ORIGINAL PAPER

Benefits and risks of commercially available coffee beverages from Western Balkan

Sanja M. Petrović[1] [ID] · Saša R. Savić[1] · Jelena B. Zvezdanović[1] · Ivana Mladenović-Ranisavljević[1] · Dragan J. Cvetković[1] · Aleksandra D. Cvetanović[2]

Abstract

Concentrations of Ag, Al, As, B, Ca, Cu, Fe, Hg, In, K, Li, Mg, Mn, Na, Ni, Pb, Sb, Zn, and caffeine were determined in 25 coffee samples collected on the Western Balkan market. Three types of coffee (black, espresso, and instant) manufactured in Serbia, Brazil, Czech Republic, Slovenia, Hungary, Poland, Romania and France have been investigated. Coffee samples were prepared as infusions in a traditional way. Minerals and caffeine content were analyzed by ICP–OES and UHPLC–MS/MS method, respectively. Among macroelements, the potassium concentration (105.35–2826.93 ppm) was the highest in all investigated samples. On the other side, microelement concentrations follow the order: Cu > Zn > Fe > B > Mn. In group of investigated heavy metals, the presence of aluminium, arsenic, and lead was detected, but below the allowed limits. Caffeine concentration in black coffee samples was the highest. Average amounts of caffeine detected in black, espresso, and instant coffees per one serving were 150.5, 108.3, and 57.1 mg, respectively. Since the recommended daily caffeine dose is 400 mg, the limiting black, espresso, and instant coffee intake should be 250, 370, and 700 ml/day, respectively (not counting the possibility of caffeine intake via other foods). To bring out strong patterns in experimental data set, Principal Component Analysis (PCA) was applied. Results from this study should be taken into account in nutritional planning.

Keywords Caffeine · Coffee · Mineral content · ICP-OES · UHPLC–MS/MS

Introduction

Coffee is one of the most commonly consumed beverages worldwide and it is ranked as the second most traded global commodity after petroleum (Parras et al. 2007). In the Balkan region, traditional black coffee is probably consumed more frequently than other types of coffee. The custom of drinking coffee is expressing not only as a beverage, but also a complex cultural concept served mainly at homes and pubs. For people in the Balkans, drinking of coffee turned into a social phenomenon that brings people together (Ranić et al. 2015). According to statistical surveys, the majority of examined population in Balkans consumes coffee products (89%), and most of consumers enjoy this drink 2–4 times

per day (66%), while 8% of them drink coffee occasionally (Vlahović et al. 2012). Numerous analyses have been performed to summarize the conclusions regarding the benefits and risks of coffee intake. Recent studies pointed to the protective effects of coffee consumption against breast cancer (Jiang et al. 2013a), esophageal cancer (Zheng et al. 2013), the incidence of type II diabetes mellitus (Jiang et al. 2013b), hypertension, and obesity (O'Keefe et al. 2013). Epidemiological data also confirmed that habitual coffee consumption has several health benefits, such as lower risks of Alzheimer's and Parkinson's disease. In addition, coffee has effect on liver function, a possible role in weight loss (increased metabolic rate, energy expenditure, lipid oxidation, and lipolytic and thermogenic activities), and decreased certain cancers developing risks (prostatic, endometrial, liver colorectal, etc.) (O'Keefe et al. 2013; Cano-Marquina et al. 2013). On the other side, coffee consumption has some health risks as bone loss and increased risk of fractures, as well as some acute effects that are mostly related to the high caffeine content: anxiety, insomnia, tremulousness, and palpitations (O'Keefe et al. 2013; Ranić et al. 2015). In terms of

✉ Sanja M. Petrović
milenkovic_sanja@yahoo.com

[1] Faculty of Technology, University of Nis, Bulevar Oslobodjenja 124, 16000 Leskovac, Serbia

[2] Faculty of Technology, University of Novi Sad, Bulevar Cara Lazara 1, 21000 Novi Sad, Serbia

composition, coffee is a complex beverage containing more than 1000 compounds of which many have a pronounced biological activity. The main and the most famous coffee ingredient is caffeine (1,3,7-trimethylxanthine) (Ranić et al. 2015; Ioannidis et al. 2014). Caffeine consumption causes addictive properties; headache, lethargy, and irritability are just some of symptoms when caffeine ingestion is abruptly discontinued (O'Keefe et al. 2013). Caffeine also enhances memory consolidation (Borota et al. 2014). However, like most bioactive compounds, excessive caffeine intake could cause headaches, nausea, anxiety, hypertension, and restlessness (Branum et al. 2014). The amount of caffeine required to produce adverse effects depends on weight, sex, age, and differences in susceptibility, but dose of 400 mg per day might be taken as safe for most healthy adults (Mitchell et al. 2014). Caffeine is present in many natural and processed products. Because of its use in pharmaceutical or cosmetic industry as well, coffee beans are exposed to the extraction procedures by ethyl acetate, methylene chloride, or CO_2 (Ramalakshmi and Raghavan 1999). Such caffeine pore coffee beans are further used for coffee production.

Besides bioactive coffee ingredients, minerals such as micronutrients are also of a great importance. They are essential for maintaining normal physiological functions and have various metabolic roles. Essential trace elements such as Cu, Se, and Zn play an important role in human biology, because they are not synthesized in the body. On contrary, toxic elements, such as Pb, Cd, and As, are not required for normal functioning of living processes because of non-beneficial health effects (Gogoasa et al. 2017; Nędzarek et al. 2013; O'Keefe et al. 2013; Zaidi et al. 2006).

Bearing in mind all the potential benefits and dangers that could be ensue by coffee consumption, there is a justified need for coffee analysis to determinate its composition. The main goal of this paper was to determine the nutrition profile and caffeine content in coffee beverages that are present and consumed in the territory of the Western Balkan.

Experimental

ICP–OES analysis

To estimate the content of macro- and microelements concentrations, the calibration standards were prepared. Multistandard IV—standard solution (Merck), which contained Ag, Al, B, Ca, Cu, Fe, In, K, Li, Mg, Mn, Na, Ni, Pb, Sb, and Zn in a concentration of 1000 ppm was used for the preparation of calibration solutions. Additional calibration standard solutions of Hg and As (Reagecon, Ireland) were prepared independently. Distilled water, purified by Fisher Chemical (HPLC grade), was used for samples dilution. The carrier gas was Argon 5.0 (99.999% purity). Working solutions were

prepared by diluting the standards, so that concentrations of standard elements, used for calibration curves construction, cover the range of the expected elements concentrations. Table 1 shows the wavelength detection of each element in the samples, correlation coefficient (R), limit of detection (LOD), as well as the range of linearity.

Sampling and sample preparation

Twenty-five different coffee samples from Balkans territory have been taken for the analysis. Before any further analysis, coffee samples were prepared by the manufacturer instructions. To compare the obtained results, the ratio of powdered coffee mass (g) and water volume (cm^3) was maintained the same in all experiments (1:10, m/v). Distillate water was used for coffee preparation. Preparation of samples was carried out by wet digestion. 1 ml of prepared coffee infusion was added to 1 ml of 65% nitric acid and heated in water bath for wet digestion in laboratory hood. After complete mineralization, samples are left for 24 h before further analysis. Before ICP–OES analysis, all samples were filtrated (0.45 μm) and diluted with distilled water purified by Fisher Chemical (HPLC grade) to the final volume of 10 ml.

