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Relationship between antioxidant capacity, chlorogenic acids and elemental composition of green coffee

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ABSTRACT

Antioxidant capacity of green coffee infusions (Arabica and Robusta of different geographical origin) has been studied e.g. with the use of Folin-Ciocalteu assay (the average: 1043 ± 577 mg GAE/L). The highest antioxidant capacity as well as concentration of three main 5-,4- and 3- caffeoylquinic acids were determined for Robusta coffee brews. According to assay used, steaming and decaffeination of Vietnam coffee beans altered the antioxidant capacity as well as the concentration of chlorogenic acids in the infusions. Additionally, the method of Cd, Cu, Mn, Pb and Se determination in green coffee beans and their infusions was optimized with the use of graphite furnace atomic absorption spectrometry. The average concentration of metals in green coffee beans was (mg/kg): Cd (0.013 ± 0.008), Cu (13.3 ± 2.8), Mn (24.1 ± 8.7), Pb (0.023 ± 0.005), Se (0.028 ± 0.010), respectively. The average leachabilities of Mn and Cu were established as 31.5% and 62.3%, respectively. The Cd, Pb and Se concentrations in the infusions were below the limits of detections.

1. Introduction

Food of plant origin contains many antioxidants and bioactive compounds such as phenolics, vitamins/provitamins as well as major, minor and trace elements. Higher intake of antioxidant-rich products is associated with lower oxidative stress in the human body. There are many evidences that diet rich in food antioxidants especially from plants, herbs, spices and beverages shows protective effect on human health and reduces the risk of various diseases (Benzie & Choi, 2014).

Popular beverages contain multitude of antioxidants and between them coffee brew showed high antioxidant capacity in *in vitro* and *in vivo* tests (Daglia, Papetti, Gregotti, Berte, & Gazzani, 2000; Shahidi & Chandrasekara, 2010). Antioxidant capacity of espresso coffee measured with the use of FRAP assay is even two fold higher in comparison to other beverages such as red wine or pomegranate juice (Carlsen et al., 2010). Coffee, prepared on filter or boiled has the same capacity as red wine (Carlsen et al., 2010). Coffee with unique aroma and flavour is one of the most popular beverages in the world. Species of *Coffea* genus *Coffea arabica* and *Coffea canephora var. robusta* belong to Rubiaceae family. Arabica usually comes from South America (i.e. Brazil) and from the uplands and mountain areas of East Africa. The main places of Robusta origin are Vietnam and the lowlands of Central and West Africa as well as South Asia (ICO, 2013).

Coffee contains antioxidants, mainly the chlorogenic acids (caffeoylquinic acids). Green coffee extracts show a hypotensive effect on rats (Suzuki, Kagawa, Ochiai, Tokimitsu, & Saito, 2002) and reduce visceral fat and body weight (Igho, Rohini, & Edzard, 2011; Shimoda, Seki, & Aitani, 2006). The other bioactive compounds with antioxidant capacity such as caffeine, theophylline and theobromine, tocopherols, cafestol, kahweol and trigonelline were also determined (Jeszka-Skowron, Sentkowska, Pyrzyńska, & De Peña, 2016; Jeszka-Skowron, Zgoła-Grześkowiak, & Grześkowiak, 2015; Kuhnert et al., 2011; Perrone, Farah Donangelo, de Paulis, & Martin, 2008).

Latest studies on chlorogenic acid (5-caffeoylquinic acid), the main component of green coffee beans, showed the protective role of this compound in neurons therefore it could prevent from neurodegenerative diseases such as ischemic stroke (Mikami & Yamazawa, 2015).

Antioxidant capacity of green coffee extracts of Arabica depends on the calcium levels (Stelmach, Pohl, & Szymczycha-Madeja, 2015). Other trace elements such as copper, manganese and

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selenium also play a significant role in oxidative metabolism - they are involved in redox processes that are essential for many metabolic pathways as well as for cellular defence against oxidative stress (Brigelius-Flohé, 2006). Simultaneously, low selenium dietary intake may result in higher cancer incidence and is associated with development of cardiovascular diseases, cirrhosis, diabetes and asthma (Fairweather-Tait et al., 2011; Navarro-Alarcon and Lopez-Martinez, 2000).

Copper is a transition metal which distorts homeostasis and it may induce oxidative stress and oxidative damage to proteins, lipids and DNA (Festa & Thiele, 2011). Cadmium and lead, so-called heavy or toxic metals, are most frequent contaminants in food products and they have influence on the quality of coffee infusions.

The aim of the study was to compare the content of minor and trace elements, three main chlorogenic acids (5-, 4- and 3-caffeoylquinic acids) and antioxidant capacity of green coffee Arabica and Robusta beans as well as infusions depending on the place of origin and method of beans preparation (decaffeinated and steamed Vietnam coffee beans). Folin-Ciocalteu (F-C), ABTS (2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt) and DPPH (2,2-diphenyl-1-picrylhydrazyl) assays were used to evaluate the antioxidant properties of coffee brews. High pressure liquid chromatography (HPLC-UV-Vis) was used to determine 5-, 4- and 3-caffeoylquinic acids in green coffee brews. Possible correlations between the content of particular compounds and antioxidant capacity were also in the scope of this study.

