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Elemental composition of green coffee and its contribution to dietary intake

Sevcan Şemen *, Selda Mercan *, Murat Yayla, Münevver Açıkkol

İstanbul University, Institute of Forensic Sciences, Forensic Toxicology Laboratories, 34098 Cerrahpaşa, İstanbul, Turkey

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ABSTRACT

The concentration of twenty-seven elements (Li, Be, B, Mg, Al, P, K, Ca, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Sn, Sb, Ba, Hg, Pb, Bi, Th, and U) in green coffee samples and their infusions were determined by using inductively coupled plasma-mass spectrometry (ICP-MS). Prior to analysis, green coffee samples were prepared by microwave digestion, while infusions were analyzed without any pre-treatment. The accuracy and precision of the proposed methods were verified by recovery experiments. Considering samples; K, Cu, and Al had the highest mean concentrations with 6714.5 $\mu g\ g^{-1}$, 12.1 $\mu g\ g^{-1}$, and 25.9 $\mu g\ g^{-1}$ among major, trace and toxic elements, respectively. The impact of brewing type on leachability of elements was also studied and the results outlined that mean leachability of elements to Turkish coffee were greater than to mud coffee. Furthermore, dietary element intakes through green coffee consumption were also estimated. This is the first study presenting wide range of elements in green coffee brews and calculating dietary intakes.

1. Introduction

Coffee is one of the most consumed beverages worldwide and ranked as the second most traded global commodity after petroleum (Parras, Martínez-Tomé, Jiménez, & Murcia, 2007). The coffee plant belongs to the genus *Coffea* (*Rubiaceae* family) that has over ninety different species, but only two of them, *Coffea arabica* (~60% of the world's production) and *C. canephora*, named also *robusta* (~40%) are widely cultivated and have economical value. The term "green coffee" refers to raw or unroasted seeds (beans) of *Coffea* fruits. The coffee that we know is produced by processing the green coffee beans in several stages. In this production process, the green coffee beans are firstly cleaned and dried, then seeds are roasted, grounded, and brewed (Farah & dos Santos, 2015; Valentin & Watling, 2013).

Green coffee has a complex chemical composition of polysaccharides, monosaccharides, lipids, sterols, fatty acids, phenolic acids, polyphenols, alkaloids, proteins, free amino acids, vitamins, and minerals (Köseoğlu Yılmaz, Hacıbekiroğlu, & Kolak, 2014; Parras et al., 2007). Additionally, it is a rich source of compounds possessing antioxidant and radical scavenging activities such as chlorogenic acids, hydroxycinnamic acids, caffeine and caffeic acid (del Castillo, Gordon, & Ames, 2005; Iwai, Kishimoto, Kakino, Mochida, & Fujita, 2004; Sato et al., 2011). However, the chemical composition and biological activity of green coffee are affected by the roasting process. During the roasting process, chlorogenic acids are particularly degraded, the content of phenolic compounds in coffee decreases as well as antioxidant capacity. As a result, green coffee beans seem to be a better source of these beneficial compounds (Brezová, Šlebodová, & Staško, 2009; Köseoğlu Yılmaz et al., 2014; Wei & Tanokura, 2015).

Although the main reasons of coffee consumption were its preferred flavor and stimulating effect of caffeine for several years, the green coffee has recently received considerable attention with chlorogenic acid in its content because of its weight-loss properties and health benefits which are currently under discussion. Recent studies suggest that chlorogenic acids have antihypertensive effects (Zhao, Wang, Ballevre, Luo, & Zhang, 2012), preventive effects on diabetes (Stefanello et al., 2014), and show a tendency to reduce visceral fat and body weight (Shimoda, Seki, & Aitani, 2006). Therefore, people prefer to consume green coffee as a dietary supplement or beverage (Onakpoya, Terry, & Ernst, 2011; Stelmach, Pohl, & Szymczycha-Madeja, 2015).