Analysis of samples

The quantitative analysis of all samples from Table 3 was performed on ICP–OES (Inductively Coupled Plasma—Optical Emission Spectrometry, ARCOS FHE12, SPECTRO, Germany), according to the manufacturer's instructions. The instrument conditions and determined parameters are given in Table 2.

UHPLC–DAD–HESI–MS/MS analysis

Preparation of calibration standards

Caffeine standard stock solution was prepared in methanol–water (50:50, v/v), at the concentration of 1000 mg/L. Calibration standards were prepared by diluting the stock solution with distillate water (LC–MS, grade). The final caffeine concentrations of calibration samples were adjusted to 1, 5, 20, 50, 200, 500, and 1000 mg/L.

Quantitative caffeine determination

Determination of caffeine content was done using caffeine peak area detected in coffee cup samples and caffeine standard calibration curve. Curve was constructed by the caffeine peak area ratio as vertical coordinate and the concentrations of the calibration standards as horizontal ordinate.

UHPLC–DAD–HESI–MS/MS analysis was performed using a Thermo Scientific liquid chromatography system

Table 1 Calibration parameters λ, nm; R; LD (µg/L) and the range of linearity (mg/L)

Element	Detection wavelength (nm)	Correlation coefficient (R)	Limit of detection (µg/L)	Linearity range (mg/L)
Ag	224.641	0.99993	14.5	1.45×10^{-2}–12.00
	328.068	0.99995	0.4	3.99×10^{-4}–12.00
Al	167.078	0.99985	0.08	7.6×10^{-5}–2.40
	394.401	0.99998	1.55	1.55×10^{-3}–12.00
As	197.262	0.99982	2.55	2.55×10^{-3}–3.60
B	182.641	0.99999	7.37	7.37×10^{-3}–12.00
	249.773	0.99999	6.43	6.43×10^{-3}–12.00
Ca	183.801	0.99995	1605	1.6–480.00
	396.847	0.99946	2.14	2.14×10^{-3}–2.41
Cu	224.70	0.99999	0.91	9.07×10^{-4}–12.00
	324.754	0.99999	0.26	2.59×10^{-4}–12.00
Fe	259.941	0.99997	0.12	1.18×10^{-4}–12.00
Hg	184.950	0.9993	0.63	6.26×10^{-4}–6.00
In	325.609	1.00000	4.00	4×10^{-3}–12.00
K	404.721	0.99998	798	0.798–300.00
	766.491	0.99999	0.38	3.78×10^{-4}–1.20
Li	323.261	1.00000	79.80	7.98×10^{-2}–12.00
	670.780	0.99997	0.06	5.75×10^{-5}–1.20
Mg	279.553	0.99997	0.11	1.15×10^{-4}–6.04
	285.213	0.99994	4028	4.03–120.00
Mn	257.611	0.99992	0.04	3.57×10^{-5}–12.00
Na	330.237	0.99994	7984	7.98–480.00
	598.592	0.99989	4.75	4.75×10^{-3}–12.00
Ni	231.604	0.99994	0.47	4.74×10^{-4}–12.00
Pb	220.353	0.99998	1.78	1.78×10^{-3}–12.00
Sb	187.115	0.99992	2.44	2.44×10^{-3}–12.00
Zn	213.856	0.99997	0.08	8.2×10^{-5}–12.00

Table 2 Operating conditions for ICP–OES analysis

Plasma Power (W)	1400
Gas flow (L/min)	
Coolant	13
Auxiliary	0.80
Nebulizer type	Cross flow
Nebulizer flow rate (L/min)	0.95
Pump speed (rpm)	30
Number of probes for each measuring	3
Plasma observation	Axial

(UHPLC) composed of a quaternary pump with a degasser, a thermostated column compartment, an autosampler, and a diode array detector connected to LCQ Fleet Ion Trap Mass Spectrometer (Thermo Fisher Scientific, San Jose, California, USA) equipped with heated electrospray ionization (HESI). Xcalibur (version 2.2 SP1.48) and LCQ Fleet (version 2.7.0.1103 SP1) software were used for instrument control, data acquisition, and data analysis. Separations were performed on a Hypersil gold C18 column (50–2.1 mm, 1.9 µm) obtained from Thermo Fisher Scientific.

The mobile phase consisted of (a) water (Fisher Chemical, HPLC grade) + 0.2% formic acid (Carlo Erba) and (b) methanol (Fisher Chemical, LC–MS grade). A linear gradient program at flow rate of 0.250 mL/min was used 0–2 min from 10 to 20% (b), 2–4.5 min from 20 to 90% (b), 4.5–4.8 min 90% (b), 4.8–4.9 min from 90 to 10%, and 4.9–12.0 min 10% (b). The injection volume was 5 µL, and the column temperature was maintained at 25 °C. The separated compounds were detected at a wavelength of 193, 272, 354, and 450 nm, and each online spectrum was recorded within the range of 150–1000 nm. The mass spectrometer was operated in positive mode. HESI-source parameters were as follows: source voltage 4.5 kV, capillary voltage 9 V, tube lens voltage 85.00 V, capillary temperature 275 °C, sheath and auxiliary gas flow (N2) 50 and 8 (arbitrary units), respectively. MS spectra were acquired by full-range acquisition covering 150–1000 m/z. For fragmentation study, a data-dependent scan was performed by deploying the collision-induced dissociation (CID). The normalized collision

Table 3 Origin of analyzed samples

Code	Sample	Origin
BC-1	Black coffee	Republic of Serbia
BC-2	Black coffee	Republic of Serbia
BC-3	Black coffee	Republic of Serbia
BC-4	Black coffee	Republic of Serbia
BIC-5	Black instant coffee	Republic of Serbia
BC-6	Black coffee	Brazil
IC-7	Instant coffee 1 in 1	Republic of Serbia
IC-8	Instant coffee 2 in 1	Czech Republic
IC-9	Instant coffee 2 in 1	Slovenia
IC-10	Instant coffee 2 in 1	Hungary
IC-11	Instant coffee 2 in 1	Republic of Serbia
IC-12	Instant coffee 2 in 1	Poland
IC-13	Instant coffee 3 in 1	Poland
IC-14	Instant coffee 3 in 1	Czech Republic
IC-15	Instant coffee 3 in 1	Slovenia
IC-16	Instant coffee 3 in 1	Romania
IC-17	Instant coffee 3 in 1	Republic of Serbia
IC-18	Instant coffee 3 in 1	Republic of Serbia
IC-19	Instant coffee 4 in 1	Republic of Serbia
EC-20	Espresso coffee	Slovenia
EC-21	Espresso coffee	Poland
EC-22	Espresso coffee	Republic of Serbia
EC-23	Espresso coffee	France
IIC-24	Instant ice coffee	Slovenia
IIC-25	Instant ice coffee	Czech Republic

energy of the CID cell was set at 25 eV. All compounds were identified according to the corresponding spectral characteristics: mass spectra, accurate mass, and characteristic fragmentation.

Principal component analysis (PCA)

Visual presentation of PCA is done using software Visual PROMETHEE Academic Edition. For the purpose of PCA analysis, 25 types of coffee are used as alternatives, while ten analyzed parameters of coffee (K, Ca, Mg, Na, Fe, Zn, Cu, As, caffeine, and location country of origin) are used as criteria. Those parameters that ICP–OES analysis confirmed to be with no or minimum content in the coffee are eliminated from the analysis.

