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Covering the different steps of the coffee processing: Can headspace VOC emissions be exploited to successfully distinguish between Arabica and Robusta?

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ABSTRACT

This work was performed to evaluate the possible application of PTR-ToF-MS technique in distinguishing between *Coffea arabica* (Arabica) and *Coffea canephora* var. robusta (Robusta) commercial stocks in each step of the processing chain (green beans, roasted beans, ground coffee, brews). volatile organic compounds (VOC) spectra from coffee samples of 7 Arabica and 6 Robusta commercial stocks were recorded and submitted to multivariate statistical analysis. Results clearly showed that, in each stage of the coffee processing, the volatile composition of coffee is highly influenced by the species. Actually, with the exception of green beans, PTR-ToF-MS technique was able to correctly recognize Arabica and Robusta samples. Particularly, among 134 tentatively identified VOCs, some masses (16 for roasted coffee, 12 for ground coffee and 12 for brewed coffee) were found to significantly discriminate the two species. Therefore, headspace VOC analyses was showed to represent a valuable tool to distinguish between Arabica and Robusta.

1. Introduction

Coffee is one of the most widely consumed beverage in the world. Coffee plants grow in the tropical areas of all continents and the total world coffee bean production in 2015 was around 8.7 million tons (ICO., 2016). Although >100 different species have been described so far (Cagliani, Pellegrino, Giugno, & Consonni, 2013), from the commercial point of view two *Coffea* species comprise almost all of the total world production: *Coffea arabica* L. var. arabica (commercially called Arabica) with 5.1 million tons (ICO, 2016), and *Coffea canephora* Pierre *ex* Froehner var. robusta (commercially called Robusta), with a production of 3.6 million tons (ICO, 2016).

Coffea arabica originated in the highlands of NW of Abissinia and SE of Sudan and was first utilized by the Arab peoples around the Red Sea (Yemen) (Smith, 1985). It is the most appreciated species worldwide. Its cultivation is suited to slopes and in altitude (>600–800 m a.s.l.), with a relatively mild climatic conditions and a well-defined dry season.

Coffea canephora var robusta is still present in wild form in the undergrowth of the tropical forests of central Africa. It is used as a substitute of Arabica for its leaf rust disease (CLR, Coffee Leaf Rust, *Hemileia vastatrix* Berk. and Br.) resistance and its good adaptability for orchards in the humid lowlands, allowing an easy mechanization of the cultivation techniques (Charrier, Lashermes, & Eskes, 2012). For these reasons, *C. canephora* is more productive and the production of Robusta coffee is more economical.

Brews from the two species differ in terms of taste and aroma. Arabica has a lower caffeine concentration, is sweeter and more fruity, while Robusta is stronger (Cagliani et al., 2013). Coffee is commonly marketed as a mixture of the two species blended in different amounts to manipulate the flavor: while Arabica is used to enhance aroma, Robusta is usually added to increase the body and foam of some coffee beverages (e.g. espresso coffee) and in instant coffee production (Smith, 1985).

In general, consumers seem to have a substantial interest in 'pure' coffee and tend to prefer coffee brewed from Arabica beans (Odello & Lavaroni, 2009). On the other hand, higher quality Arabica coffees have a premium price on the wholesale market (2–

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10 times the price of Robusta) and, consequently, there is a growing financial motivation to unlawfully replace Arabica with Robusta or to add the lower value Robusta coffee to 100% Arabica pure coffee. It is therefore evident that the assessment of coffee authenticity is of great importance for quality, economical and legal reasons. Therefore, the market demands a fast, time-effective and easy to use tool for the authentication of the original matrix of commercial beans throughout the multiple processing steps, from green coffee beans to brewed coffee.

Green coffee beans cannot be consumed as such, but need to undergo different processes necessary for the formation of the typical coffee aroma. One of the crucial steps is represented by the roasting process, which transforms the green coffee seed, characterized by almost no flavor beyond a quite unpleasant taste, into an aromatic, complex coffee bean. During the roasting procedure, a wide range of reactions lead to a drastic generation of numerous chemical compounds, both volatile and non-volatile: the former are responsible for the aroma and the latter for the basic taste sensations of sourness, bitterness and astringency (Buffo & Cardelli-Freire, 2004). Moreover, grinding of roasted coffee is strictly necessary for the preparation of the final beverage for consumption, as well as for releasing the developed aromatic compounds and for perceiving higher intensities of aroma in the final drink. Brewing is another crucial step in extracting the aromatic compounds from ground coffee into the water matrix of the beverage (Bhumiratana, Adhikari, & Chambers, 2011).