Additionally, green coffee has a total element content of approximately 5% (m/m), including essential, non-essential and toxic ones. These contents depend mainly on growing origin of the coffee which is the factor primarily associated with soil type, coffee variety, field practices, climate and processing (Debastiani,

* Corresponding authors.
E-mail addresses: sevcansemen@gmail.com (S. Şemen), mercans@istanbul.edu.tr (S. Mercan).

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dos Santos, Yoneama, Amaral, & Dias, 2014; Pohl, Stelmach, Welna, & Szymczycha-Madeja, 2013). Besides, the soil and water pollution, use of inorganic fertilizers and/or some pesticides increase the total content of heavy metals in soil and, consequently, cause metal accumulation in crops as well as food chain (dos Santos, dos Santos, Conti, dos Santos, & de Oliveira, 2009; Santos, Lauria, & Porto da Silveira, 2004). Inorganic contamination can occur during the production and storage processes of coffee as well (dos Santos & de Oliveira, 2001; Pohl et al., 2013).

The concentration of various elements in green coffee have been determined using different analytical techniques such as atomic absorption spectrometry (AAS), (flame - FAAS-, high resolution-continuum source -HR-CS FAAS-, and solid sampling electrothermal -SS-ET AAS-) (Amorim Filho, Polito, & Gomes Neto, 2007; Krivan, Barth, & Morales, 1993; Oleszczuk et al., 2007; Stelmach et al., 2015), particle induced X-ray emission (PIXE) (Debastiani et al., 2014), instrumental neutron activation analysis (INAA) (Krivan et al., 1993), inductively coupled plasma-optic emission spectrometry (ICP-OES) (Martín, Pablos, & González, 1998; Oleszczuk et al., 2007; Valentin & Watling, 2013) and inductively coupled plasma-mass spectrometry (ICP-MS) (Rodrigues et al., 2011; Santato, Bertoldi, Perini, Camin, & Larcher, 2012; Valentin & Watling, 2013). In recent years, ICP-MS has become a widely used technique in food analysis as well as coffee (Millour et al., 2011; Santos et al., 2004). Lower detection limits, high sensitivities, simultaneous multi-element measurement capability and wider linear dynamic ranges make the technique more preferable than the other techniques such as AAS and ICP-OES (Jarošová, Milde, & Kuba, 2014; Nardi et al., 2009).

The common objective of the above cited articles was to analyze the elements in coffee samples in order to examine the origin and the authenticity of the green coffee. Because, minerals are more stable than organic compounds and reflect the soil type and growing conditions (Oliveira, Ramos, Delerue-Matos, & Morais, 2015). Besides, inorganic elements play an important role in nutrition and influence human health in different ways (Oliveira et al., 2012; Santos et al., 2004). Therefore, considering the increasing consumption, the levels of major, trace (essential/non-essential) and toxic elements present in green coffee and its infusions have to be determined and kept under control in terms of its safety.

In this context, the only study was carried out by Stelmach et al. (2015) on the quantitative determination of elements in green coffee brews. In the stated study, 5 nutritionally important elements (Ca, Cu, Fe, Mg, and Mn) were determined using HR-CS FAAS technique beside antioxidant activity (Stelmach et al., 2015). No research study has been conducted for analyzing essential, non-essential and toxic elements in green coffee and its infusions using ICP-MS according to the literature search results within the published literatures. Besides, daily mineral intake calculations were generally established for roasted and instant coffee samples (Grembecka, Malinowska, & Szefer, 2007; Oliveira et al., 2012). The only study conducted in Turkey by Özdestan (2014) reported concentration of five minerals (Mg, Mn, Zn, Na, K) for roasted Turkish coffee and brews, and listed daily mineral intakes through consumption. The contribution of green coffee to dietary element intake according to nutritional and toxicological reference values has not been reported yet in the literature.

The main goals of this study were i) to determine the inorganic composition of commercially available green coffee samples with 27 elements (Li, Be, B, Mg, Al, P, K, Ca, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Sn, Sb, Ba, Hg, Pb, Bi, Th, and U) using ICP-MS, ii) to compare different brewing methods including mud (mug) and Turkish coffee without additional extraction step prior to analysis and to evaluate the leaching percentages of elements from ground coffee samples to infusions, iii) to estimate the dietary element intake through green coffee consumption based on nutritional and toxicological reference values for the first time.