Results and discussion

Content of Ag, Al, As, B, Ca, Cu, Fe, Hg, In, K, Li, Mg, Mn, Na, Ni, Pb, Sb and Zn was investigated in 25 coffee samples found on Western Balkans market. Total elements concentrations were determined in representative and most popular

coffee brands. The amount of detected elements was compared between taken samples, as well as literature data to see how differences in origin of coffee samples affect human health. Analysis results are presented in Table 4.

Among the investigated macroelements (K, Ca, Mg, and Na), potassium content in the range of 105.35–2826.93 ppm was the highest in all samples. The recommended daily intake of potassium varies from 0.4 to 4.7 g depending on years and gender (WHO 2011). Its sufficient concentration is significant for body acid–base balance maintenance as well as osmotic pressure, the nerve impulse transmission of muscle contraction, and has an impact on carbohydrate metabolism and membrane transport (Veljković and Vučković 2010).

After potassium, the highest mineral concentration is detected for calcium in the range of 413–992.51 ppm. In investigation carried out on Mexico market, the calcium content in coffee was between 1490 and 1970 ppm (Vega-Carrillo et al. 2002). The implemented Portugal and Polish market investigations of Oliveira and associates (2012) as well as Grembecka et al. (2007) reported calcium presence in the range of 430–1140 ppm and 650–2650 ppm, respectively. Brazil coffee samples have contained calcium in the range of 1060–1890 ppm (Dos Santos and de Oliveira 2001).

Sodium as well as potassium is the most common cation in the body that participates in water metabolism, contraction of muscles, allows the transfer of carbon dioxide to the lungs, etc. (Barker and Pilbeam 2015). After calcium, the sodium content is also considerable (80.7–790.7 ppm) in all investigated coffee samples.

Compared with other macroelements, magnesium presence is detected in reduced amounts. Magnesium participates in regulation of protein synthesis, muscle, and nerve function and blood pressure (Barker and Pilbeam 2015). Magnesium is included in the active transport across the cell membrane, which is an important process for nerve impulses conducting and normal heart rhythm maintenance. The recommended daily intake of Mg is about 400 mg (Guerrera et al. 2009). In this study, the highest concentration of magnesium (495.78 ppm) was detected in instant coffee that was made in Serbia. Magnesium was detected in India and Brazil coffee samples in concentrations between 2000–3100 and 2120–4150 ppm, respectively (Dos Santos and de Oliveira 2001, Suseela et al. 2001). The coffee samples originated from Portugal market contained Mg in the range of 1160–5470 ppm (Oliveira et al. 2012). On the other side, the detected amounts of magnesium in coffee samples from Mexico in the range of 32.0–458.0 ppm are nearest to the results presented in this work (Vega-Carrillo et al. 2002). The detected macroelements that present > 99% of the entire mineral composition of coffee infusions are represented by order: K > Ca > Mg > Na. The obtained results are in accordance with published results of coffee analysis of

Table 4 Concentrations (ppm) of macro- and microelement in coffee samples as a result of ICP–OES analysis

Code	Ag	Al	As	B	Ca	Cu	Fe	In	K
BC-1	$<3.99\times10^{-4}$	$<7.6\times10^{-5}$	$<2.55\times10^{-3}$	0.73	706.22	1.22	0.56	0.01	958.38
BC-2	$<3.99\times10^{-4}$	$<7.6\times10^{-5}$	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	882.14	0.63	$<1.18\times10^{-4}$	$<4\times10^{-3}$	1930.5
BC-3	$<3.99\times10^{-4}$	$<7.6\times10^{-5}$	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	649.87	0.95	$<1.18\times10^{-4}$	$<4\times10^{-3}$	1802.3
BC-4	$<3.99\times10^{-4}$	$<7.6\times10^{-5}$	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	946.67	1.26	$<1.18\times10^{-4}$	$<4\times10^{-3}$	2171.1
BIC-5	$<3.99\times10^{-4}$	0.58	$<2.55\times10^{-3}$	0.51	992.51	0.99	0.87	$<4\times10^{-3}$	1429.69
BC-6	$<3.99\times10^{-4}$	$<7.6\times10^{-5}$	0.16	1.93	729	1.02	2.17	$<4\times10^{-3}$	2052.97
IC-7	$<3.99\times10^{-4}$	0.86	$<2.55\times10^{-3}$	1.19	666.48	1.05	4.67	$<4\times10^{-3}$	2826.93
IC-8	$<3.99\times10^{-4}$	$<7.6\times10^{-5}$	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	672.4	9.99	$<1.18\times10^{-4}$	$<4\times10^{-3}$	1196.8
IC-9	$<3.99\times10^{-4}$	$<7.6\times10^{-5}$	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	612	9.6	$<1.18\times10^{-4}$	$<4\times10^{-3}$	1810.02
IC-10	$<3.99\times10^{-4}$	$<7.6\times10^{-5}$	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	582	1.2	0.65	$<4\times10^{-3}$	423.64
IC-11	$<3.99\times10^{-4}$	$<7.6\times10^{-5}$	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	554.1	6.2	$<1.18\times10^{-4}$	$<4\times10^{-3}$	1645.1
IC-12	$<3.99\times10^{-4}$	$<7.6\times10^{-5}$	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	503.6	1.3	$<1.18\times10^{-4}$	$<4\times10^{-3}$	1156.5
IC-13	$<3.99\times10^{-4}$	$<7.6\times10^{-5}$	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	692.4	5.4	$<1.18\times10^{-4}$	$<4\times10^{-3}$	1137.4
IC-14	$<3.99\times10^{-4}$	$<7.6\times10^{-5}$	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	495	0.63	$<1.18\times10^{-4}$	$<4\times10^{-3}$	1089.3
IC-15	$<3.99\times10^{-4}$	0.21	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	696.7	0.92	0.99	$<4\times10^{-3}$	588.86
IC-16	$<3.99\times10^{-4}$	0.31	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	554.1	1.21	0.79	$<4\times10^{-3}$	358.33
IC-17	$<3.99\times10^{-4}$	0.26	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	588	0.92	0.78	$<4\times10^{-3}$	536.13
IC-18	0.02	0.13	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	642.12	1.09	1.22	$<4\times10^{-3}$	2052.97
IC-19	$<3.99\times10^{-4}$	0	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	413	0.22	$<1.18\times10^{-4}$	$<4\times10^{-3}$	1122.9
EC-20	$<3.99\times10^{-4}$	0.77	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	428	1.18	1.17	$<4\times10^{-3}$	476.53
EC-21	$<3.99\times10^{-4}$	1.46	0.13	0.83	504	1.09	1.22	$<4\times10^{-3}$	580.57
EC-22	$<3.99\times10^{-4}$	$<7.6\times10^{-5}$	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	466.9	0.13	$<1.18\times10^{-4}$	$<4\times10^{-3}$	1523.2
EC-23	$<3.99\times10^{-4}$	1.26	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	650.22	1.23	0.74	$<4\times10^{-3}$	274.27
IIC-24	$<3.99\times10^{-4}$	$<7.6\times10^{-5}$	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	486.87	0.86	$<1.18\times10^{-4}$	$<4\times10^{-3}$	105.35
IIC-25	$<3.99\times10^{-4}$	$<7.6\times10^{-5}$	$<2.55\times10^{-3}$	$<6.43\times10^{-3}$	502.4	1.64	$<1.18\times10^{-4}$	$<4\times10^{-3}$	1004.85

