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Differentiation of roasted and soluble coffees through physical fractionation of selected essential and nonessential metals in their brews and exploratory data analysis

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ABSTRACT

An analytical scheme for physical fractionation of Al, Ba, Ca, Co, Fe, K, Mg, Mn, Na, Ni, Sr and Zn in ground roasted and soluble coffees brews was proposed. It was based on ultrafiltration through five ultrafiltration membranes having molecular weight cut-offs of 5, 10, 30, 50 and 100 kDa. The highest "> 100 kDa" and the lowest "< 5 kDa" molecular weight fractions were established to differentiate the studied coffees brews the most. Al, Cu, Fe and Ni were mostly associated with the "> 100 kDa" fraction, while Co, K, Mg and Na – with the "< 5 kDa" fraction. For Ba, Ca, Mn, Sr and Zn, "> 100 kDa" and "< 5 kDa" fractions contributions were equally accounted. The physical fractionation pattern of selected metals was convenient for discovering important features of brews of both coffee types and differences between them by principal component analysis and then classifying them by linear discriminant analysis.

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1. Introduction

Being increasingly consumed, ground roasted and soluble coffees (GCs and SCs) occupy a special and unique place in everyday live and hot beverages drinking habits of the world population. Because coffee consumption can not cause any concern about quality and nutritional safety, the chemical composition of coffee products rises special consumers awareness and is more and more often of great scientific interest [1–16].

Considering essential and nonessential metals effects in humans, element analysis of GCs brews [1,5,9,10,12,13,17] is important in reference to nutritional impact that these metals have and a degree with which they are released during brewing and potentially available for the human body. As above-cited papers show, coffee brews analysis on the metals content is not very common. When it is carried out, the obtained results, i.e. total metals concentrations, are taken to estimate the extent to which roasted coffee brews consumption covers the recommended daily intakes (RDIs) of many important metals (i.e. Ca, Cu, Fe, K, Mg, Mn, Na and Zn), assuming that they are completely bioaccessible and bioavailable [5,9,12,13,17]. In the case of SCs it is also assumed that coffee powder taken for preparing the brews is entirely digestible

[5,8,16]. In both cases, information derived from element analysis of brews of both coffee types is used to evaluate their nutritional status with regards to the essential and nonessential metals uptake and their contribution to RDIs through the daily coffee intake.

Considering metals speciation, the abovementioned treatment is not entirely justified and can not be decisive in terms of their actual uptake with coffee. Recently in our group, after undertaking enzymatic digestion with simulated gastric and intestinal juices followed by ultrafiltration (UF) through a 5-kDa molecular weight cut-off (MWCO) semi-permeable membrane, it has been shown that the concentrations of selected essential metals, namely Ca, Fe, Mg and Mn, in the bioaccessible fraction separated from GCs [13] and SCs [14] brews differ noticeably from their total concentrations. This is primarily associated with a variety of Ca, Fe, Mg and Mn physicochemical forms present in both coffee beverages. In reference to this, the information about metals speciation and/or fractionation rather than about their total content should be considered when assessing nutritional quality and safety of coffee brews. Surprisingly, the posted problem on metals speciation and/or fractionation in coffee brews is not firmly established in food chemistry and analysis related research.

To the best of our knowledge, there are only two works that report so far on chemical and physical partitioning of Mn in GCs brews [10] by using solid phase extraction (SPE) and UF, respectively, and chemical fractionation of Ca, Fe, Mg and Mn in SCs brews [11] by using SPE. For that reason, we recognize that

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knowledge about the type of speciation forms of essential and non-essential metals that are bound to endogenous bioligands of different functionality and their distribution in coffee brews are critical to indirectly predict metals bioaccessibility in coffee and to anticipate the actual metals impact on consumers' health.

The first objective of the present work was to assess in GCs and SCs brews the characteristic physical fractionation profiles of some selected physiologically and nutritionally relevant metals (Ca, Cu, Fe, K, Mg, Mn, Na and Zn) and few accepted as being nonessential (Al, Ba, Co, Ni and Sr). These data could be used to indirectly predict their actual bioaccessibility from both popular coffee beverages. The research hypothesis adopted in this work assumed that coffee brews and their eventual nutritional effects may differ not only due to the total concentrations of metals included in brews but primarily due to the type and contribution of speciation forms in which these metals exist and are bioaccessible. Therefore, the second objective was to verify if information about distinct physical fractions of the studied metals could better indicate important differences between brews of both coffee types by principal component analysis (PCA) and classify and discriminate them by linear discriminant analysis (LDA) as compared to the total concentrations of these metals. Because it was expected that the number of possible metals species in analyzed GCs and SCs brews would be great, it was presumed that a better approach to separate and determine the existing metals species would be their operational speciation tending to distinguish the metals fractions associated with organic compounds having certain molecular weight (MW) and functionality. Hence, a five-stage ultrafiltration-centrifugation procedure with UF membranes of certain MWCOs, i.e. 5, 10, 30, 50 and 100 kDa, was used to comprehensively partition the Al, Ba, Ca, Co, Fe, K, Mg, Mn, Na, Ni, Sr and Zn species in GCs and SCs brews due to their MW.

