determine the contents of Cd, Pb and As in the samples of green coffee, bags and their respective infusions by atomic absorption spectrometry with graphite furnace (ETAAS). Three brands available in local commerce were treated in two different ways. One method consisted of preparing the infusion and the other, an acid digestion of the contents of the green coffee bag. The contents of As, Pb and Cd were measured using the calibration line method. An acceptable percentage recovery was obtained. All the green coffee brands analyzed presented contents of Cd and As below 1.0μg.g^{-1}, while the Pb values were lower than 3.0μg.g^{-1}. These contents do not exceed the limits established by the regulations in force. The infusions also gave low levels of said metals, below the established limits. The study of the contribution of these heavy metals by the consumption of green coffee indicates that adverse effects on health are unlikely to occur.

Keywords: Cadmium; Lead; Arsenic; Green coffee; Infusions

Introduction

Coffee is one of the world's most popular beverages. The green coffee is the bean picked from the fruit of the coffee tree before they are submitted to the roasted process; therefore it conserves its organoleptic properties and active principles. The benefits of the consumption of their infusions are mainly related to the presence of chlorogenic acids that have antioxidant activity. Due to the habitual consumption of coffee, the presence of essential, non-essential and toxic elements began to be studied to optimize its quality, nutritional value and certain sensorial properties [1]. Different analytical techniques were used to determine elemental contents in coffee [2]. Nutrient elements were determined by flame atomic absorption spectrometry (Ca, Mg, Fe, Cu, Mn and Zn) and flame atomic emission photometry (Na and K) after preparing the samples by two different wet digestion procedures [3]. The mineral composition of 14 elements (Ca, Mg, K, Na, P, Co, Mn, Fe, Cr, Ni, Zn, Cu, Cd and Pb) by FAAS in coffee marketed in Poland and its infusions was studied [4]. Ca, Cu, Fe, Mg and Mn contents in green coffee infusions by FAAS were analyzed and the rate of the extraction of these elements were determined concluding that the rate was different according to the preparation method [5]. Two digestion procedures for coffee samples using diluted nitric acid in closed vessels for inductively coupled plasma optical emission spectrometry were evaluated: one using microwave-assisted heating and the other using pressurized bomb [6]. Besides, methods for elemental determination of green coffee, without digestion step, using direct solid sampling electro thermal atomic absorption spectrometry have been developed [7].

The presence of some minor and trace elements in excess, such as Al, Cd, Ni, Sb, Sn, Pb and As in coffee or its infusions can be toxic to health therefore, its concentrations in the product and during the production of coffee should be strictly controlled [2]. Cr, Ni, Cd and Pb were quantified by optical emission spectrometry of inductively coupled plasma ICP-OES in Brazilian coffee [8] and trace element contents of five brands of Indian instant coffee (Ca, Cr, Fe, K, Mg, Mn, Ni, Cd and Pb) using atomic absorption spectrometry and differential pulse anodic stripping voltammetry were analyzed [9].

The content of essential and non-essential metals in infusions of green coffee and instant coffee

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has been well studied in different parts of the world. However, the bibliographic references about the content of toxic metals in green coffee marketed in Argentina are scarce.

The present paper reports levels of some toxic metals (Cd, Pb and As) in green coffee and their infusions, commercially available in Tucumán province from Argentina by electro thermal atomic absorption spectrometry. Besides, the intake of these elements was calculated considering the daily consumption of their infusions. The data obtained were compared with the established limits by the legislation.

Materials and Methods

Instrumentation

For the elemental determination, a Perkin-Elmer atomic absorption spectrometer (Norwalk, CT, USA) AAnalyst 100 was used equipped with deuterium background corrector, graphite furnace HGA 800 and autosampler AS-72. All measurements were made with hollow cathode lamps of each element, 0.7nm bandwidth, 10mA lamp current and pyrolitic graphite furnace with integrated platform (part N° B3000407, Perkin-Elmer). 99.9% high purity argon was used as purge gas. The analytical readings were made at 228.8nm, 283.3nm and 193.7nm for Cd, Pb and As respectively.