Code	Li	Mg	Mn	Na	Ni	Pb	Sb	Zn	Hg
BC-1	$<5.75\times10^{-5}$	242.02	0.9	83.46	$<4.74\times10^{-4}$	$<1.78\times10^{-3}$	$<2.44\times10^{-3}$	1.11	0.05
BC-2	$<5.75\times10^{-5}$	203.0	$<3.57\times10^{-5}$	80.7	$<4.74\times10^{-4}$	$<1.78\times10^{-3}$	$<2.44\times10^{-3}$	0.95	$<6.26\times10^{-4}$
BC-3	$<5.75\times10^{-5}$	179.69	$<3.57\times10^{-5}$	787.3	$<4.74\times10^{-4}$	$<1.78\times10^{-3}$	$<2.44\times10^{-3}$	0.85	$<6.26\times10^{-4}$
BC-4	$<5.75\times10^{-5}$	333.69	$<3.57\times10^{-5}$	790.7	$<4.74\times10^{-4}$	$<1.78\times10^{-3}$	$<2.44\times10^{-3}$	0.97	$<6.26\times10^{-4}$
BIC-5	$<5.75\times10^{-5}$	242.98	0.98	98.39	$<4.74\times10^{-4}$	$<1.78\times10^{-3}$	$<2.44\times10^{-3}$	1.06	$<6.26\times10^{-4}$
BC-6	0.18	356.66	0.76	117.7	$<4.74\times10^{-4}$	$<1.78\times10^{-3}$	$<2.44\times10^{-3}$	1.23	$<6.26\times10^{-4}$
IC-7	$<5.75\times10^{-5}$	495.78	1.12	116	$<4.74\times10^{-4}$	0.01	$<2.44\times10^{-3}$	1.32	$<6.26\times10^{-4}$
IC-8	$<5.75\times10^{-5}$	156.54	$<3.57\times10^{-5}$	90.67	$<4.74\times10^{-4}$	$<1.78\times10^{-3}$	$<2.44\times10^{-3}$	1.26	$<6.26\times10^{-4}$
IC-9	$<5.75\times10^{-5}$	129.8	$<3.57\times10^{-5}$	506.6	0.12	$<1.78\times10^{-3}$	$<2.44\times10^{-3}$	1.35	$<6.26\times10^{-4}$
IC-10	$<5.75\times10^{-5}$	99.03	$<3.57\times10^{-5}$	501.25	$<4.74\times10^{-4}$	$<1.78\times10^{-3}$	$<2.44\times10^{-3}$	1.45	0.06
IC-11	$<5.75\times10^{-5}$	102.6	$<3.57\times10^{-5}$	83.1	$<4.74\times10^{-4}$	$<1.78\times10^{-3}$	$<2.44\times10^{-3}$	1.44	$<6.26\times10^{-4}$
IC-12	$<5.75\times10^{-5}$	223.6	$<3.57\times10^{-5}$	265.9	$<4.74\times10^{-4}$	$<1.78\times10^{-3}$	$<2.44\times10^{-3}$	1.12	$<6.26\times10^{-4}$
IC-13	$<5.75\times10^{-5}$	655.1	$<3.57\times10^{-5}$	229.3	$<4.74\times10^{-4}$	$<1.78\times10^{-3}$	$<2.44\times10^{-3}$	9.55	$<6.26\times10^{-4}$
IC-14	$<5.75\times10^{-5}$	105.48	$<3.57\times10^{-5}$	821	$<4.74\times10^{-4}$	$<1.78\times10^{-3}$	$<2.44\times10^{-3}$	1.17	$<6.26\times10^{-4}$
IC-15	0.2	107.27	$<3.57\times10^{-5}$	376.27	$<4.74\times10^{-4}$	$<1.78\times10^{-3}$	$<2.44\times10^{-3}$	1.34	$<6.26\times10^{-4}$
IC-16	$<5.75\times10^{-5}$	88.68	$<3.57\times10^{-5}$	412.6	$<4.74\times10^{-4}$	0.01	$<2.44\times10^{-3}$	1.32	$<6.26\times10^{-4}$
IC-17	$<5.75\times10^{-5}$	91.37	$<3.57\times10^{-5}$	162.39	$<4.74\times10^{-4}$	$<1.78\times10^{-3}$	$<2.44\times10^{-3}$	1.14	$<6.26\times10^{-4}$
IC-18	$<5.75\times10^{-5}$	100.87	$<3.57\times10^{-5}$	123.76	$<4.74\times10^{-4}$	$<1.78\times10^{-3}$	$<2.44\times10^{-3}$	1.16	$<6.26\times10^{-4}$
IC-19	$<5.75\times10^{-5}$	105.84	$<3.57\times10^{-5}$	103.1	$<4.74\times10^{-4}$	$<1.78\times10^{-3}$	$<2.44\times10^{-3}$	9.88	$<6.26\times10^{-4}$
EC-20	$<5.75\times10^{-5}$	89.02	$<3.57\times10^{-5}$	290.2	$<4.74\times10^{-4}$	0.1	$<2.44\times10^{-3}$	1.18	$<6.26\times10^{-4}$
EC-21	$<5.75\times10^{-5}$	88.15	$<3.57\times10^{-5}$	345.16	$<4.74\times10^{-4}$	0.06	$<2.44\times10^{-3}$	0.98	$<6.26\times10^{-4}$
EC-22	$<5.75\times10^{-5}$	342.51	$<3.57\times10^{-5}$	160.7	$<4.74\times10^{-4}$	0.3	$<2.44\times10^{-3}$	1.06	$<6.26\times10^{-4}$
EC-23	$<5.75\times10^{-5}$	81	$<3.57\times10^{-5}$	177.88	$<4.74\times10^{-4}$	0.01	$<2.44\times10^{-3}$	1.18	$<6.26\times10^{-4}$

Table 4 (continued)

Code	Li	Mg	Mn	Na	Ni	Pb	Sb	Zn	Hg
IIC-24	$<5.75\times10^{-5}$	78.73	$<3.57\times10^{-5}$	97.83	$<4.74\times10^{-4}$	$<1.78\times10^{-3}$	$<2.44\times10^{-3}$	1.13	$<6.26\times10^{-4}$
IIC-25	$<5.75\times10^{-5}$	89.5	$<3.57\times10^{-5}$	208.6	$<4.74\times10^{-4}$	$<1.78\times10^{-3}$	$<2.44\times10^{-3}$	0.76	$<6.26\times10^{-4}$

macroelements detected in roosted coffee of various brands at the Romanian market (Gogoasa et al. 2013).

The amounts of zinc in all coffee samples were between 0.76 and 9.88 ppm. Zinc is essential for normal biomembrane and brain function as well as for treatment of mental disorders (e.g., schizophrenia). It is also necessary for metabolism of proteins and carbohydrates, prostate function, and many other biological functions. In addition, zinc is required for DNA synthesis, and plays a major role in development and functioning of reproductive organs. Zinc is an essential oligoelement important for the membrane stabilization and the activity of metalloenzymes (alkaline phosphatase, alcohol dehydrogenase, carbonic anhydrase, lactate dehydrogenase, superoxide dismutase as well as RNA and DNA polymerases) (Veljković and Vučković 2010). Recent data indicate that lack of this vital element is common in 48% of all global population (Oteiza and Mackenzie 2005). Recommended daily allowance of zinc is 12–15 mg (WHO 1989).