2. Materials and methods

2.1. Chemicals

2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS), 2,2-diphenyl-1-picrylhydrazyl (DPPH), chlorogenic acids (5-, 4- and 3-caffeoylquinic acids), gallic acid and Folin-Ciocalteu reagent were purchased from Sigma-Aldrich Chemical Co. (Steinheim, Germany). MS-grade acetonitrile, potassium persulfate (di-potassium peroxdisulfate), and methanol were obtained from POCH (Gliwice, Poland).

Working standard solutions of the elements were obtained by appropriate dilution of the stock standard solutions (1000 mg/L solution of Cd, Cu, Mn, Pb and Se in 0.5 mol/L nitric acid, Merck, Darmstadt, Germany). All working standard solutions were prepared daily; the appropriate stock solution was diluted with high-purity water. Chemical modifier solutions: palladium 10.0 ± 0.2 g/L $Pd(NO_3)_2$, magnesium 10.0 ± 0.2 g/L $Mg(NO_3)_2$ and phosphate 100.0 ± 2 g/L $NH_4H_2PO_4$ were purchased from Merck. *Ca.* 14 mol/L HNO_3 and *ca.* 10 mol/L H_2O_2 of the highest quality (Suprapur, Merck) were used for digestion of the samples. High purity water: deionized and doubly distilled water (quartz apparatus, Bi18, Heraeus, Hanau, Germany) was also used throughout the experiments.

2.2. Material

The accuracy of the elements determination procedure was studied using several certified reference materials (CRMs) with the certified reference values of analytes (Cd, Cu, Mn, Pb and Se). The following materials were chosen: SRM 1567a (Wheat flour), SRM 1549 (Nonfat milk powder) from the National Institute of Standards and Technology (Gaithersburg, USA) and INCT-OBTL-5 (Oriental Basma Tobacco Leaves), INCT-SBF-4 (Soya Bean Flour) and INCT-TL-1 (Tea Leaves) from Institute of Nuclear Chemistry and Technology (Warsaw, Poland). All solid reference materials were used as bottled, without further grinding and sieving.

Fourteen green coffee samples from different regions of the world were provided by Strauss Café Poland (Swadzim/Poznań, Poland). It included Arabica green coffee beans from Brazil (TG), Rwanda (Ordinary), China, Laos, Guatemala (SGH) and Peru (HB) as well as Robusta green coffee beans from Uganda (Bugishu, SC12), Indonesia, Vietnam (Gr2, decaffeinated Gr2, steamed Gr2), India (Cherry) and Laos (FAQ). The geographical origin of the samples and their types were confirmed by the supplier. The samples were ground in a laboratory mill and digested without sieving (according the procedure described in the section 2.4.1.)

2.3. Instrumentation for determination of elements and antioxidant capacity

Determination of selected elements was performed with an AAS 5EA spectrometer (ET AAS) (Analytik Jena GmbH, Jena, Germany) equipped with deuterium source background correction, a transversely heated graphite atomizer and an MPE5 autosampler. Pyrolytically coated graphite tubes were employed exclusively. Appropriate hollow cathode lamps (Photron, Narre Warren, Australia) were used as the radiation sources. Compressed argon of UHP 5.5 purity obtained from Air Products (Warsaw, Poland) was employed as a protective and purge gas. For wet digestion of certified reference materials and coffee samples a UniClever focused microwave sample preparation system (Plazmatronika, Wrocław, Poland) operating at 2450 MHz and 300 W maximum output was used. The computer-controlled system with continuous temperature, pressure and microwave power monitoring was equipped with high-pressure vessel made from modified PTFE (poly(tetrafluoroethylene) modified with perfluoro(propylvinyl ether) and water cooling system. The vessel capacity was 110 mL and the maximum pressure and maximum temperature were 10.1 MPa and 300 °C, respectively.

All spectrophotometric determinations connected with antioxidant capacity were performed with the use of Beckman UV–Vis Spectrophotometer 7500DU (Brea, CA, USA) with glass cuvettes of 1 cm length. Spectra were recorded in the range from 380 to 800 nm with 0.2 nm resolution. All determinations were carried out in triplicate.

Coffee samples (beans) were ground in a laboratory mill IKA (Staufen, Germany) A11 basic designed with a grinding chamber mad of Tefcel (PTFE, glass fiber-reinforced) with stainless steel inlet.

2.4. Analytical procedures for elements determination

2.4.1. Microwave-assisted digestion of CRMs and coffee beans samples

Approximately 0.500 g of powdered certified reference material or ground coffee beans sample was placed in the vessel of the microwave digestion system and moistened by 1 mL of 10 mol/L H_2O_2. Then, 5 mL of 14 mol/L HNO_3 were added. The sample was heated for 20 min at 300 W. After digestion, the clear digested solution was transferred into 10 mL calibrated flask and diluted to volume with high-purity water. Before further analysis this solution was appropriately diluted depending on the concentration levels of the elements. A corresponding blank was also prepared according to the above microwave-assisted digestion procedure. It was performed to correct possible contamination from the reagents used for the sample preparation.

2.4.2. AAS determination procedures

In the course of the study a graphite furnace was used for atomization of the analytes. In order to determine the elements in the coffee beans samples after digestion, 20 μL (or 30 μL for Se determination) of the solution was injected into the graphite tube for ET AAS determination under the optimized conditions. In order to improve the removal of matrix without losing the analyte in the