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Analytical Methods

Espresso beverages of pure origin coffee: Mineral characterization, contribution for mineral intake and geographical discrimination

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ABSTRACT

Espresso coffee beverages prepared from pure origin roasted ground coffees from the major world growing regions (Brazil, Ethiopia, Colombia, India, Mexico, Honduras, Guatemala, Papua New Guinea, Kenya, Cuba, Timor, Mussulo and China) were characterized and compared in terms of their mineral content. Regular consumption of one cup of espresso contributes to a daily mineral intake varying from 0.002% (sodium; Central America) to 8.73% (potassium; Asia). The mineral profiles of the espresso beverages revealed significant inter- and intra-continental differences. South American pure origin coffees are on average richer in the analyzed elements except for calcium, while samples from Central America have generally lower mineral amounts (except for manganese). Manganese displayed significant differences ($p < 0.05$) among the countries of each characterized continent. Intercontinental and inter-country discrimination between the major world coffee producers were achieved by applying canonical discriminant analysis. Manganese and calcium were found to be the best chemical descriptors for origin.

1. Introduction

Coffee world total production has been increasing in the last 5 years (ICO, 2013). Coffee is one of the most important commodities both for producers, that is, countries in the tropical and subtropical areas with coffee as their main agriculture export product, and for manufacturers, which are mainly located in Europe and North America, where coffee is roasted, mixed and packed. It is not unusual that coffee is subject to adulteration throughout its production chain, mainly in the mislabelling of the product to conceal its true botanical and/or geographical origin (Alonso-Salces, Serra, Reniero, & Héberger, 2009). Chemical analyses constitute an important tool for quality control in the food industry where on-line, fast and simple methods are required. Recently, some studies have been reported in order to identify the fraudulent addition of common coffee adulterants, such as barley (Ebrahimi-Najafabadi et al., 2012), roasted corn and coffee husks (Reis, Franca, & Oliveira, 2013) to green coffee. Many others focus their attention on the discrimination of green and roasted coffee varieties, namely *Coffea arabica* and *Coffea canephora* var. *robusta* using different chemical components (Alonso-Salces et al., 2009; Alves, Casal, Alves, & Oliveira, 2009; Bertrand et al., 2008; Cagliani, Pellegrino, Giugno, & Consonni, 2013; Choi, Choi, Park, Lim, & Kwon, 2010; Garrett, Vaz, Hovell, Eberlin, & Rezende, 2012; Gordillo-Delgado, Marín, Cortés-Hernámdez, Mejía-Morales, & García-Salcedo, 2012; Pacetti, Boselli, Balzano, & Frega, 2013; Rodrigues et al., 2009; Wang, Fu, & Lim, 2011; Özdestan et al., 2013). However, studies concerning the characterization of espresso coffee beverages consumed worldwide, and prepared from roasted ground coffees, are limited. Downey and Boussion (1996) investigated the potential of near-infrared reflectance spectroscopy for the authentication of coffee bean variety based on the analysis of the dried coffee extract prepared from pure *arabica*, pure *robusta* and blends of these two varieties. Garrett et al. (2012) evaluated the use of direct-infusion electrospray ionization–mass spectrometry data combined with the partial least-squares multivariate calibration technique to detect and quantify the *arabica* coffee adulterations by *robusta* coffee in drinking espresso coffee blends. Mineral content has been also used to evaluate the authenticity and geographical origin of coffee samples. The content of selected minerals and trace elements in coffee beverages reflects the soil type and the environmental growing conditions. Moreover, minerals are significantly more stable in the food commodity than vitamins or other organic compounds (Anderson & Smith, 2002; Grembecka, Malinowska, & Szefer, 2007) and they are usually determined more easily with less expense. Some authors characterized the mineral content of coffees and were able

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to discriminate some of them based on coffee species (Grembecka et al., 2007; Martín, Pablos, & González, 1998, 1999), green, organic, ground, flavored and soluble coffee (Barbosa et al., 2013; dos Santos & de Oliveira, 2001; Fernandes et al., 2005; Grembecka et al., 2007; Martín et al., 1998, 1999; Morgano, Pauluci, Mantovani, & Mory, 2002; Oliveira et al., 2012; Suseela, Bhalke, Kumar, Tripathi, & Sastry, 2001; Vega-Carrillo, Iskander, & Manzanares-Acuña, 2002) and geographical origin (Anderson & Smith, 2002; Bertrand et al., 2008; Krivan, Barth, & Morales, 1993; Oleszczuk et al., 2007). Information describing digested green and roasted ground coffee beans or infusions of instant coffees was found; none regarding espresso beverages (consumed global, and from pure sources) has been published. Concerning pure origin coffees (instant or coffee beans) specific elemental data was not found for Mussulo (Africa), or Asian coffees from Timor and China.

