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Analytical Methods

Simple ICP-OES based method for determination of selected elements in brewed ground and soluble coffees prior to evaluation of their intake and chemical fractionation

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ABSTRACT

A simple method of simultaneous determination of aluminum (Al), barium (Ba), calcium (Ca), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn), nickel (Ni), strontium (Sr) and zinc (Zn) in brews of ground and soluble coffees was proposed. It relied on acidification of brews with HNO_3 to 1.3 mol L^{-1} and their analysis by inductively coupled plasma optical emission spectrometry. Precision of 0.1–9% and detection limits from 0.07 ng mL^{-1} (Sr) to 3 ng mL^{-1} (Ni) were achieved. Trueness of the method was verified by comparison of results with those achieved with wet digestion and by the recovery study, and was better than 5%. Additionally, chemical fractionation by tandem solid phase extraction with reverse-phase and strong cation-exchange extraction tubes was carried out. Differences in chemical fractionation patterns, particularly the residual fraction, was useful for differentiation of ground and soluble coffees by analysis of variance, principle component analysis and hierarchical clustering analysis.

1. Introduction

It seems that global consumption of ground coffee (GC) shall reach a record of 158.5 million (60 kg) bags in 2017/2018 (USDA, 2017). Soluble coffee (SC) popularity also increases in this global market and its growth is predominantly coming out from Asiatic and Middle East countries, where consumers find it as an attractive and easy in preparation beverage that helps in getting energy and refreshing taste (R& M, 2017).

Unfortunately, despite such high consumption of both types of coffees in the world, element analysis of brewed GCs and SCs is infrequent in related literature. Nevertheless, importance of such kind of analysis is not to be overestimated because it is used to evaluate nutritional value of coffee beverages and minerals intake associated with their habitual drinking as well as to verify quality and safety of coffee products in reference to presence of some hazardous elements. Spectrochemical analysis of brewed GCs and SCs is commonly carried out by using flame atomic absorption spectrometry (FAAS) (Ashu & Chandravanshi, 2011; Grembecka, Malinowska, & Szefer, 2007; Oliveira et al., 2012; Oliveira, Ramos, Delerue-Matos, & Morais, 2015; Onianwa, Adetola, Iwegbue, Ojo, & Tella, 1999; Ozdestan, 2014; Pohl, Stelmach, & Szymczycha-Madeja, 2014a, 2014b; Pohl, Szymczycha-Madeja, Stelmach, & Welna, 2016; Ranic et al., 2015; Stelmach, Pohl, & Szymczycha-Madeja, 2013; Stelmach, Szymczycha-Madeja, & Pohl, 2016; Szymczycha-Madeja, Pohl, Welna, Stelmach, & Jedryczko, 2016). Inductively coupled plasma optical emission spectrometry (ICP-OES) (Dos Santos & de Oliveira, 2001; Fernandes et al., 2005; Jaganyi, Vanmare, & Clark, 1999; Pohl et al., 2016; Santos, Lauria, & da Silveira, 2004; Szymczycha-Madeja et al., 2016; Welna, Szymczycha-Madeja, & Zyrnicki, 2013) or inductively coupled plasma mass spectrometry (ICP-MS) (Nedzarek et al., 2013; Santos et al., 2004) are less frequently applied for that purpose. Element analysis of brews of green coffee by FAAS (Stelmach, Pohl, & Szymczycha-Madeja, 2015), graphite furnace atomic absorption spectrometry (GFAAS) (Jeszka-Skowron, Stanisz, & de Pena, 2016) or ICP-MS (Semen, Mercan, Yayla, & Acikkol, 2017) is also reported.

Considering pretreatment of brewed GCs and SCs proposed in cited works, it commonly appears to be protracted and hence, can be a potential source of contamination of samples and/or losses of elements. Accordingly, infusions of GCs are decomposed in mixtures of concentrated HNO_3 and $HClO_4$ (Ashu & Chandravanshi, 2011; Nedzarek et al., 2013) or concentrated HNO_3 and 30% H_2O_2 (Welna et al., 2013). They are also evaporated to dryness followed by ashing of residues left and dissolution of resulting ashes in solutions of HNO_3 or HCl

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(Grembecka et al., 2007; Onianwa et al., 1999; Ozdestan, 2014; Ranic et al., 2015; Santos et al., 2004). SCs are wet digested in mixtures of concentrated HNO_3 and 30% H_2O_2 (Dos Santos & de Oliveira, 2001; Welna et al., 2013) or dry ashed (Grembecka et al., 2007).