2. Experimental

2.1. Spectrochemical measurements

A Perkin-Elmer single-beam spectrophotometer, model 1100B, with an air-acetylene flame was used to measure concentrations of Ca and Mg (by flame atomic absorption spectrometry, FAAS), and of K and Na (by flame atomic emission spectrometry, FAES). The manufacturer recommended settings were used, i.e. analytical lines: 422.7 nm (Ca), 766.5 nm (K), 285.2 nm (Mg), 589.0 nm (Na), spectral band-passes: 0.7 nm (Ca, K, Mg, Na), the lamp current: 15 mA (Ca, Mg), the acetylene flow rate: 2.4 L min⁻¹, the air flow rate: 8.0 L min⁻¹, the burner height: 6 mm. Concentration ranges for working calibration standard solutions were within 0.05–2.0 µg mL⁻¹. Five-point calibration curves were used for quantification. Absorbance readings were background-corrected and averaged for three replicates acquired in a time-average integration mode with the integration time: 3 s

Remaining metals, i.e. Al, Ba, Co, Cu, Fe, Mn, Ni, Sr and Zn, were measured using an Agilent bench-top inductively coupled plasma optical emission spectrometer (ICP-OES), model 720, with an axial plasma torch. Instrument manufacturer recommended operating parameters were applied, i.e. the RF power: 1200 W, the Ar plasma gas flow rate: 15.0 L min⁻¹, the Ar auxiliary gas flow rate: 1.5 L min⁻¹, the Ar nebulizing gas flow rate: 0.75 L min⁻¹, the sample/standard solution introduction flow rate: 0.75 mL min⁻¹, instrument stabilization and solution uptake delays: 15 and 30 s, respectively, rinse and replicate times: 10 and 1 s, respectively, the number of replicates: 3. Intensities of the most prominent atomic (I) and ionic (II) emission lines of studied metals were acquired, including 396.2 nm (Al I), 455.4 nm (Ba II), 238.9 nm (Co II), 324.8 nm (Cu I), 259.9 nm (Fe II), 257.6 nm (Mn II), 231.6 nm (Ni II),

407.8 nm (Sr II) and 213.8 nm (Zn I). Concentration ranges for working calibration standard solutions were within 0.01–5.0 µg mL⁻¹. Five-point calibration curves were used for measurements. Intensity readings were background-corrected using a seven-point fitted background correction (FBC) technique.

2.2. Reagents and samples

Merck Millipore (KGaA, Darmstadt, Germany) Emsure concentrated HNO₃ (14.5 mol L⁻¹) was used. De-ionized water (18.3 MΩ cm) was obtained from an EasyPure™ water purification system (Barnstead Corp., USA) and used throughout. A Merck Millipore Certipur^R multi-element stock (1000 µg mL⁻¹) ICP standard solution IV was taken to prepare all working calibration standard solutions for FAAS, FAES and ICP-OES measurements.

The research material was eight commercially available GCs, i.e. GC1–GC8, and their soluble equivalents, i.e. SC1–SC8, sold under the same names. In addition, two SCs (SC9, SC10) with finely ground roasted coffee beans were selected.

2.3. Sample preparation

2.3.1. Coffee brewing

For coffee brewing, coffees as received were taken following the producers recommendations about water temperatures and coffee to water proportions. In the case of GCs brews, coffee portions (6.0 g) were placed into 400-mL glass beakers, poured with 200 mL of boiling de-ionized water, mixed using stirring rods, covered with watch glasses and left to infuse for 10 min. Resultant coffee brews were separated from grounds by decantation through 390 grade quantitative filter papers (Munktell and Filtrak, Germany). In the case of SCs, coffee portions (6.0 g) were also placed into 400-mL glass beakers, poured with 250 mL of hot de-ionized water (90–95 °C) and completely dissolved by mixing with the aid of glass stirring rods. To remove any tiny particles, resultant coffee brews were centrifuged for 10 min at maximal speed of 14,006 rpm using a MPW-352 centrifuge (MPW Medical Instruments, Poland) with a fixed angle (30°) 8 × 30 mL rotor (radius 87 mm). Supernatants were collected and saved for further analysis.

2.3.2. Physical fractionation

Sartorius (Sartorius Stedim Biotech GmbH, Germany) Vivaspin 20 centrifugal tubes with polyethersulfone (PES) twin vertical membranes of 5, 10, 30, 50 and 100 kDa MWCO were used to partition metals species in coffee brews into physical fractions having different MW ranges by means of ultrafiltration-centrifugation (at speed of 9069 rpm at 30 min). The fractionation procedure was as follows: a coffee brew portion was ultrafiltrated at first through a 100 kDa MWCO membrane using four respective UF tubes, each one treating at once 14 mL of the coffee brew. Ultrafiltrates were collected into 50-mL conical bottom tubes, then removed and combined. Next, a 5-mL portion of the resulting “< 100 kDa” ultrafiltrate was sampled prior to FAAS, FAES and ICP-OES analysis on the Al, Ba, Ca, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Sr and Zn content. The remaining “< 100 kDa” ultrafiltrate was subsequently ultrafiltrated using four UF tubes having lower MWCO, i.e. 50 kDa. Again, ultrafiltrates were taken and combined, followed by sampling a 5-mL portion of the resulting “< 50 kDa” ultrafiltrate prior to FAAS, FAES and ICP-OES analysis. The abovementioned steps were repeated using UF tubes with membranes of 30, 10 and 5 kDa MWCO. Each time, 5-mL portions of “< 30 kDa”, “< 10 kDa” and “< 5 kDa” ultrafiltrates were taken and saved for element analysis. A schematic diagram of the physical fractionation procedure is given in Fig. 1. For each coffee, the whole fractionation procedure was repeated three times (n=3) using freshly prepared brews.

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