Espresso Machine and Coffee Composition

Chapter · December 2015

DOI: 10.1016/B978-0-12-409517-5.00028-0

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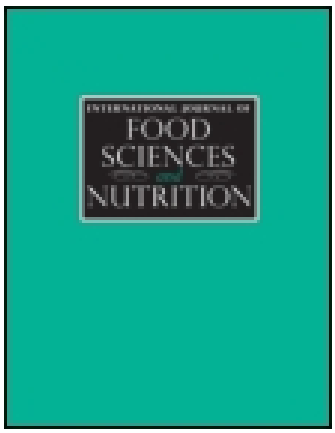

International Journal of Food Sciences and Nutrition
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/iijf20

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Published online: 15 Jul 2015.

INTERNATIONAL JOURNAL OF FOOD SCIENCES and NUTRITION

http://informahealthcare.com/ijf
ISSN: 0963-7486 (print), 1465-3478 (electronic)

Int J Food Sci Nutr, 2015; 66(5): 505–513
 DOI: 10.3109/09637486.2015.1064871

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FOOD COMPOSITION AND ANALYSIS

The influence of different types of preparation (espresso and brew) on coffee aroma and main bioactive constituents

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Abstract

Coffee is one of the most popular hot drinks in the world; it may be prepared by several methods, but the most common forms are boiled (brew) and pressurized (espresso). Analytical studies on the substances responsible for the pleasant aroma of roasted coffee have been carried out for more than 100 years. Brew coffee and espresso coffee (EC) have a different and peculiar aroma profile, demonstrating the importance of the brewing process on the final product sensorial quality. Concerning bioactive compounds, the extraction mechanism plays a crucial role. The differences in the composition of coffee brew in chlorogenic acids and caffeine content is the result of the different procedures of coffee preparation. The aim of the present review is to detail how the brewing process affects coffee aroma and composition.

Keywords

Caffeine, chlorogenic acids, *Coffee arabica* and *Coffee canephora*, coffee aroma, espresso coffee machine, espresso coffee

History

Received 6 February 2015
Revised 24 April 2015
Accepted 18 June 2015
Published online 14 July 2015

Introduction

The consumption of coffee, one of the most popular hot drinks in the world, is continually increasing (Butler, 1999; Illy & Viani, 1995a; Maeztu et al., 2001a). According to the latest statistics from the International Coffee Organization (ICO), ~1.4 billion cups of coffee a day are consumed worldwide; prepared in a number of procedures, it is the second-most popular beverage in the world, after tea. It is consumed for its pleasant aroma directly estimated through the nostrils. Moreover, coffee brew has been proposed as an important source of antioxidants (Pulido et al., 2003; Svilaas et al., 2004), which are very important chemicals for the prevention of several chronic diseases, associated with oxidative stress, such as cancer, cardiovascular, inflammatory, and neurogenerative pathologies (Aruoma, 1999; Beal, 1995; Dorea & da Costa, 2005). The antioxidant capacity of coffee brew is attributed to antioxidants originally present in coffee beans, such as phenolic compounds, as well as to roasting-induced antioxidants, like melanoidins and other Maillard Reaction Products (MRP) (Borrelli et al., 2002; Crozier et al., 2009; Del Castillo et al., 2002). The caffeine content in coffee has been studied extensively from the pharmacological point of view, but less attention has been paid to its potential antioxidant activity that may be overshadowed by phenolic compounds and MRP. Additionally, coffee contains a wide number of very important bioactive compounds, such as tocopherols, diterpenes like cafestol and kahweol, and many others that cannot be detailed in this work.

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In fact, the aim of this review is to report the differences in aroma composition and bioactive compounds, such as chlorogenic acids and caffeine, in brew coffee and espresso coffee (EC).

Overview on coffee preparation

Coffee may be brewed in several methods, with the most common being boiled brew and pressurized EC.

Preparation of boiled coffee brew

The earliest method for brewing coffee was by boiling, the most commonly known example being Turkish coffee, prepared by grinding or pounding the beans to a fine powder, then adding it to water in a pot and bringing it to a boil for no more than an instant. This produces a strong coffee with a layer of foam on the surface and sediment (not meant for drinking) that settles on the bottom of the cup.

