Food Chemistry 214 (2017) 218–226

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Coffee aroma: Chemometric comparison of the chemical information provided by three different samplings combined with GC–MS to describe the sensory properties in cup

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ARTICLE INFO

Article history:
Received 24 March 2016
Received in revised form 11 July 2016
Accepted 11 July 2016
Available online 12 July 2016

Keywords:
Aroma and flavor
HS-SPME
SBSE
GC–MS
Chemometric
Sensory properties
Coffee

ABSTRACT

This study is part of a wider project aiming to correlate the chemical composition of the coffee volatile fraction to its sensory properties with the end-goal of developing an instrumental analysis approach complementary to human sensory profiling. The proposed investigation strategy compares the chemical information concerning coffee aroma and flavor obtained with HS-SPME of the ground coffee and *in*-solution SBSE/SPME sampling combined with GC–MS to evaluate their compatibility with the cupping evaluation for quality control purposes. Roasted coffee samples with specific sensory properties were analyzed. The chemical results obtained by the three samplings were compared through multivariate analysis, and related to the samples' sensory attributes. Despite the differences between the three sampling approaches, data processing showed that the three methods provide the same kind of chemical information useful for sample discrimination, and that they could be used interchangeably to sample the coffee aroma and flavor.

1. Introduction

The quality of a cup of coffee and its distinctive sensory properties depend on the entire production chain. Some of the major factors influencing the final product are: geographical origin, climate, species, harvesting methods, technological processing (mainly roasting and grinding), storage conditions, and last but no less important, the brewing method (International Trade Centre., 2011; Sunarharum, Williams, & Smyth, 2014).

Aroma and flavor are undoubtedly important hedonic aspects of a good coffee (Sunarharum et al., 2014), and thus these two aspects should be carefully considered in coffee classification during coffee-bean selection, in addition to their physical aspects, such as size, color and defective beans (http://www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_tc_browse.htm?commid=47950S).

The Cupping Protocol of the Specialty Coffee Association of America (SCAA) (http://www.scaa.org/PDF/resources/cupping-protocols.pdf) provides an international standard for cup evaluation that, besides aroma and taste, also considers kind of roasting, equipment, and cupping preparation, among other factors. Assessment of sensory attributes consists of scoring the aroma, by smelling the dry milled sample and water infusion (Steps 1 and 2) and the flavor plus other attributes, such as aftertaste, acidity, body, and balance, by tasting the brew (Step 3).

A number of studies, some of them involving molecular sensory science, have been carried out to understand the chemistry behind the overall sensory perception given by a cup of coffee, in order to identify and define key aroma and flavor compounds (Blank, Alina, & Grosch, 1992; Czerny & Grosch, 2000; Flament, 2002; Frank, Zehentbauer, & Hofmann, 2006; Nebesny & Budryn, 2006; Nebesny, Budryn, Kula, & Majda, 2007; Budryn, Nebesny, Kula, Majda, & Krysiak, 2011; Sunarharum et al., 2014). Different analytical platforms have been used to study coffee aroma; gas-chromatography mass spectrometry and/or olfactometry (GC–MS, GC-O) were the analytical techniques of choice. Conversely, several sampling approaches were used to extract and concentrate the flavor components directly from the ground coffee (powder) and/or from the coffee brew, including steam distillation (SD), solvent extraction (SE), fractionation of solvent extracts, simultaneous distillation–extraction (SDE), supercritical fluid extraction (SFE), pressurized-fluid extraction, Soxhlet extraction, solvent-assisted flavor evaporation (SAFE), microwave-assisted hydrodistillation

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http://dx.doi.org/10.1016/j.foodchem.2016.07.088
0308-8146/

(MAHD), headspace (HS) techniques, and solid-phase microextraction (SPME) (Picó, 2012). Whatever the approach, sample preparation is still the bottle-neck of the analytical process, since it must provide a consistent and meaningful picture of the sensory-informative components. An effective sample preparation technique requires some key requisites, including (a) the possibility of tuning extraction selectivity by modifying physico-chemical characteristics of extractants and sampling conditions; (b) use of methods involving mild interactions to limit artifact formations (e.g. partition (sorption) *versus* adsorption as extraction mechanism); (c) the possibility of full automation, and of integrating the extraction step with the analytical system.

However, both compositional data and sensory information alone do not fully explain the importance of key compounds, nor indicate which of them cause distinct sensory attributes. Recently, Dunkel et al. (2014) considered more than 10,000 volatiles detected in food, and determined that the specific odor code of a food is due to between 3 and 40 key odorants. Moreover, flavor implies a multisensory process involving distinct sensory properties (mainly odors and tastes) that are closely integrated and reinforce one another (Chiralertpong, Acree, Barnard, & Siebert, 2008; Köster & Mojet, 2007). These interactions may be due to different compounds that mutually influence the perceived flavor, involving interactions between odorants (odor synesthesia) and/or odorants and tastes (chemesthesis) (Prescott, 2015). An important contribution to clarifying how our sense of olfaction deconvolves a complex food odor at the molecular level has been made by the genetic codification of the olfactory receptors, and the exploration of the chemistry-biology synergism of olfaction (Dunkel et al., 2014; Sunarharum et al., 2014). Very recently, Geithe et al. demonstrated that a recombined butter aroma, resulting from four odor-active compounds, each tested on *in vitro* class-I odor receptors, showed different and concentration-dependent patterns of activation (Geithe, Andersen, Malki, & Krautwurst, 2015).