At the stage of unroasted seeds, Arabica can be distinguished from Robusta by examining the morphological characteristics (e.g. size and shape of the cotyledons). However, in the case of roasted, ground and brewed coffee, the two species can be discriminated only by means of sensory evaluation or chemical analyses. In sensory assessments, the procedure is difficult and not completely reliable; professional tasters are able to guess Arabica/Robusta coffee blend composition with an error of about 20% (Wermelinger, D'Ambrosio, Klopprogge, & Yeretzian, 2011). Alternatively, several literature studies report chemical approaches to identify specific indicators to distinguish between Arabica and Robusta (Cagliani et al., 2013; Romano et al., 2014), such as certain concentrations of caffeine (Ky et al., 2001), amino acids (Casal, Alves, Mendes, Oliveira, & Ferreira, 2003), fatty acids (Alves, Casal, Oliveira, & Ferreira, 2003) and tocopherol (Alves, Casal, Alves, & Oliveira, 2009). Although chemical analyses could be more reliable than sensory evaluation, they have the disadvantage to be elaborated and time-consuming methodologies requiring an adequate sample preparation. The availability of a fast analytical method to be used in common screening for coffee quality control and to prevent possible frauds would be desirable and economically important.

Proton Transfer Reaction – Time of Flight – Mass Spectrometry (PTR-ToF-MS) has the advantage to enable real-time analysis of volatile organic compounds (VOCs) without the need of sample pretreatment. It is a promising approach widely used, in recent years, in food science to discriminate among plant materials as different as cultivars of pepper, wood cores, saffron, etc. (Infantino et al., 2015; Masi et al., 2016; Taiti et al., 2015). In the complex universe of aroma coffee research, PTR-ToF-MS allowed to differentiate specialty (organic and conventional) coffees (Özdestan et al., 2013), to discriminate coffee brews by means of nose-space analysis (Romano et al., 2014), to characterize different commercial stocks of Arabica (Yener et al., 2014) and to distinguish the kinetics of aroma (López, Wellinger, Gloess, Zimmermann, & Yeretzian, 2016). To the best of our knowledge, until now PTR-ToF-MS has never been applied to coffee species discrimination. Actually, some authors employed gas chromatography-mass spectrometry (GC–MS) to compare the volatile fractions of Arabica and Robusta beans, showing the predominance of some different odorants in coffee samples of the two coffee species (Blank, Sen, & Grosch, 1991; Mondello et al., 2005). However, these investigations were restricted to a reduced number of samples and the authors did not take into account each step of the coffee processing. Moreover, although reliable and, in many cases, indispensable, GC–MS technique has the limitation of the long time needed for sample preparation and analyses.

In the present work, PTR-ToF-MS was used for the aroma characterization of coffee samples of *C. arabica* and *C. canephora* var. robusta, from the green beans to the brewed coffee. The aim of this investigation was to evaluate the possibility to employ PTR-ToF-MS as a rapid and simple technique for the discrimination of coffee samples from the two species in each step of the coffee chain, based on their VOC fingerprinting. In addition, the major compounds that contribute to the determination of differences were tentatively identified and evaluated.

2. Materials and methods

2.1. Coffee samples

Commercial certified stocks of *C. arabica* (7 stocks) and *C. canephora* var. robusta (6 stocks) were used for VOCs analysis. Each coffee stock belonged to different commercial products. Green and medium-dark roasted bean samples of each stock were supplied by Caffè Magnelli S.r.l. (Florence, Italy) and stored in vacuum-sealed bags in the dark at room temperature (21 °C) before the relative analysis. An aliquot of roasted beans of each stock were ground using an electric coffee grinder (Moulinex AR 11, Groupe SEB, France).

From each coffee stock, 7 different samples were prepared and used for VOCs analysis, taking aliquots of 20 g for green or roasted beans and 5 g for roasted ground coffee.

2.2. Coffee brew

The most common way to make coffee at home in Italy is with the Moka stove-top coffee maker (Caporaso, Genovese, Canela, Civitella, & Sacchi, 2014). For the analyses, coffee was brewed using an Italian 2-serving Moka (Bialetti, Brescia, Italy). The coffee was prepared in accordance with the indications reported by Navarini, Nobile, Pinto, Scheri, and Suggi-Liverani (2009). For each coffee batch, brew samples were prepared using 10 g of roasted ground coffee and 100 ml of bottled water (Ca^{2+} 13 mg/L, Na^{2+} 2.3 mg/L, Mg^{2+} 1.4 mg/L, K^{+} 0.5 mg/L, HCO_3^- 38 mg/L, SO_4^{2-} 6.3 mg/L and NO_3^- 1 mg/L, as reported on the bottle label). The Moka was placed on an electric hot plate at a temperature of 150 °C for about 10 min, until the coffee reached the "Strombolian" phase (so-called because the hot air and steam start to spurt from the nozzle). This phase indicates that all of the water has finished rising from the bottom chamber, through the coffee grounds and into the top chamber. At this point, the coffee maker was removed from heat to prevent burning the coffee. After having gently stirring the brew with a spoon, 50 ml were transferred in a glass cup for headspace analysis as soon as the temperature dropped to around 40 °C. For each coffee stocks, 7 samples of brew were prepared and analyzed.

2.3. VOC analysis

VOC measurements were performed using a commercial PTR-ToF 8000 model, from Ionicon Analytik GmbH (Innsbruck, Austria) in its standard configuration and using H_3O^+ as reagent ion for the proton-transfer reaction. The ionization conditions for all measurements in the drift tube were the following: 110 °C drift tube temperature, 2.30 mbar drift pressure and 550 V drift voltage and E/N