



Analytical Methods

Simplified sample treatment for the determination of total concentrations and chemical fractionation forms of Ca, Fe, Mg and Mn in soluble coffees



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ABSTRACT

A simpler, and faster than wet digestion, sample treatment was proposed prior to determination of total concentrations for selected macro- (Ca, Mg) and microelements (Fe, Mn) in soluble coffees by flame atomic absorption spectrometry. Samples were dissolved in water and acidified with HNO₃. Precision was in the range 1–4% and accuracy was better than 2.5%. The method was used in analysis of 18 soluble coffees available on the Polish market. Chemical fractionation patterns for Ca, Fe, Mg and Mn in soluble coffees, as consumed, using a two-column solid-phase extraction method, determined Ca, Mg and Mn were present predominantly as cations (80–93% of total content). This suggests these elements are likely to be highly bioaccessible.

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1. Introduction

Considering statistical data on exports, imports, and re-exports of soluble coffee during the period 1990–2011, these coffee-based products are remarkably popular in many countries (International Coffee Organization, 2013). As reported by International Coffee Organization (2013), the global trade in soluble coffee has grown rapidly since 2000 and with that increased consumption of soluble coffees. Control of soluble coffee chemical composition is important because the concentration of all soluble components, including hazardous substance, increase during production (Chu, 2012).

Determination of micro- and trace elements in soluble coffee is of particular interest because of the need to understand better variations among samples of different origin or industrial processing (dos Santos & de Oliveira, 2001; Pohl, Stelmach, Welna, & Szymczycha-Madej, 2013). Unfortunately, studies devoted to the measurement of minerals and other nutrients or bioactive compounds in soluble coffee are relatively scarce. Methods used to determine concentrations of different elements in soluble coffee include flame atomic absorption spectrometry (FAAS) (Grembecka, Malinowska, & Szefer, 2007; Oliveira et al., 2012;

Onianwa, Adetola, Iwegbue, Ojo, & Tella, 1999; Suseela, Bhalke, Vinod Kumar, Tripathi, & Sastry, 2001), graphite furnace atomic absorption spectrometry (GFAAS) (Oliveira et al., 2012), inductively coupled plasma optical emission spectrometry (ICP-OES) (dos Santos & de Oliveira, 2001; Fernandes et al., 2005) and instrumental neutron activation analysis (INAA) (Vega-Carrillo, Iskander, & Manzanares-Acuna, 2002; Zaidi, Fatima, Arif, & Qureshi, 2006).

In the case of FAAS, sample pre-treatment is laborious because it relies on dry-ashing (Onianwa et al., 1999; Suseela et al., 2001) and subsequent digestion of the resulting mineral residues in acid (e.g., HNO₃ with HClO₄, Onianwa et al., 1999 or HCl, Suseela et al., 2001) followed by re-constitution in water or dilute HNO₃ (Grembecka et al., 2007). In the case of ICP-OES, soluble coffees are wet-digested in mixtures of HNO₃ and H₂O₂ using closed vessel microwave assisted systems (dos Santos & de Oliveira, 2001; Fernandes et al., 2005). For these reasons, the development of alternatives for complete decomposition prior to elemental analysis is important for future research since it would allow simpler, more rapid and more convenient determination of soluble coffee composition. Using methods with simplified pre-treatments would reduce the risk of contamination and/or the loss of substances of interest, particularly those at low concentrations.

It is worth noting that, when recommended dietary allowances (RDAs) and adequate intakes (AIs) for macro- and micro-elements

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(Ca, Fe, K, Mg, Mn, Na, P) are assessed, intake from soluble coffee is assumed to be 100% (Grembecka et al., 2007; Oliveira et al., 2012; Suseela et al., 2001; Zaidi et al., 2006). Thus, it is important the composition of soluble coffees is accurately reported. Daily mineral intakes (DMIs) are usually low, but uptake may be affected by consumption and composition of soluble coffees. Elements present in coffee take different forms, based on hydrophobicity, charge and size. They may also differ in bioaccessibility. To the best of our knowledge, no scientific work has been published on identification and/or quantification of element species and form in soluble coffee. The prediction of uptake of elements from these beverages, and likely health benefits or reduction in disease risk, associated with consumption of soluble coffee is important for diet-health research.

The aim of the present contribution was to (i) evaluate suitability of a simplified sample treatment prior to determination of Ca, Fe, Mg and Mn total concentrations in soluble coffees, available on Polish market, by FAAS and (ii) assess the partitioning profile of these elements, using operational speciation by two-column solid-phase extraction (SPE), and predict the possible bioaccessibility of these macro- and micro-elements in soluble coffees as consumed.

2. Experimental

2.1. Solutions, reagents and materials

Re-distilled water was used in all preparations. Mixed working standard solutions of Ca, Fe, Mg and Mn were prepared using TraceCERT single-element stock standard solutions (1000 mg L^{-1}) provided by Sigma–Aldrich Chemie GmbH (Steinheim, Germany). These working standards were freshly prepared and used for 5-point calibration of the FAAS instrument. Solutions were not acidified and contained the elements under study in the following ranges: $0.01\text{--}1 \text{ mg L}^{-1}$ (Ca, Mg) and $0.01\text{--}2 \text{ mg L}^{-1}$ (Fe, Mn). Additionally, solutions containing 30 (Ca), 0.7 (Fe), 70 (Mg) and 0.5 (Mn) mg L^{-1} , respectively, were prepared to study sorption and desorption properties of the SPE tubes. These solutions were acidified using potassium hydrogen phthalate ($\text{C}_8\text{H}_5\text{KO}_4$)-HCl (pH 4.0) and $\text{C}_8\text{H}_5\text{KO}_4$ -NaOH (pH 4.5 and 5.0) buffers.