Although several studies have sought to clarify the link between sensory properties and chemical composition, including through multivariate data analysis (MVA) (Bhumiratana, Adhikari, & Chambers, 2011; Liberto et al., 2013; Michishita et al., 2010; Ribeiro, Augusto, Salva, & Ferreira, 2012; Ribeiro, Augusto, Salva, Thomaziello, & Ferreira, 2009; Ruosi et al., 2012; Science, Pérez-Martínez, Sopelana, de Peña, & Cid, 2008; Sunarharum et al., 2014), the challenge of explaining the pleasure of a coffee-experience at the molecular level still remains, mostly because of the limits of the strategies used to collect information (number and kind of samples, standardization of the samples, precision and accuracy) (Ongo et al., 2012).

This study is part of a wider project exploring the correlation between the chemical composition of coffee volatile fraction and the sensory properties of the beverage; the end-goal is to develop an instrumental analysis approach complementary to human sensory profiling (Bhumiratana et al., 2011; Chiralertpong et al., 2008; Lindinger et al., 2008; Michishita et al., 2010). In particular the study compares chemical information related to coffee aroma and flavor obtained with three different sampling approaches, combined in on-line or in off-line mode with GC–MS, taking the SCAA protocols for cup evaluation as reference. Because of the wide range of volatility, water solubility, and concentration of the most significant components of the coffee matrix, three different sampling approaches were tested for the reliability of characterization of the aroma and flavor profiles, and to evaluate their compatibility with the cupping evaluation in coffee selection for quality control. Aroma evaluation (steps 1 and 2 of the SCAA cupping protocol) was associated to Headspace Solid Phase Microextraction (HS-SPME) of roasted coffee powders and the corresponding brews; aroma and taste evaluation (step 3) was combined with *in*-solution sampling of the brew by SBSE (Stir Bar Sorptive Extraction). The ability of each optimized method to discriminate and describe the investigated samples was compared by multivariate analysis, to determine whether it provided consistent and/or complementary information also in connection to the sample sensory properties defined by a trained panel according to SCAA cupping protocols.

2. Materials and methods

2.1. Reagents and matrices

Coffees samples, consisting of roasted coffee ground to suit a coffee-filter machine, were kindly supplied over a period of 9 months by Lavazza Srl (Turin, Italy).

Eight coffee samples with distinctive sensory notes, originating from different countries (Ethiopia, Papua New Guinea, Colombia, Brazil, India, Indonesia, Java, and Uganda), of the species *Coffea Arabica* L. (Arabica) and *Coffea canephora Pierre* (Robusta), were analyzed (Table 1). Each coffee origin was analyzed in five replicates; each replicate was produced by a fresh cycle of roasting and grinding, starting from the same batch of green coffee beans (n = 40). The roasting degree of each sample was carefully measured by ground bean light reflectance, with a single-beam Neuhaus Neotec Color Test II instrument (Genderkesee, Germany) at a wavelength of 900 nm on 25–30 g of ground coffee. Roasting degree was set at 55°Nh, in order to be close to the international standardization protocol for cupping (SCAA, 2015). Samples were roasted within 24 h prior to cupping, and left for at least 8 h to stabilize. For clarity of exposition, samples in the text are labeled with their origins.

The coffee brew was prepared from 18 g of coffee powder and 300 mL of water, using a Lavazza "Xlong" coffee filter machine. Tridecane (n-C_{13}) in Dibuthylphtalate (DBP), used as internal standard (ISTD), were purchased from Sigma-Aldrich (Milan-Italy).

2.2. Sample preparation techniques

HS-SPME of the coffee powder: 1.500 ± 0.010 g of powder were weighed in a septum-sealed gas vial (20 mL); the resulting headspace was sampled through the PDMS/DVB SPME fiber for 40 min at 50 °C with an agitation speed of 350 rpm. The internal standard was loaded onto the fiber (Wang, O'Reilly, Chen, & Pawliszyn, 2005) in advance by sampling 5 μL of a 1000 mg/L solution of n-C_{13} in DBP into a 20 mL headspace vial for 20 min at 50 °C, agitation speed of 350 rpm.

HS-SPME of the brew: a volume of 4.5 mL of brew in a septum-sealed gas vial (20 mL) were sampled through the SPME fiber for 40 min at 50 °C with an agitation speed of 350 rpm. The internal standard was loaded onto the SPME fiber in advance by sampling 5 μL of a 1000 mg/L n-C_{13} in DBP solution in a 20 mL headspace vial for 20 min at 50 °C, agitation speed of 350 rpm (Wang et al., 2005).

Table 1
List and characteristics of the coffee samples used in this study.

Sample acronym	Sample Name	Species	Treatment	Sensorial Attribute
BRA	BRAZIL LA2	Arabica	Natural	Nutty, quite acid, rich
COL	COLOMBIA CL1	Arabica	Washed	Flowery, Acid
JAV	JAVA WB1 MB	Robusta	Washed	Nutty
UGA	UGANDA STD	Robusta	Natural	Spicy
PNG	PAPUA NG Y	Arabica	Washed	Fruity
INDIA	INDIA ARAB CHERRY	Arabica	Natural	Astringent, quite bitter
INDO	INDONESIA EK1	Robusta	Natural	Woody, Bitter
KAFA	ETIOPIA KAFA GR. 3	Arabica	Natural	Flowery/Fruity, rather Acid