Iron is responsible for some enzymes activities that generate energy. The presence of iron in this study was in the range of 0–4.67 ppm, which is much lower compared to the coffee samples found on the most of previously investigated markets. The coffee from Nigerian market showed iron concentration of 6.3–174 ppm (Onianwa et al. 1999). Suseela and collaborators were reported that on Indian market in coffee samples iron was detected in the range of 15.5–91.5 ppm. In coffee samples found on Pakistan market, detected iron presence was in the range of 62.3–83.2 ppm (Zaidi et al. 2006). Oliveira and collaborators recorded the presence of iron at Portugal market (13.7–108 ppm), until Dos Santos and de Oliveira (2001) have found iron in Brazilian coffee in concentration range of 14–451 ppm. On Poland market, Grembecka and associates (2007) detected iron in the range of 29.3–58.7 ppm.

The presence of copper in coffee samples was also detected (0.13–9.99 ppm). Obtained concentrations of copper are consistent with results reported by Mehra and Baker (2007), where the obtained Cu amount was between 2 and 20 ppm. Contrary to the investigation of coffee infusions made of coffee from Brazilian market (Pigozzi et al. 2018), where Cu were not detected, coffee sample that originate from Brazil (BC-6) from this study showed its occurrence at the concentration of 1.02 ppm. Copper, with vitamin C and zinc, is responsible for maintaining elasticity of fibres, which provides better skin structure support. According to

WHO (1989), the recommended daily dosage of copper is 1 mg (WHO 1989). The lack of copper has the effect of anaemia, hair depigmentation, and bones deformities. Diet that is deficient in particular essential elements as Cu, Fe, and Zn can enhance the accumulation of some toxic metals as Cd or Pb, which can influence trace-element metabolism (Alonso et al. 2004).

The boron content was detected in the range of 0.51–1.93 ppm. In the report of Krejcová and Cernohorský (2003), boron content was in the range of 0–1.93 ppm which is in agreement with obtained results (Table 4). Boron contributes to the functioning and the absorption of calcium, magnesium, and phosphorus. Its deficiency can cause bone demineralization. The recommended daily intake of boron is not precisely defined, but the maximum allowable daily intake ranges from 6 to 20 mg (Devirian and Volpe 2003).

Manganese is included in bone forming, lipid metabolism, energy production, and synthesis of nucleotides. In this study, the obtained values for manganese content were in the range of 0–1.12 ppm. On Pakistan, Brazilian, Indian, Poland, and Portugal markets, manganese is detected in higher concentrations (3.6–39.9 ppm) compared to the results from our study (Zaidi et al. 2006; Oliveira et al. 2012).

Heavy metals belong to a special group that is classified as the most dangerous inorganic environment pollutant elements, because they are non-biodegradable with a tendency towards bioaccumulation and expression of toxic effects even at very low concentrations. Some heavy metals such as copper, zinc, manganese, and iron are among the group of trace microelements, because even they are toxic in higher concentrations, at lower concentrations, are necessary for the growth and development of plant and other living organisms. Among others, the accumulation of heavy metals in plants depends on the affinity of plant to absorb appropriate metal. The presence of Al, As, Hg, Ni, Pb, and Sb was also examined in all coffee samples, while the presence of Hg, Ni and Sb was below the limit of detection.

Aluminium was detected in amount of 0.13–1.46 ppm. Aluminium is included as cofactor in the guanine nucleotide binding which is necessary for the metabolism of proteins. Increased content of this element in patient kidneys can significantly damage the skeleton due to the negative impact on the process of bone formation, leading to the osteomalacia occurrence.

Lead is considered to a very toxic element that affects the brain function and nervous system reduces the level of

intelligence, perception, and memory mode and most severe can cause death (Petrović et al. 2015). According to Serbian regulations (1992), the concentration of lead is strictly controlled and the maximum allowed quantity of lead in coffee is 1 ppm. The presence of lead is detected in six investigated samples, mainly in espresso type of coffee with maximum concentration of 0.3 ppm. If we keep in mind that allowed amount of lead is 1 ppm, it could be concluded that investigated coffees are not dangerous to a human health. In addition, having in mind the maximum content of Pb, Ni, Cu, and Zn establish by Brazilian legislation in roasted ground coffee samples of 0.5, 5, 30, and 50 ppm, respectively (Pigozzi et al. 2018), the detected concentrations of Pb in this work as well as other adduced elements were below the prompt limits.

Arsenic is one of the most toxic and carcinogenic element of the second group of p elements, which occurs in inorganic and organic form. Arsenic and manganese in the soil are often found together with iron, mainly pyrite and arsenopyrite. They can also be found in the form of different arsenic sulphide minerals. In this study, arsenic is detected only in two coffee samples at concentrations of 0.13 and 0.16 ppm. Since allowed arsenic concentration in coffee is 1 ppm (Serbian regulations 1992), it could be concluded that investigated coffees do not represent a risk to human health in terms of this element.

Bearing in mind the importance of caffeine, second aim of this study was to determine content of caffeine in coffees that were placed on Western Balkans market. Three types of coffee samples: black, espresso, and instant coffee have been investigated using of LC–MS method. The experiment was designed in a manner that first subjected caffeine standard is compared to other coffee samples in continuation.

Obtained chromatogram of the standard caffeine solution, shown in Fig. 1, distinguished one intense peak at retention time of 5.93 min which originates from caffeine. Another confirmation is caffeine PDA spectrum (Fig. 1b) with absorption maximum at 272 nm that is in accordance with literature data (Atomssa and Gholap 2011; Dobrinas et al. 2013). After MS fragmentation of peak at m/z 195.13, six new fragment ions at m/z 176.79, 162.83, 161.47, 138.11, 110.01, and 95.84 were obtained (Fig. 1c). The resulting caffeine fragment ions are in agreement with previously published results by Liu et al. (2013).