Reagents used for sample preparation were ACS grade 30% (m/m) H_2O_2 and 65% (m/m) HNO_3 solutions supplied by J.T. Baker (Deventer, Netherlands). In addition, a 36.5–38.0% (m/m) HCl solution from J.T. Baker, and methanol from POCh (Gliwice, Poland), was used for pre-condition of the SPE tubes.

For the chemical fractionation of Ca, Fe, Mg and Mn, by two-column SPE, two types of 6-mL Sigma–Aldrich Discovery® SPE tubes were used, i.e., DSC-18 and DSC-SCX. These contained polymerically bonded octadecyl and sulphonic acid groups on silica supports, respectively. They both had a bed weight of 500 mg and the particle size of supporting silica gel was of $50 \mu\text{m}$. SPE tubes were initially pre-conditioned; DSC-18 beds were washed with 10 mL of methanol and 10 mL of water and DSC-SCX tubes were washed with 5 mL of a 2 mol L^{-1} HCl solution and 20 mL of water. Pre-conditioning reagents and water were passed through SPE tubes at a flow rate of $5\text{--}6 \text{ mL min}^{-1}$ using disposable 20-mL syringes and tube adapters.

2.2. Apparatus

All quantifications of Ca, Fe, Mg and Mn in soluble coffees (as consumed), as well as effluents and eluates resulting from chemical fractionation, were carried out using a Perkin Elmer 1100B FAAS instrument equipped with a deuterium lamp (DL) for background correction. The spectrometer was filled with a standard

Ti single-slot 10-cm long burner head for air– C_2H_2 flame and a wetttable inert plastic coated burner–mixing chamber with an end cap and a drainage assemblage. A steel nebuliser and a multi-vane flow spoiler were used for sample introduction by pneumatic nebulisation. A fuel lean flame was used as recommended by the manufacturer. To obtain maximum response, the burner height and the C_2H_2 flow rate were optimised. Operating conditions used were: air flow rate, 8 L min^{-1} ; C_2H_2 flow rate, 1.4 L min^{-1} ; burner height, 5.5 mm; wavelengths, 422.7 (Ca), 248.3 (Fe), 285.2 (Mg) and 279.5 (Mn), respectively; slit widths, 0.2, 0.7, 0.2 and 0.7 nm (Ca, Fe, Mg and Mn); lamp currents, 15, 30, 15 and 30 mA (Ca, Fe, Mg and Mn); solution aspiration rate, 4.5 mL min^{-1} ; measurement time, 3 s; and the number of replicates, 3.

2.3. Sample preparation

Commercial soluble coffees were purchased from supermarkets in Wrocław, the largest city in western Poland (Lower Silesia region). The coffees (16) were labelled as containing 100% natural coffee; two (C7, C12) contained finely ground green coffee beans (35%) and roasted coffee beans (15%), respectively, making 18 samples in total. Before analysis, samples were ground using an octagonal agate mortar and an agate pestle.

Three different sample preparation procedures were applied. For open-vessel wet-digestion (A), ground samples (0.5 or 1 g) were weighed into glass beakers and 5 mL concentrated HNO_3 added. Samples were covered with watch glasses and hot plate digested. Initially, the digestion was carried out at a low heat, but the temperature was gradually increased to $\sim 100^\circ\text{C}$ until the solutions were almost evaporated. After cooling, 5 mL H_2O_2 were added to and the samples heated, allowing the volume of sample solutions to decrease but not dry out. Finally, remnants were re-constituted with water, transferred to 50 mL volumetric flasks and made up to volume with water. For water dissolution (B), ground samples (0.5, 1 and 2 g) were weighed into 50 mL screw-capped tubes and dissolved in hot water ($\sim 70^\circ\text{C}$). The resulting solutions were cooled and the volume adjusted to 50 mL with water. The final sample preparation procedure was similar to procedure B (water dissolution) but, before being made up to volume with water, 3.5 mL concentrated HNO_3 were added to the samples to a final HNO_3 concentration of 1 mol L^{-1} .

External calibration with working standards solutions was used for the quantification of Ca, Fe, Mg and Mn concentrations by FAAS. Analysis was made against appropriate blanks, based on the method used. In each case, three samples were prepared and analysed in parallel. Final results were blank-corrected and averaged. The content of Fe and Mn were measured directly in samples whilst samples were diluted 20 and 50 times, respectively for Ca and Mg.

2.4. Chemical fractionation

To fractionate Ca, Fe, Mg and Mn in soluble coffees as consumed, and determine the contribution of fractionated forms of these elements, grouped in three different fractions, samples (4 g of coffee per 200 mL of hot water) were subjected to the following: 15 mL were placed in syringe barrels and passed through DSC-18 SPE tubes at $5\text{--}6 \text{ mL min}^{-1}$. Resulting effluents were collected and saved (5 mL portions) for FAAS analysis to determine the total concentrations of Ca, Fe, Mg and Mn not retained by DSC-18 sorbent. Considering total concentrations of the elements of interest in soluble coffees, contributions from the hydrophobic fraction (HF) were evaluated. The remaining 10 mL portions were placed in syringe barrels and passed through DSC-SCX SPE tubes, at $5\text{--}6 \text{ mL min}^{-1}$, to retain cationic species of Ca, Fe, Mg and Mn. Effluents from these SPE tubes were also collected and subjected

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