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Prediction of key aroma development in coffees roasted to different degrees by colorimetric sensor array

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ABSTRACT

We developed a colorimetric sensor array (CSA) that is sensitive to highly contributory volatile compounds of coffee aroma for discrimination of coffee samples roasted to different roast degrees. Strecker aldehydes and α-diketones were significantly higher for the medium roast than the other roast degrees. The development of several sulfur compounds was pronounced in the medium-dark and dark roasts, except for dimethyl sulfide, which was only detected in the light roast. The CSA method coupled with principal component analysis or hierarchical cluster analysis successfully distinguished the roasted coffee samples according to roast degree. Partial least squares regression results showed that the CSA responses were well-correlated with the concentrations of volatile compounds in the coefficient of determination (r_p^2) range of 0.686–0.955. These results demonstrate that the CSA rapidly responded to coffee aroma compounds and was capable of predicting coffee aroma development.

1. Introduction

The ultimate purpose of roasting coffee beans is to impart desired flavors for consumers by causing various physical and chemical changes in the coffee beans. The color and characteristic flavor of coffee beans are developed *via* a complex series of reactions involving precursors in green beans, such as the Maillard reaction, Strecker degradation, breakdown of amino acids, and interactions between intermediate decomposition products (Baggenstoss, Poisson, Kaegi, Perren, & Escher, 2008; Buffo & Cardelli-Freire, 2004; Wang & Lim, 2014).

Numerous studies have focused on roasting (e.g., roast degree and roasting time and temperature profiles) because of the significant impact of roasting on the formation of several hundreds of chemical compounds associated with coffee flavor that are directly linked to coffee quality (Baggenstoss et al., 2008; Gloess et al., 2014; Santos et al., 2016; Sunarharum, Williams, & Smyth, 2014). Flavor is a combination of aroma, taste, texture, and mouthfeel and chemesthesis or trigeminal sensations; among these, aroma is the most important component, allowing consumers to recognize coffee flavors (Sunarharum et al., 2014). In this regard, Bhumiratana, Adhikari, and Chambers (2011) found that a light roast gives sweet, cocoa, and nutty aromas, whereas a dark roast produces burnt/acrid, ashy/sooty, sour, pungent, coffee, and roasted aromas. Bhumiratana et al. (2011), Schenker et al. (2002) reported that a more complex aroma profile was exhibited at a medium degree of roast, for which the highest increase in the concentration of aroma compounds was observed. A previous study by Baggenstoss et al. (2008) showed that rapid roasting (high temperature-short time roasting) led to considerable differences in aroma formation compared to slow roasting (low temperature-long time roasting). Thus, it is important to develop an optimal roasting profile to satisfy consumer preferences while maintaining the quality of coffee products. In addition, monitoring the quality of coffee product is required to meet consumer expectations; a rapid analytical tool is needed to detect coffee flavor development during roasting and identify different coffee products with different roasting profiles (Dorfner, Ferge, Yeretzian, Kettrup, & Zimmermann, 2004; Gloess et al., 2014).

More than 800 volatile compounds have been identified in roasted coffees (Buffo & Cardelli-Freire, 2004; Czerny, Mayer, & Grosch, 1999). Despite the complexity of coffee flavor, previous investigations revealed that as few as 20–30 volatile compounds are predominantly responsible for the characteristic coffee aroma (Blank, Sen, & Grosch, 1992; Czerny et al., 1999; Semmelroch, Laskawy, Blank, & Grosch, 1995). Sulfur compounds such as sulfides and thiols, particularly 2-furfurylthiol, are the most important aroma compounds in coffee because of their extremely low odor thresholds and concentrations, resulting in a greater olfactory contribution to coffee flavor (Baggenstoss et al., 2008; Dulsat-

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Serra, Quintanilla-Casas, & Vichi, 2016; Sunarharum et al., 2014). Strecker aldehydes, such as methylpropanal, 2-methylbutanal, and 3-methylbutanal, were found to be potent compounds affecting coffee aroma (Czerny et al., 1999; Holscher & Steinhart, 1992). Czerny et al. (1999) through sensory analyses determined that these Strecker aldehydes are responsible for malty notes. α-Dicarbonyls such as 2,3-butanedione and 2,3-pentanedione have been proposed as indices for aroma freshness of coffee brews by Pérez-Martínez, Sopelana, De Pena, and Cid (2008), who reported that decreases in these compounds in coffee brews was dependent on storage period, which significantly affected several sensory notes.

The volatile compounds responsible for coffee aroma are typically investigated using various forms of headspace sampling methods, mainly solid-phase microextraction (SPME) and gas chromatography (GC) coupled to either mass spectrometry (MS) or flame ionization detector (FID) (Cheong et al., 2013; Lee, Cheong, Curran, Yu, & Liu, 2015; Yang et al., 2016). GC-based methods are the commonly used techniques, but component-by-component analysis has important limitations and must be conducted by a skilled operator; the operations are also cumbersome and time-consuming. A sensor-based method may overcome these limitations. In several studies, an electronic nose (E-nose) system was used either to monitor and predict coffee roasting or to differentiate different coffee samples (Gardner, Shurmer, & Tan, 1992; Romani, Cevoli, Fabbri, Alessandrini, & Dalla Rosa, 2012). Suslick, Feng, and Suslick (2010) successfully applied a colorimetric sensor array (CSA) technique to differentiate between coffee samples. These sensor-based methods are advantageous for discrimination of similar complex mixtures such as coffee because they are faster, easier to use, and less costly compared to conventional analytical methods. Moreover, the CSA technique is a promising analytical tool based on strong chemical interactions between a sensor and analytes, including Brønsted and Lewis acid-base, hydrogen bonding, dipolar, and π–π interactions, rather than weak interactions, including van der Waals and physical adsorption, on which E-nose is exclusively based (Askim, Mahmoudi, & Suslick, 2013). In addition, the CSA technique successfully discriminated complex food matrices in beverages such as beers (Zhang, Bailey, & Suslick, 2006), soft drinks (Zhang & Suslick, 2007), and green teas (Huo et al., 2014). CSA-based methods have also shown potential for recognizing changes in the volatile compositions of foodstuffs, such as those in vinegar during fermentation (Guan et al., 2014), and in fish (Zaragozá et al., 2013), pork (Huang et al., 2014), and cooked chicken during storage (Kim, Li, Lim, Kang, & Park, 2016).