Since the main goal of this work was to compare the content of caffeine in three different coffee types, three representative UHPLC chromatograms of black (a), espresso (b), and instant (c) coffee sample are shown in Fig. 2. To compare the results of caffeine content taking into account the type of coffee, the average caffeine content was calculated using the data from Table 4 that are consolidated with obtained median value by coffee type. Average amount of calculated caffeine content detected in black, espresso,
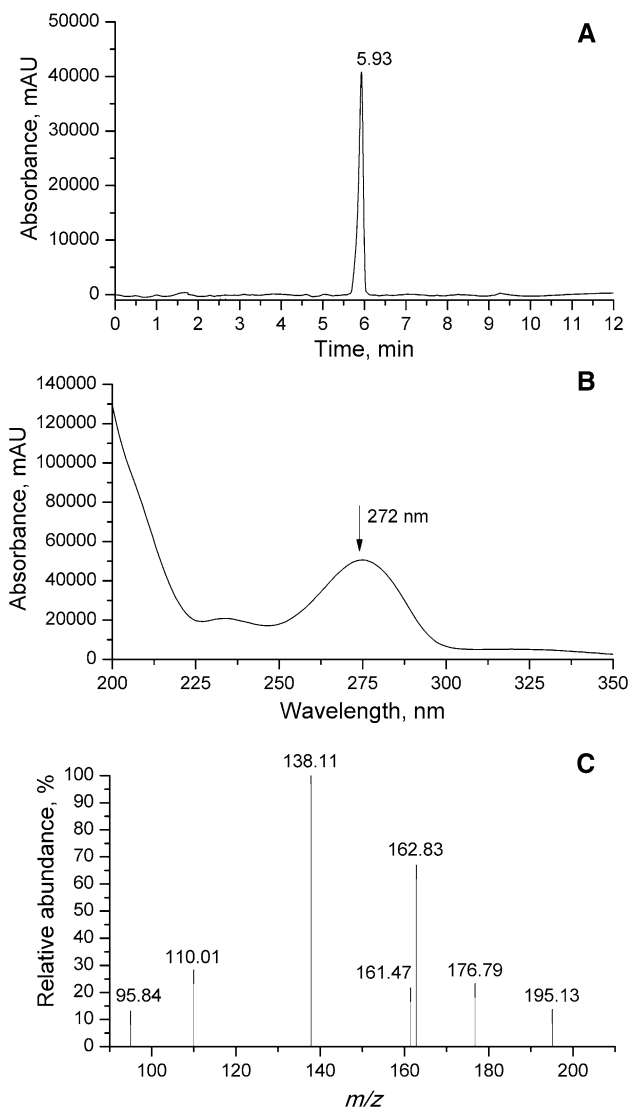

Fig. 1 UHPLC chromatogram of caffeine standard solution (**a**), PDA spectrum of the main peak detected at 5.92 min (**b**), and corresponding caffeine mass spectrum (**c**)

and instant coffees per one serving was 150.5, 108.3, and 57.1 mg, respectively. Based on the obtained results, it can be concluded that espresso and instant coffees have higher average caffeine content compared to the black coffees. This is in accordance with results published by de Mejia and collaborators (2014), where detected caffeine amount in black, espresso, and instant coffees was 95–330, 50–150, and 30–70, respectively.

European Food Safety Authority has recommended a single dose of caffeine up to 200 mg for an average 70 kg adult as clinically non-harmful dose. In addition, daily caffeine intake from all sources up to 400 mg for adults might be taken as safe (excluding pregnant women).

Recent studies have shown that children (2–12 years) and adolescents (13–17 years) can metabolize caffeine more

Fig. 2 Representative UHPLC chromatograms of black (**a**), espresso (**b**), and instant (**c**) coffee beverage
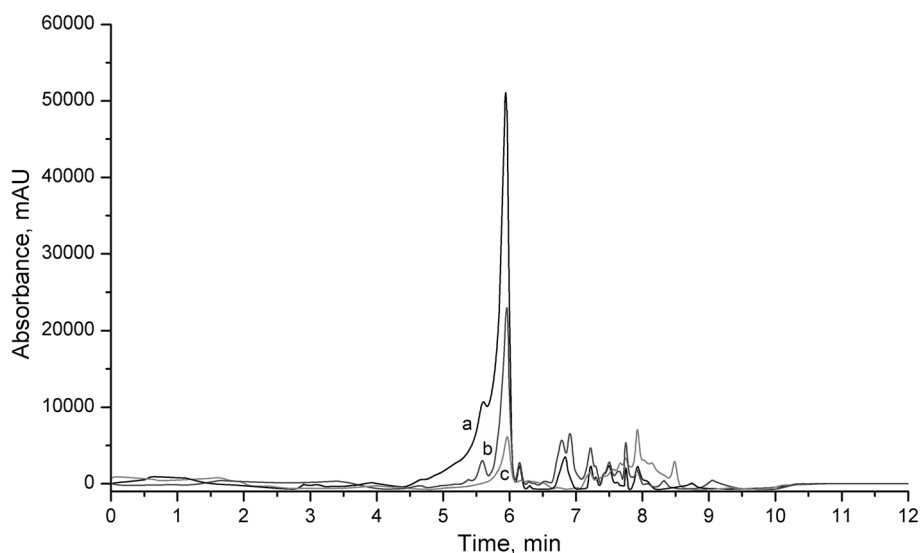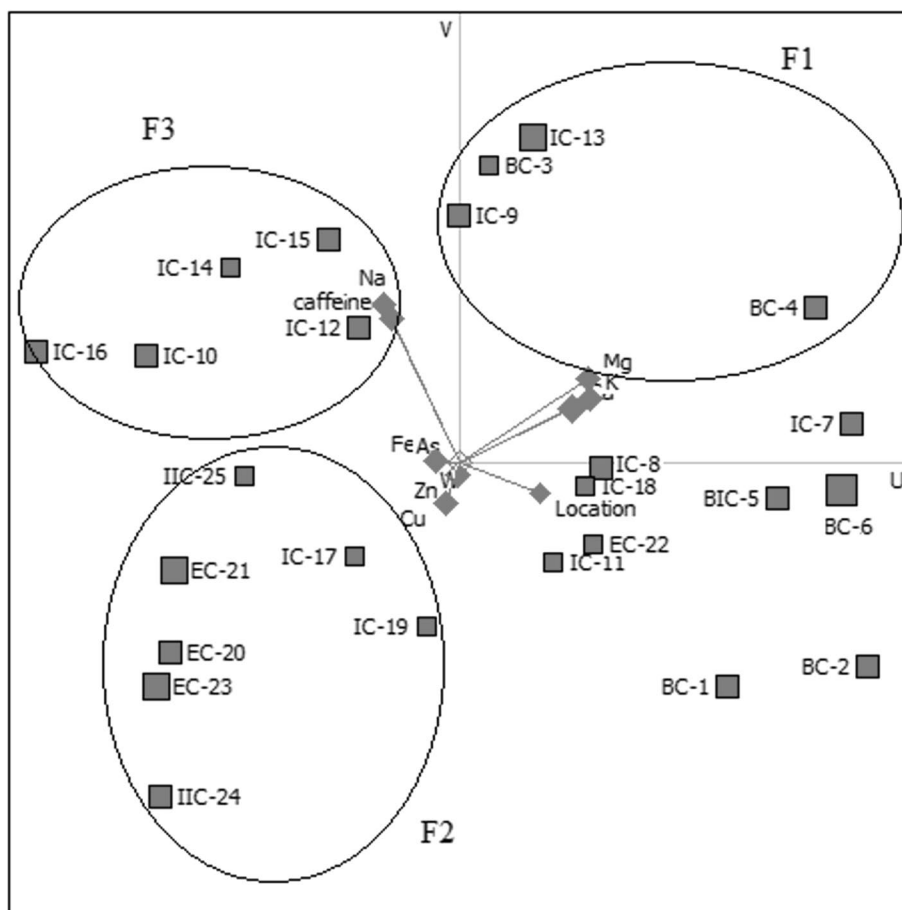

Fig. 3 Principal component analysis (PCA) plot. The analysis was done using 25 types of coffee as alternatives

rapidly than adults. In general, children consume caffeine less (24–37 mg/day) than adults (Mitchell et al. 2014; De Mejia and Ramirez-Mares 2014), but on the other side, children and adolescents, including those diagnosed as hyperactive, are sensitive to the effects of caffeine same as adults. In adolescents, the consumption of sweetened coffee and energy drinks as the principal sources of caffeine intake have been increased (83.2 mg/day). However, the estimated values are below current suggested maximal level for adolescents (100–175 mg/day depending on body weight 40–70 kg) (Mitchell et al. 2014).