2. Experimental

2.1. Reagents, standards, calibration solutions and samples

In this study, Nitric acid 65% (v/v) and H_2O_2 30% (v/v) solutions were purchased from Merck Suprapur® (Merck, Darmstadt, Germany). Certificated calibration solution (10 mg mL^{-1}) and Mercury (Hg) (1000 mg mL^{-1}) used were purchased from High-Purity Standards, Charleston, SC; Indium (In) and Gallium (Ga) (1000 mg mL^{-1}) were used as internal standards (IS) (Absolute Standards, Inc., Hamden, CT, USA). All measurements were carried out using argon (>99.999% purity, Okser, Turkey) as plasma gas.

All glassware and polypropylene materials were cleaned by soaking them in 10% (v/v) HNO_3 solution, thoroughly rinsed with ultra-pure water and dried before use. Nitric acid solutions for dilution (2%) and cleaning (10%) were freshly prepared.

The calibration solutions were prepared daily in 2% HNO_3 by incremental amount as 0.1, 0.5, 1, 2, 5, 10, 25, 50, 100, 150 ng mL^{-1} for Li, Be, Al, Cr, Mn, Co, Ni, Cu, As, Se, Sr, Mo, Cd, Sb, Ba, Pb, Bi, Th, U and 20, 50, 100, 150, 200, 250, 300, 400 ng mL^{-1} for B, Mg, P, and Zn. Calibration range for Hg was set as 2, 5, 10, 15, 25, and 35 ng mL^{-1}. Only K, Ca, and Sn elements were calculated semi-quantitatively. All calibration solutions were added internal standards (20 ng mL^{-1} of Ga and In) and were prepared in triplicate.

Twelve green coffee samples examined in the study were purchased from different herbalist and coffee stores in Istanbul, Turkey. Samples were already in grounded form, thus additional grinding process was not applied. Before sample preparation, samples were oven-dried at 75 °C overnight.

2.2. Instrumentation

ICP-MS experiments were carried out on a Thermo Scientific X Series II (Thermo Fisher Scientific, Bremen, Germany) equipped with a CETAC (Omaha, Neb., USA) auto- sampler model ASX 520. A short-term stability test was performed using a tuning standard solution (High-Purity Standards, Charleston, SC) containing 10 μg/mL of Ba, Be, Bi, Ce, Co, In, Pb, Li, Ni, and U in 2% HNO_3, covering the whole range of masses. Details of experimental conditions were as follows: radio frequency power was 1400 W, plasma gas flow was 13 L min^{-1}, auxiliary gas flow was 0.8 L min^{-1}, nebulizer (concentric) gas flow was set 0.86 L min^{-1}, 100 sweeps/replicate were used, 3 sample replicates were chosen, spray chamber (cyclonic) temperature was set at 3 °C, dwell time was 0.01 s, and sample uptake was 60 s.

A closed vessel microwave digestion system (Mars, CEM, Matthews, NC, USA) equipped with control sensor of pressure and temperature was used for sample digestion. A Millipore Direct-Q®3 UV purification system (Millipore, Molsheim, France) was used to obtain ultra-pure water (18.2 MΩ cm).

2.3. Microwave assisted sample digestion

Prior to analysis, a dry mass of 0.5 g of each green coffee samples were accurately weighed into Teflon digestion vessel, 7 mL of HNO_3 (65%, v/v) and 1 mL of H_2O_2 (30%, v/v) were added, and then the closed vessels were placed inside the microwave oven for digestion. The samples were digested by a four-step temperature program. In the first step, the temperature was linearly increased to 90 °C in 4 min. In the second step, it was kept at 90 °C for 2 min. In the third step, the temperature was linearly increased up to 180 °C in 4 min and in the last step, it was kept