Mineral content is usually assessed by atomic absorption spectrometry (AAS), a sensitive and highly selective tool suitable for the determination of many elements at trace and ultra-trace levels. The most significant drawback of the AAS is the lack of multi-elemental analysis. However, high-resolution continuum source atomic absorption spectrometry (HR-CS-AAS), which uses a continuum radiation source in contrast to a line source, generates a spectrum with a continuous spectral distribution over a broad wavelength range (Welz et al., 2010). This recent AAS technique combines graphite furnace and flame system, in tandem, and is equipped with a high-resolution double monochromator and a charge-coupled device array detector (Welz et al., 2010). The main advantages of HR-CS-AAS *vs* traditional AAS are: (i) the need for only one single lamp for all elements and wavelengths; (ii) since any wavelength between 190 and 900 nm can be accessed, the same equipment can be used for molecular absorption spectrometry, making possible the determination of non-metals; (iii) the visibility of the spectral environment of the analytical line at high resolution greatly helps in method development and to avoid spectral interferences; (iv) advanced simultaneous background correction automatically eliminates lamp flicker noise and continuous background absorption (Welz et al., 2010). HR-CS-AAS was recently applied to different food matrices, namely in yogurt (Brandao, de Jesus, da Silva, & Ferreira, 2010), wheat flour foods (Ting, Li-jiao, & Ru-gang, 2011), milk powder and vegetables (Ozbeck & Akman, 2013), cereals, vegetables, beverages, sea foods and dairy products (Ting, Li-jiao, Jun, & Ru-gang, 2012), instant coffees and coffee substitutes (Oliveira et al., 2012), as well as in wine, beans, grain products and mineral waters (Huang, Becker-Ross, Florek, Heitmann, & Okruss, 2005). No study using HR-CS-AAS describes analysis of espresso coffee.

The main goal of this work was to characterize espresso beverages prepared with pure origin roasted coffees from Africa (Kenya, Mussulo and Ethiopia), South America (Colombia and Brazil), Central America (Honduras, Cuba, Mexico and Guatemala), Asia (China, India and Timor) and Oceania (Papua New Guinea). The selected samples are representative of current espresso coffees, generally consumed worldwide, as well as in Portugal. This study also included the application of the novel HR-CS-AAS to quantify the relevant macronutrients (calcium (Ca), magnesium (Mg), potassium (K), sodium (Na) and phosphorous (P)) and micronutrients (iron (Fe) and manganese (Mn)) in the espresso coffee beverages without sample preparation except dilution and acidification. The inter- and intra-continental mineral composition variability and the daily mineral intake promoted by the consumption of these beverages were evaluated. The suitability of using mineral contents of espresso coffee beverages as chemical descriptors to differentiate their continental and specific origin (country) was demonstrated. Consequently, a straightforward, simple, fast and inexpensive method was established for detection of fraud involving mislabelling of geographical origin.

2. Materials and methods

2.1. Reagents

A Milli-Q water purification system (Millipore, Molsheim, France) was used to obtain ultrapure water (18.2 $M\Omega\,cm^{-1}$ resistivity). Standard solutions of Ca, Mg, Fe and Mn were prepared from the 1000 mg/L stock solutions (Panreac, Barcelona, Spain). K, Na and P standard solutions were obtained by potassium chloride (99.5%, Riedel-de Haën, Seelze, Germany), sodium chloride (99.8%, Riedel-de Haën, Seelze, Germany) and potassium dihydrogen phosphate (99.5%, Riedel-de Haën, Seelze, Germany) dissolution in ultrapure water, respectively. All standard solutions were acidified with 1% (v/v) suprapur hydrochloric acid (Sigma–Aldrich, Steinheim, Germany), except for P analysis. For quantification by HR-CS-AAS, 1% (w/v) caesium chloride (Sigma–Aldrich, Steinheim, Germany) was used as an ionization chemical suppressor. The color development reagent for P determination was prepared as described in 4500-P standard (Greenberg, Clesceri, & Eaton, 1992) by the addition of ammonium molybdate tetrahydrated (99.0%, Merck, Darmstadt, Germany) and ammonium metavanadate (99.0%, Merck, Darmstadt, Germany). All glassware and polypropylene material were soaked in nitric acid (10% v/v) for at least 24 h, thoroughly rinsed with ultrapure water and dried before use.

2.2. Sampling and preparation of espresso coffee beverages

A total of 39 distinct pure origin roasted and ground coffee samples were analyzed. Samples were obtained from two well-known international companies that specialize in import and selection of the best coffee crops from the world's leading producers. Geographical authenticity was established according to the information given by the importers (Table 1). Pure origin coffee samples from Colombia, Brazil and India were only available as 5 g ground coffee capsules; the beverages were prepared with ultra-pure water with a Siemens espresso machine (TK30). The other espresso coffee drinks were prepared using 6 g ground coffee weighed accurately (Mettler Toledo AG-MS205DU, Switzerland) and prepared using a different espresso machine (Krups, 880). Coffee samples were extracted immediately using ultra-pure water in the machines. After extraction and cooling of the beverages, the final volumes were adjusted to 40 mL with ultra-pure water.

2.3. Mineral analysis

Ca, Mg, Na, K, Fe and Mn quantifications were carried out using an Analytik Jena ContrAA 700 HR-CS-AAS spectrometer equipped

Table 1
Identification and geographical origin of the characterized pure origin coffees.

Samples	Origin	Variety
1, 14, 27	Kenya (Africa)	*Arabica* and *robusta* coffee
2, 15, 28	Papua New Guinea (Oceania)	*Arabica* and *robusta* coffee
3, 16, 29	Timor (Asia)	Arabic coffee
4, 17, 30	Mussulo (Africa)	*Arabica* coffee
5, 18, 31	Colombia (South America)	*Arabica* coffee
6, 19, 32	India (Asia)	*Arabica* and *robusta* coffee
7, 20, 33	Brazil (South America)	*Arabica* coffee
8, 21, 34	Honduras (Central America)	Arabic coffee
9, 22, 35	Guatemala (Central America)	Arabic coffee
10, 23, 36	Cuba (Central America)	Arabic coffee
11, 24, 37	Mexico (Central America)	Arabic coffee
12, 25, 38	China (Asia)	Arabic coffee
13, 26, 39	Ethiopia (Africa)	Arabic coffee