It is easy to predict that advances in simpler and faster sample preparation procedures of brews of GCs and SCs prior to their multi-element analysis are important for future research and development, i.e., fast multi-element analysis of a high number of brewed GCs and SCs for reliable control of their safety and quality or collection of data for chemometric classification or categorization. Such new, validated methods (with reduced number of manipulations and amount of reagents) shall certainly increase the sample throughput, decrease costs of analysis and improve quality of results because of lower risk of contamination of samples and losses of elements. When reported in related literature, simplified sample preparation procedure of brewed GCs and SCs prior to their element analysis usually concern measurements made by FAAS and determination of a limited group of elements, i.e., Ca, Fe, K, Mg, Mn, Na and P (Oliveira et al., 2012, 2015), Ca, Cu, Fe, Mg, Mn and Zn (Stelmach et al., 2013), Ca, Fe, K, Mg and Na (Szymczycha-Madeja et al., 2016); Ca, Fe, Mg and Mn (Pohl et al., 2014a; Stelmach et al., 2016), Ca, K, Mg and Na (Pohl et al., 2016) or Mn (Pohl et al., 2014b). In case of ICP-OES, just few papers are focused on determination of K, Mg, Mn and P (Jaganyi et al., 1999), Ca, Cu, Fe, K, Mg, Mn, Na, Pb, S, Se, Si, Sn, Sr and Zn (Fernandes et al., 2005) or Al, Ba, Cd, Co, Cr, Mn, Ni, Pb, Sr and Zn (Szymczycha-Madeja et al., 2016). Unfortunately, it is difficult to accept that in case of simplified sample preparation procedures proposed prior to spectrochemical analyses, these methods were not validated at all as in case of ICP-OES (Fernandes et al., 2005; Jaganyi et al., 1999) or only the recovery study was performed as in case of FAAS (Oliveira et al., 2012, 2015). Only in few cases, trueness of these simplified sample preparation procedures combined with detection by ICP-OES (Szymczycha-Madeja et al., 2016) or FAAS (Pohl et al., 2014a, 2014b; Stelmach et al., 2013, 2016) was assessed by comparison of results obtained with these methods and reference methods including complete destruction of coffee matrix and release of elements at the step of the sample preparation. On the basis of main provisions of the ISO 5725-4:1994 standard, results obtained with a measurement method can be compared to two different types of references: a reference measurement method and a certified reference material (CRM). Since a CRM of coffee is not available, the use of an appropriate reference method can confirm reliability of results obtained with the aid of the measurement method (ISO, 1994).

Considering speciation of elements in brewed GCs and SCs, information about possible forms of elements present in these beverages and intaken by coffee drinkers is negligible and quite inconsistent. To the best of our knowledge, chemical partitioning of Ca, Fe, Mg and Mn in brews of SCs by means of solid phase extraction (SPE) (Pohl et al., 2014a) in addition to physical fractionation of Al, Ba, Ca, Co, Fe, K, Mg, Mn, Na, Ni, Sr and Zn in brews of GCs and SCs by ultrafiltration (UF) (Pohl et al., 2016) were reported so far. It could be expected that chemical fractionation of elements in brewed GCs and SCs would enable to gain knowledge about possible fractionation forms of different chemical nature (hydrophobicity, charge) and functionality. In this way, it would be possible to indirectly predict bioavailability of elements from brewed GCs and SCs and better anticipate their actual safety and quality. Additionally, dissimilar distribution of given chemical fractions, also known as fractionation patterns, would be distinctive for a given type of coffee and therefore would help in better classifying and/or discriminating samples of both types of coffees by pattern recognition methods.