Daily intake of three-to-four 200 ml cups of coffee (a total of 500 mg/day of caffeine) may be considered as moderate amount (110–345 mg/day) for most adults and appears to be associated with a neutral to potentially beneficial effect on health.

To emphasize variation and bring out strong patterns in a data set, statistical method Principal Component Analysis (PCA) was further applied. It represents a projection of sets of alternatives (types of coffee) as *n* points in the *k*-dimensional space, where *n* represents the number of alternatives, and *k* the number of criteria.

Based on the position of the criteria, an evident pattern is observed concerning groups of criteria of macroelements (K, Ca, Mg, and Na) that correlate with each other. They are grouped with the corresponding analyzed types of coffees as Cluster F1 in Fig. 3. In addition, a group of criteria of microelements (Fe, As, Zn, Cu) that are strongly correlated and thus discriminate the alternatives in the same manner is grouped along with the following alternatives and marked as Cluster F2. Cluster F3-gathered types of coffee with the smallest content of caffeine. Agreement between the Location criteria and the other criteria is weak, i.e., they are not correlated, since they are not close to each other in the presented visual projection plane (Fig. 3). In addition, caffeine and location are in the opposite directions in the plane, which means that they are conflicting criteria and not correlated whatsoever. Therefore, PCA analysis gathered types of coffee according to the content of caffeine, macro-, and microelements, which is in accordance with presented experimental results obtained by ICP–OES and UHPLC–MS/MS analysis (Tables 4 and 5).

Conclusions

To summarize, the main goal of this study was to provide a composition of coffee infusions that were prepared according to widespread procedure in a domestic environment on Balkan territory, and without sugar addition. Obtained results showed that coffee samples found on Balkans market are generally rich in the content of potassium (105.35–2826.93 ppm) and calcium (413–992.51 ppm). On the other hand, in terms of heavy metal presence, the estimated concentrations were in allowed amounts in all investigated samples. Variation in nutrient content of coffee infusions between samples might be a consequence of different ways of preparation, different coffee brands, or different water types used for coffee preparation. In this study, the impact of macro- and microelements from water to the final nutrition content is negligible, since distillate water has been used for coffee infusions preparation. Consumption of coffee in the amount of one cup per day could be considered as significant in terms of potassium and calcium contribution

Table 5 Content of caffeine in coffee samples (mg/per cup)

Code	Sample	Origin	Content
BC-1	Black coffee	Republic of Serbia	147.1
BC-2	Black coffee	Republic of Serbia	151.7
BC-3	Black coffee	Republic of Serbia	142.3
BC-4	Black coffee	Republic of Serbia	153.3
BIC-5	Black instant coffee	Republic of Serbia	63.4
BC-6	Black coffee	Brazil	158.2
IC-7	Instant coffee 1 in 1	Republic of Serbia	63.6
IC-8	Instant coffee 2 in 1	Czech Republic	58.4
IC-9	Instant coffee 2 in 1	Slovenia	57.8
IC-10	Instant coffee 2 in 1	Hungary	53.7
IC-11	Instant coffee 2 in 1	Republic of Serbia	58.9
IC-12	Instant coffee 2 in 1	Poland	56.1
IC-13	Instant coffee 3 in 1	Poland	51.3
IC-14	Instant coffee 3 in 1	Czech Republic	50.4
IC-15	Instant coffee 3 in 1	Slovenia	47.8
IC-16	Instant coffee 3 in 1	Romania	49.2
IC-17	Instant coffee 3 in 1	Republic of Serbia	58.2
IC-18	Instant coffee 3 in 1	Republic of Serbia	59.8
IC-19	Instant coffee 4 in 1	Republic of Serbia	62.1
EC-20	Espresso coffee	Slovenia	110.3
EC-21	Espresso coffee	Poland	103.1
EC-22	Espresso coffee	Republic of Serbia	108.5
EC-23	Espresso coffee	France	111.4
IIC-24	Instant ice coffee	Slovenia	68.6
IIC-25	Instant ice coffee	Czech Republic	54.4

to recommended daily intake. On the other side, results of LC–MS investigations showed that black coffee has the high content of caffeine (150.5 mg/cup), compared to espresso (108.3 mg/cup) and instant (57.1 mg/cup) coffee. If we do not count the potential availability of caffeine intake from other drinks and food, since the recommended daily dose of caffeine is 400 mg, 250 ml of black coffee, 370 ml of espresso, and 700 ml of instant coffee should be the limiting volume per day for adult person. Results of PCA analysis showed that there is no clear evidence of strong correlation impedance between types of coffee and country of their origin, though observed types of coffee can be gathered in three clusters (according to content of caffeine, macro- and microelements), where these criteria discriminate different types of coffee in the same way.

Bearing in mind the importance of minerals for the normal biological function of the human organism, as well as the numerous positive effects that caffeine causes, coffee from the Western Balkans market can be recommended for daily consummation. Results from this study could be useful for accurate determination of macro-, micronutrients and caffeine for dietary intake that might help adequate nutritional recommendation and health policies at the national

level. In addition, results from this study should be taken into account in nutritional planning or a valuable tool in clinical trials.

References

Alonso J, Angermeyer MC, Bernert S, Bruffaerts R, Brugha TS, Bryson H, de Girolamo G, de Graaf R, Demyttenaere K, Gasquet I (2004) Prevalence of mental disorders in Europe: results from the European study of the epidemiology of mental disorders (ESEMeD) project. Acta Psychiatr Scand 109:21–27. https://doi.org/10.1111/j.1600-0047.2004.00327.x

Atomssa T, Gholap AV (2011) Characterization of caffeine and determination of caffeine in tea leaves using UV-Vis spectrometer. Afr J Pure Appl Chem 5:1–8

Barker AV, Pilbeam DJ (2015) Handbook of plant nutrition. CRC Press, Boca Raton

Borota D, Murray E, Keceli G, Chang A, Watabe JM, Ly M, Toscano JP, Yassa MA (2014) Post-study caffeine administration enhances memory consolidation in humans. Nat Neurosci 17:201–203. https://doi.org/10.1038/nn.3623

Branum AM, Rossen LM, Schoendorf KC (2014) Trends in caffeine intake among US children and adolescents. Pediatrics 133:386–393. https://doi.org/10.1542/peds.2013-2877

Cano-Marquina A, Tarín JJ, Cano A (2013) The impact of coffee on health. Maturitas 75:7–21. https://doi.org/10.1016/j.maturitas.2013.02.002

De Mejia EG, Ramirez-Mares MV (2014) Impact of caffeine and coffee on our health. Trends Endocrinol Metab 25:489–492. https://doi.org/10.1016/j.tem.2014.07.003

Devirian TA, Volpe SL (2003) The physiological effects of dietary boron. Crit Rev Food Sci Nutr 43:219–231. https://doi.org/10.1080/10408690390826491

Dobrinas S, Soceanu A, Popescu V, Stanciu G, Smalberger S (2013) Optimisation of a UV-VIS spectrometric method for caffeine analysis in tea, coffee and other beverages. Sci Study Res 14:71–78