The aim of this study was to develop a simple and rapid CSA-based method to differentiate between coffee samples roasted to different roast degrees. The array was fabricated using 2,4-dinitrophenylydrazine (DNPH) as an aldehyde- and ketone-specific sensing material and 5,5′-dithiobis(2-nitrobenzoic acid) (DTNB) as a thiol- and sulfide-specific sensing material so that the sensor array would be more sensitive to important coffee aroma compounds, such as Strecker aldehydes, α-diketones, thiols, and sulfides, than to other chemical species in roasted coffee. We demonstrated the potential of the CSA method to detect important volatile compounds known as 'key odorants' by determining the good relationships between GC and CSA methods using partial least square regression (PLSR).

2. Materials and methods

2.1. Sample preparation

Arabica green coffee beans, which were harvested in the Chiapas of Mexico at an altitude of 1300–1600 m and processed by the washed method, were purchased from an importer. Coffee roasting was conducted using a Hottop roaster (Model KN-8828P; Chang Yue Industrial Co., Tainan, Taiwan). Approximately 250 g green beans were poured into the roasting chamber at 75 °C, as recommended by the manufacturer, and roasted using the automatic roasting program. Once the temperature of the roasting chamber on the display reached 187 °C (light roast), 202 °C (medium roast), 217 °C (medium-dark roast), or 225 °C (dark roast), the roasted coffee beans were ejected from the roasting chamber into the cooling tray for automatic cooling for 5 min. The roasted beans were cooled for an additional 30 min at room temperature (approximately 25 °C) and finely ground using a coffee grinder (Model Super Jolly Electronic; Mazzer Luigi S.R.L., Venice, Italy) immediately before each usage. Roasting degrees were established based on roasting progress: light roast, the point at the beginning of the first crack; medium roast, the point at the peak of the first crack; medium-dark roast, the point at the beginning of the second crack; dark roast, the point at the end of the second crack.

2.2. Color values, weight loss, and moisture content of the samples

The L^*, a^*, and b^* values of the samples were analyzed using a chromameter (Model CR-400; Konica Minolta Sensing, Inc., Tokyo, Japan) (Wang & Lim, 2014). L^* indicates the lightness (0, black and 100, white). a^* is red/green coordinate (+, red and −, green) and b^* is yellow/blue coordinate (+, yellow and −, blue). Approximately 12 g of each ground roasted coffee sample were placed in a Petri dish (ø = 60 mm) and covered with the lid of a Petri dish to level the surface. After removing each lid, the L^*, a^*, and b^* values of different three areas on the surface in the Petri dish were measured and averaged. The mean for each sample was obtained from triplicate measurements. The weight loss of each sample was measured immediately after cooling and was expressed as the mean obtained from triplicate measurements. The moisture content of the samples was determined using a moisture analyzer (Model MX-50; A & D Co., Ltd., Seoul, Korea). The values were measured seven times for each sample and averaged.

2.3. Determination of volatile compounds

2.3.1. Extraction of volatile compounds by headspace solid-phase microextraction (HS-SPME)

Approximately 2.0 g of ground roasted coffee sample were transferred into a 20-mL headspace-vial containing a magnetic stir bar and then 6 mL of saturated sodium chloride solution and 10 μL of fluorobenzene solution (50 mg/L in methanol) as an internal standard were added. The vial was tightly capped with a silicon septum and allowed to equilibrate for 90 min at room temperature under constant agitation on a magnetic stirrer (Model MS-300HS; Misung Scientific Co., Ltd., Seoul, Korea). Next, an 85-μm Carboxen/polydimethylsiloxane (CAR/PDMS) SPME fiber (Supelco, Bellefonte, PA) was exposed to the headspace of the vial for 20 min at room temperature under stirring. After extraction, the fiber was inserted into the injection port of the GC for 10 min at 230 °C (Akiyama et al., 2003; Petisca, Pérez-Palacios, Pinho, & Ferreira, 2014).

2.3.2. Gas chromatography-flame ionization detection (GC-FID)

Analyses were performed on a model 7890 GC (Agilent Technologies, Santa Clara, CA) with a DB-WAX column (60 m × 0.25 mm × 0.25 μm, Agilent Technologies). The flow of helium carrier gas was 1.0 mL/min and split mode (10:1) was used. The oven temperature was maintained at 50 °C for 2 min and then increased at 5 °C/min until 230 °C. The detector was maintained at 250 °C.

2.3.3. Quantification of volatile compounds

To calculate the concentrations of the ten targeted volatile compounds, calibration curves were determined by adding each mixed-solution of authentic volatile compounds of known concentration with the internal standard to a deodorized coffee sample as a blank matrix (Du, Song, Baldwin, & Rouseff, 2015). The blank matrix was obtained by pumping the volatile compounds in ground light-roasted coffee in a vacuum oven at room temperature for 12 h. The mixed-authentic standard solutions, containing ranges of 233.5–7472.5 mg/L for 2-