The default temperature program provided by the manufacturer was used in all cases. The drying temperature (120°C), cooling prior to atomization (20°C) and cleaning (2600°C) were the same for the three elements. While the temperatures of pyrolysis and atomization varied: 850 and 1650°C for Cd, 700 and 1800°C for Pb and 800 and 2300°C for As.

Reagents solutions and samples

A NANOpure water purification system (Barnstedt, IA, USA) was used to obtain ultrapure water (18Ωcm resistivity). 65% Nitric acid, analytical grade (Merck, Darmstadt, Germany) redistilled in quartz sub-boiling distiller and hydrogen peroxide 100vol. was used for the digestion of the samples. A nitrate of Mg and Pd solution (Perkin-Elmer) was used as matrix modifier for As, and ammonium dihydrogen phosphate for Cd and Pb.

Three intermediate standards were prepared with 5% (v/v) nitric acid: one of 1mg.L^{-1} from a standard solution of Cd 1000mg.L^{-1} traceable to SRM from NIST Merck; another of 10mg.L^{-1} from a standard solution of Pb 1000mg.L^{-1} traceable to SRM of NIST Merck and the last one of 150 mg.L^{-1} from a standard solution of As 1000mg.L^{-1} traceable to SRM by Perkin-Elmer Pure.

Three different brands of green coffee in bags and their infusions available in local commerce were analyzed.

Sample preparation

The three green coffees brands in bags were treated in two different ways. One method (P_1) consisted in preparing an infusion. In a beaker, 200mL of deionized water was boiled on a hotplate. Then, the bag of green coffee was immersed, leaving it to rest for 20minutes. It was allowed to cool and was transferred to a previously decontaminated plastic container. In the other method (P_2), an acid digestion of the green coffee bag content was performed. The contents of the bag (approximately 2g) were weighed in an analytical balance, 20mL of nitric acid was added and it was heated to 180°C in a hot plate for one hour. It was allowed to cool and then 2mL of 100vol. hydrogen peroxide was added. The mixture was again heated to dryness; 2.5mL of nitric acid was aggregated, filtered into a 50mL volumetric flask and brought to volume with deionized water. A preparation blank solution was made in parallel.

The accuracy of the method was determined by calculating the recovery prior to the chemical treatment of the samples. 2μg.L^{-1} of Cd, 20μg.L^{-1} of Pb and 50μg.$L^{-1}$of As were added to the sample. The recovery was also calculated after the chemical digestion treatment, adding 2μg.L^{-1}, 30μg.L^{-1} and 50μg.L^{-1} of Cd, Pb and As respectively.

Elemental analysis

The determination of cadmium, lead and arsenic was carried out by atomic absorption spectrometry with electro thermal vaporization (ETAAS). In each case, calibration lines were built and worked with appropriate sensitivities. For the analysis of each element, three to six readings were made to each of the green coffee samples.

Cadmium determination

Dilutions of the Cd solution of 1mg.L^{-1} were made to obtain two solutions of 1μg.L^{-1} and 5μg.L^{-1} respectively. The calibration line was constructed from the standard solution of 5μg.L^{-1} with the autosampler of the equipment in the range of 1 to 5μg.L^{-1}. The linear regression analysis was performed (-0.0033 + 0.1054 [Cd]) and a correlation coefficient equal to r=0.9996 was obtained. The sensitivity of the equipment was controlled with the standard of 1μg.L^{-1}, giving a good sensitivity for the determination of cadmium. The Limit of Detection (LOD) was calculated as three times the signal of the blank, obtaining a value of 0.2μg.L^{-1} and the Limit of Quantification (LOQ) was calculated as ten times the blank signal, obtaining a value of 1μg.L^{-1}.

Lead determination

Dilutions of the Pb solution of 10mg.L^{-1} were made to obtain two solutions of 20μg.L^{-1} and 100μg.L^{-1} respectively. The sensitivity of the equipment was controlled with the standard solution of 20μg.L^{-1} and the calibration line was constructed with the 100μg.L^{-1} in the range of 10 to 100μg.L^{-1}. The linear regression analysis (0.0127 + 0.0056 [Pb]) was performed and a value of r=0.9991 was obtained. The Limit of Detection (LOD) gave equal to 4μg.L^{-1}, while the Limit of Quantification (LOQ) gave a value of 10μg.L^{-1}.