Dos Santos EJ, de Oliveira E (2001) Determination of mineral nutrients and toxic elements in Brazilian soluble coffee by ICP-AES. J Food Compos Anal 14:523–531. https://doi.org/10.1006/jfca.2001.1012

Gogoasa I, Pirvu A, Alda LM, Velciov A, Rada M, Bordean DM, Moigradean D, Simion A, Gergen I (2013) The mineral content of different coffee brand. J Hortic For Biotechnol 17:68–71

Gogoasa I, Adina B, Adina N, Maria R, Antoanela C, Liana A (2017) Determination of trace elements in commercially available instant coffees. J Hortic For Biotechnol 21:1–5

Grembecka M, Malinowska E, Szefer P (2007) Differentiation of market coffee and its infusions in view of their mineral composition. Sci Total Environ 383:59–69. https://doi.org/10.1016/j.scitotenv.2007.04.031

Guerrera MP, Volpe SL, Mao JJ (2009) Therapeutic uses of magnesium. Am Fam Physician 80:157–162

Ioannidis K, Chamberlain SR, Müller U (2014) Ostracising caffeine from the pharmacological arsenal for attention-deficit hyperactivity disorder—was this a correct decision? A literature review. J psychopharmacol (Oxford) 28:830–836. https://doi.org/10.1177/0269881114541014

Jiang W, Wu Y, Jiang X (2013a) Coffee and caffeine intake and breast cancer risk: an updated dose–response meta-analysis of 37 published studies. Gynecol Oncol 129:620–629. https://doi.org/10.1016/j.ygyno.2013.03.014

Jiang X, Zhang D, Jiang W (2013b) Coffee and caffeine intake and incidence of type 2 diabetes mellitus: a meta-analysis of prospective studies. Eur J Nutr 53:25–38. https://doi.org/10.1007/s00394-013-0603-x

Krejčová A, Černohorský T (2003) The determination of boron in tea and coffee by ICP–AES method. Food Chem 82:303–308. https://doi.org/10.1016/S0308-8146(02)00566-6

Liu Y, Li X, Yang C, Tai S, Zhang X, Liu G (2013) UPLC–MS-MS method for simultaneous determination of caffeine, tolbutamide, metoprolol, and dapsone in rat plasma and its application to cytochrome P450 activity study in rats. J Chromatogr Sci 51:26–32. https://doi.org/10.1093/chromsci/bms100

Mehra A, Baker CL (2007) Leaching and bioavailability of aluminium, copper and manganese from tea (Cameliasinensis). Food Chem 100:1456–1463. https://doi.org/10.1016/j.foodchem.2005.11.038

Mitchell DC, Knight CA, Hockenberry J, Teplansky R, Hartman TJ (2014) Beverage caffeine intakes in the US. Food Chem Toxicol 63:136–142. https://doi.org/10.1016/j.fct.2013.10.042

Nędzarek A, Tórz A, Karakiewicz B, Clark JS, Laszczyńska M, Kaleta A, Adler G (2013) Concentrations of heavy metals (Mn Co, Ni, Cr, Ag, Pb) in coffee. Acta Biochim Pol 60:623–627

O'Keefe JH, Bhatti SK, Patil HR, Dinicolantonio JJ, Lucan SC, Lavie CJ (2013) Effects of habitual coffee consumption on cardiometabolic disease, cardiovascular health, and all-cause mortality. J Am Coll Cardiol 62:1043–1051. https://doi.org/10.1016/j.jacc.2013.06.035

Oliveira M, Casal S, Morais S, Alves C, Dias F, Ramos S, Mendes E, Delerue-Matos C, Oliveira MBPP (2012) Intra-and interspecific mineral composition variability of commercial coffees and coffee substitutes: contribution to mineral intake. Food Chem 130:702–709. https://doi.org/10.1016/j.foodchem.2011.07.113

Onianwa PC, Adetola G, Iwegbue CMA, Ojo MF, Tella OO (1999) Trace heavy metals composition of some Nigerian beverages and food drinks. Food Chem 66:275–279. https://doi.org/10.1016/S0308-8146(98)00257-X

Oteiza P, Mackenzie G (2005) Zinc, oxidant-triggered cell signaling and human health. Mol Aspects Med 26:245–255. https://doi.org/10.1016/j.mam.2005.07.012

Parras P, Martínez-Tomé M, Jiménez AM, Murcia MA (2007) Antioxidant capacity of coffees of several origins brewed following three different procedures. Food Chem 102:582–592. https://doi.org/10.1016/j.foodchem.2006.05.037

Petrović S, Savić S, Dimitrijević M, Petronijević Ž (2015) The determination of macro and microelements in chamomile teas (Matricaria Chammomilla L.). Adv Technol 4:54–63. https://doi.org/10.5937/savteh1502037P

Pigozzi MT, Passos FR, Mendes FQ (2018) Quality of commercial coffees: heavy metal and ash contents. J Food Qual. https://doi.org/10.1155/2018/5908463

Ramalakshmi K, Raghavan B (1999) Caffeine in coffee: its removal. Why and how? Crit Rev Food Sci 39:441–456. https://doi.org/10.1080/10408699991279231

Ranić M, Konić-Ristić A, Takić M, Glibetić M, Pavlović Z, Pavlović M, Dimitrijević-Brankovic S (2015) Nutrient profile of black coffee consumed in Serbia: filling a gap in the food composition database. J Food Compos Anal 4:61–69. https://doi.org/10.1016/j.jfca.2014.11.008

Serbian regulations (1992) Regulation on quantities of pesticides, metals and metalloids and other toxic substances, chemotherapeutics, anabolics and other substances that can be found in food. Official Gazette of SRY no. 5/92

Suseela B, Bhalke S, Vinod Kumar A, Tripathi RM, Sastry VN (2001) Daily intake of trace metals through coffee consumption in India.

Food Addit Contam A 18:115–120. https://doi.org/10.1080/02652030010008814

Vega-Carrillo HR, Iskander FY, Manzanares-Acuna E (2002) Elemental content in ground and soluble/instant coffee. J Radioanal Nucl Ch 252:75–80. https://doi.org/10.1023/A:1015235704300

Veljković D, Vučković GN (2010) Minerali u ishrani. Hemijski pregled 51:14–19

Vlahović B, Jeločnik M, Potrebić V (2012) Preferences of coffee consumers on Serbian market. Econ Agric 59:37–49

WHO (1989) Toxicological evaluation of certain food additives and contaminants. Geneva: 33rd meeting of the Joint FAO/WHO Expert Committee on Food Additives

WHO (2011) Review and updating of current WHO recommendations on salt/sodium and potassium consumption. Switzerland, Geneva

Zaidi JH, Fatima I, Arif M, Qureshi IH (2006) Determination of trace elements in coffee beans and instant coffee of various origins by INAA. J Radioanal Nucl Ch 267:109–112. https://doi.org/10.1007/s10967-006-0015-y

Zheng JS, Yang J, Fu YQ, Huang T, Huang YJ, Li D (2013) Effects of green tea, black tea, and coffee consumption on the risk of esophageal cancer: a systematic review and meta-analysis of observational studies. Nutr Cancer 65:1–16. https://doi.org/10.1080/01635581.2013.741762