Therefore, the aim of this work was to simplify the sample preparation procedure of GCs and SCs brews prior to their routine (fast and uncomplicated because omitting sample decomposition) analysis by ICP-OES on the content of selected major, minor and trace elements (Al, Ba, Ca, Cu, Fe, Mg, Mn, Ni, Sr and Zn) and validate the new method. The second aim was to partition of studied metals by SPE using a tandem assemblage with DSC-18 tubes followed by DSC-SCX tubes to get unique fractionation patterns of studied elements in both types of coffees. Finally, information about distinguished chemical fractions of Al, Ba, Ca, Cu, Fe, Mg, Mn, Ni, Sr and Zn (hydrophobic, HF; cationic, CF; residual, RF) achieved using the mentioned SPE approach was used to build the data matrix and indicate differences between brews of both coffee types by principle component analysis (PCA). Outcomes of this chemometric analysis were compared with those obtained using total concentrations of Al, Ba, Ca, Cu, Fe, Mg, Mn, Ni, Sr and Zn.

2. Experimental

2.1. Apparatus

Concentrations of studied elements in all brews of GCs and SCs in addition to effluents and eluates resulting from tandem SPE chemical fractionation were determined using an Agilent bench-top optical emission spectrometer of inductively coupled Ar plasma (Ar-ICP-OES), model 720. The spectrometer was equipped with a high-resolution Echelle-type polychromator and a VistaChip II solid-state charge-transfer device detector. Solutions of standards and samples were introduced by pneumatic nebulization with an Agilent OneNeb concentric nebulizer and a single-pass glass cyclonic spray chamber. The spectrometer was operated at the following settings: forward power – 1.2 kW, plasma gas flow rate – 15.0 L min^{-1}, auxiliary gas flow rate – 1.5 L min^{-1}, nebulizing gas flow rate – 0.75 L min^{-1}, solution uptake rate – 0.75 mL min^{-1}, waste drainage rate – 1.5 mL min^{-1}. Instrument stabilization and solution uptake delay were 15 and 30 s, respectively. The following analytical lines (I and II denote atomic and ionic emission lines, respectively) were selected for measurements: Al I 396.2 nm, Ba II 455.4 nm, Ca I 422.7 nm, Cu I 324.8 nm, Fe I 248.3 nm, Mg I 285.2 nm, Mn II 257.6 nm, Ni II 231.6 nm, Sr II 407.8 nm and Zn I 213.8 nm. Intensities of these lines were read 3 times within integration time of 1 s. Seven-point external calibration curves within the concentration range of 0.01–10 μg mL^{-1} were used for quantification of studied elements.

2.2. Materials and reagents

Sigma-Aldrich Discovery DSC-18 (octadecyl groups polymerically bonded on a silica support, volume 6 mL, sorbent mass 500 mg) and DSC-SCX (benzene sulfonic groups polymerically bonded on a silica support) SPE tubes connected in series were used to fractionate elements species and retain them from brews of GCs and SCs *via* hydrophobic interactions and cation-exchange, respectively. Prior to ICP-OES analysis, samples of brews of GCs and SCs and effluents of DSC-18 and DSC-SCX SPE tubes were acidified using concentrated HNO_3 (65.0%). Concentrated HCl (37.0–38.0%) was used to prepare a 2.0 mol L^{-1} HCl solution used for elution of elements species from DSC-SCX SPE tubes. Both acids were Emsure® ACS premium grade and purchased from Merck Millipore (Poland). Standard solutions for calibration were prepared by stepwise dilution of a Merck Millipore CertiPur® multi-element stock (1000 μg mL^{-1}) ICP standard solution IV. De-ionized water was used throughout.

2.3. Preparation of coffee brews

Popular in Poland and other EU countries GCs (GC1-GC8) and SCs (SC1-SC10) were selected for this study. As declared by producers, SC9 and SC10 contained up to 30% of natural GC powders. 6-g portions of GCs as received were placed in 400-mL beakers and poured with 250 mL of hot de-ionized water (95 °C). After mixing with a glass bar, beakers were covered with watch glasses and let for 5 min to infuse coffee portions. Afterwards, brews were separated from grounds by decanting them through pre-cleaned 390-grade quantitative filter papers (Munktell & Filtrak). Resulting filtrates were centrifuged at