Arsenic determination

From the solution of As of concentration equal to 150 mg.L^{-1} a solution of 100μg.L^{-1} was prepared to control the sensitivity of the equipment, obtaining an adequate value. A calibration line between 30 and 150μg.L^{-1} was made using the equipment autosampler. The equation of the line (0.0772 + 0.003 [As]) was obtained by linear regression and a value of r=0.9921. The calculated LOD value was 15μg.L^{-1}, while the LOQ was 30μg.L^{-1}.

Results and Discussion

The concentrations of Cd obtained are below the LOD in two of the three green coffee brands studied, both in the contents of the bag and in their infusions. For the third mark, the contents of the sachet gave a Cd value equal to 0.038μg.g^{-1}, with a precision of 9.7%, in terms of RSD. The level of Cd obtained is below the limits established by the AECOSAN (2014) [10] for food supplements of 1.0μg.g^{-1}. The infusion of this last mark gave a Cd value equal to 0.376μg.L^{-1} with a precision of 11.7%, in terms of RSD. This concentration value is lower than the limits established by the Argentine Food Code (CAA, 2012) [11] for drinking water of 5μg.L^{-1}. No Cd limit values were found

Table 1: Descriptive statistical analysis of lead results in three green coffee brands.

	*N	Mean ($\mu g.g^{-1}$)	Deviation	95% Confidence interval for the mean		Minimum ($\mu g.g^{-1}$)	Maximum ($\mu g.g^{-1}$)
				Lower limit	Upper limit		
Brand 1	6	0.825	0.0980	0.722	0.928	0.725	1.00
Brand 2	3	1.05	0.00818	1.03	1.07	1.04	1.05
Brand 3	3	0.747	0.0140	0.712	0.782	0.737	0.763
Total	12	0.861	0.134	0.776	0.946	0.725	1.05

*N: Number of results obtained for each brand.

Table 2: Analysis of variance (ANOVA) for lead data.

	Sum of squares	Degrees of freedom	Quadratic mean	F	Significance
Between groups	0.149	2	0.075	13.840	0.002
Within groups	0.049	9	0.005	-	-
Total sum of squares	0.198	11	-	-	-

for coffee infusions in Argentine legislation. In January 2009, the European Food Safety Authority (EFSA) [12] established a Tolerable Weekly Intake (TWI) for cadmium of 2.5$\mu g.kg^{-1}$ body weight. The Cd intake was calculated for each 200mL infusion cup, which gave a Cd value equal to 0.0752μg. If you consider the consumption of two cups of green coffee infusion per day, for a person of average weight of 70Kg (BW), the consumption would be 0.15μg of Cd per day and 1.05μg per week. This value is below the indicated TWI limit.

The concentrations of Pb obtained for the three analyzed brands of green coffee gave average values of 0.825$\mu g.g^{-1}$, 1.05$\mu g.g^{-1}$ and 0.747$\mu g.g^{-1}$ that are below the limits established by the AECOSAN(2015) [13] in food supplements of 3.0$\mu g.g^{-1}$. The precision, in terms of RSD, was between 1 to 12%. The results of Pb in the infusions of the three brands gave below the LOD (4$\mu g.L^{-1}$), being also lower than the limits in drinking water established by the CAA (2012) [11] of 5$\mu g.L^{-1}$.

Cd (0.005-0.019$\mu g.g^{-1}$) and Pb (0.23-0.31$\mu g.g^{-1}$) levels in instant coffee were reported lower than the data obtained in the present work [14]. This could be a consequence of the loss of analyte in the coffee roasting process because the high temperatures cause a series of physical and chemical changes in the beans of coffee. In Brazilian coffee tissues, higher Cd values were obtained by FAAS, between 0.70-0.75$\mu g.g^{-1}$ while Pb was below 0.01$\mu g.g^{-1}$ [15]. Cd and Pb were not detected by flame atomic absorption spectrometry in three brands of Ethiopian coffee powder and its infusions [16].

In all the samples of green coffee analyzed the levels of As were lower than the LOD, results that agree with those of other authors [17], who report arsenic levels in ground coffee below the LOD of INAA. The limit of as allowed in food is related to the consumption of it. In Bangladesh, rice consumption is high, approximately 450g. day^{-1} per person, so the permitted levels are between 110 and 550$\mu g.Kg^{-1}$ [18]. While in other countries such as Brazil the level established for as by the legislation for tea, mate, coffee and derivatives is 1$\mu g.g^{-1}$, since its consumption is much lower [19].

Accuracy was estimated by calculating analyte recoveries in different stages of the chemical treatment giving satisfactory results in a range of 87 to 98%.

To estimate the transfer of these metals from the contents of the green coffee bag to their infusion, the transfer rate (T %) was calculated using equation (1) [20].

$$T\% = c_2 . v . 100 / c_1 . m \quad \text{.....(1)}$$

c_2 = concentration of the studied element in the infusion [$\mu g.L^{-1}$]

v = volume of the infusion [L]

c_1 = concentration of the studied element in the raw material [$\mu g.g^{-1}$]

m = quantity of raw material used to prepare the infusion [g]

The transfer rate of Cd and As could not be calculated because most of the green coffee brands studied gave concentrations below the LOD. The rate of transfer of Pb gave 39%, value that is within the range from 4.8 to 52.4%, obtained for others authors for infusions of herbs and fruits [21].

Statistical analysis

The statistical analysis of the data was performed only for lead. Arsenic values are not available because there was not detected by the technique used and there are cadmium values only in one brand.

The average values of lead obtained and their standard deviations are indicated in Table1. The maximum and minimum values of lead for each brand of green coffee analyzed and the confidence limits for 95% probability are also shown. The data is shown with three significant figures.

The levels of Pb ($\mu g.g^{-1}$) obtained in the different brands of green coffee were compared by means of one-way ANOVA, using the software SPSS 25.0 for Windows, and the results are shown in Table 2.

A statistical Analysis of Variance (ANOVA) at 95% confidence level of the determination of lead, indicated that there is no significant difference between the means of each brand ($p<0.05$).

Risks evaluation

The evaluation of the potential risk for human health was carried out according to the Estimated Daily Intake (EDI) and the risk quotient (HQ% hazard quotient) [20]. The EDI was calculated using C_1 which is the concentration of Pb in green coffee ($\mu g.g^{-1}$), the Maximum Daily Consumption (MDC) of green coffee, the transfer rates (T% transfer rate) of Pb and the average body weight (BW average body weight). If a person of 70Kg takes two cups of infusion per day, one can consider a MDC of 4g corresponding to two bags of green coffee.

The EDI was calculated by means of equation (2), giving a value of 0.0184$\mu g\ kg^{-1}\ BW^{-1}\ day^{-1}$.

$$EDI = C_1 . MDC . T / BW \quad \text{.....(2)}$$

The risk quotient (HQ %) was calculated using equation (3).

HQ = EDI / ADI. 100…….(3)

The Acceptable Daily Intake (ADI) value is established by the European Food Safety Authority (EFSA, 2012) [12], whose value is 0.5μg kg^{-1} BW^{-1} day^{-1}. A hazard ratio less than or equal to 1 indicates that adverse effects are unlikely to occur, so it can be considered to have negligible risk. HQs greater than 1 do not indicate statistical probabilities of damage occurring, but a statement of how much the exposure exceeds the reference concentration. The quotient of risk obtained, HQ%, gave equal to 3.68%. This figure is in the range of 1 to 10%, which indicates that the danger associated with the incorporation of the element is moderate [22]. The HQ of 0.0368 was similar to that reported, 0.0244 for lead, by other authors in fish [23].

Conclusions

The different brands of green coffee bags available in Tucumán, Argentina, present in their content Cd levels below 1.0μg.g^{-1}, Pb below 3.0μg.g^{-1} and as contents less than 1.0μg.g^{-1}. All these values are beneath the limits established by the international regulations.

Also, the infusions prepared from the samples of green coffee in bags have values of Cd, Pb and As below the limit established for drinking water of 5μg.L^{-1}, 50μg.L^{-1} and 10μg .L^{-1} respectively.

The study of the transfer of these metals to the infusions, by calculating the EDI and the HQ%, indicates that the consumption of 2 cups of green coffee per day, of a person of average body weight of 70kg, provide low heavy metals contents and are unlikely to produce adverse health effects.

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