A popular method for brewing coffee is by steeping it in a device such as a French press (also known as a *cafetière*, coffee press or coffee plunger). Ground coffee and boiling water are combined in a cylindrical vessel and left to brew for a few minutes. A circular filter, that fits tightly in the cylinder and is fixed to a plunger, is pushed down from the top through the liquid to force the grounds to the bottom. As the coffee grounds are in direct contact with the water, most of the active substances pass in the beverage, making it stronger and leaving more sediment than in coffee made by any kind of automatic coffee machine. The coffee is poured from the container, with the filter retaining the grounds at the bottom.

Another common brewing technique is the drip method, in which boiling water is poured into a container with a perforated base, above a filter containing coffee, and is given ~5 min to seep through the filter and drip into a container below. Similar to the

drip method is the filter method, often used in automatic coffee machines, in which heated water flows down over the filter containing the coffee, and the brewed coffee streams into a container below.

Preparation of pressurized coffee brew (EC)

Another method uses high pressure to produce EC, widespread in southern Europe, Central America and other areas. It is prepared from roasted and ground coffee beans and the pressure of the EC machine induces percolation of a limited amount of hot water through a ground coffee cake in a short time to yield a small cup of a concentrated foamy drink (Illy & Viani, 1995a). The preparation of EC is influenced by factors related to coffee, water composition, and other technical conditions related to the machine (Andueza et al., 2003; Navarini et al., 2001; Petracco, 2001).

The most common espresso machine is made with a pump, which provides continuous flow of water (Odello & Odello, 2006). With this volumetric pump, water is brought to the desired pressure (usually ~9 bar) and then forced through a heat exchanger, which brings water to the chosen temperature (usually between 91 and 96 °C) (Caprioli et al., 2012). Then, the water proceeds towards the filter-unit, which is composed of a fixed part into which the filter-holder is fitted snugly. This, which in turn contains the filter with the cake of coffee, must be between 76 and 80 °C. Water is sprayed evenly over the coffee surface inside the filter, and then a pre-infusion of a few seconds takes place, when the coffee absorbs some milliliters of water and swells. This allows the coffee surface to reach the required permeability, and the extraction of the most prized espresso components begins. It is one of the strongest tasting forms of coffee, with a distinctive flavor and cream, a layer of emulsified oils in the form of colloidal foam floating over the liquid. Certified Italian EC has to conform to the strict production specifications issued by the Italian Espresso National Institute and approved by a Third-Party Body, and it is safeguarded and promoted through a product certification (certificate of product conformity Csqa n. 214: 24 September 1999, DTP 008 Ed.1). The following are some important conditions to be applied to obtain a Certified Italian Espresso, though these alone would not be adequate to fulfill the quality requirements: ground coffee: 7 ± 0.5 g, exit temperature of water from the unit 90 ± 2 °C, temperature of the drink in the cup 67 ± 3 °C, entry water pressure 9 ± 1 bar, percolation time 25 ± 2.5 s, viscosity at 45 °C > 1.5 mPa, total fat >2 mg/ml, caffeine <100 mg/cup, milliliters in the cup (including foam) 25 ± 2.5 ml (Odello & Odello, 2006).

Influence of different type of preparation on aroma profiles

Main components of coffee aroma

For over 100 years, various analytical studies have been carried out on the substances responsible for the pleasant aroma of roasted coffee. The flavor of coffee brew depends mainly on the type of coffee used to prepare it. From *Coffee arabica* and *Coffee canephora* var. robusta ground roasted coffee, different aromatic profiles in coffee brew were obtained.

Bernheimer (1880) was the first to report the identification of some coffee volatiles, e.g. methylamine and pyrrole. Afterward, the composition of the volatile fraction of coffee has been studied for years, and several hundreds of compounds have been identified as constituents of coffee aroma (Holscher & Steinhart, 1992; Sanz et al., 2001, 2002a). The main constituents are aldehydes, ketones, furans, pyrazines, pyridines, phenolic compounds, indoles, lactones, esters and benzothiazines. Most of these compounds, which are produced during the roasting process, have been known as products from Maillard reaction between amino acids and sugars, Strecker degradation, degradation of sugars, minor lipid degradation and interaction between intermediate decomposition products. Some volatile compounds, such as caffeic acid, quinic acid and chlorogenic acids, do not arise from the Maillard reaction, but are natural constituents of coffee beans, produce a significant amount of total volatiles (Illy & Viani, 1995a; Moon & Shibamoto, 2010).

Although the volatile fraction in coffee is very complex, some researchers proposed that only some compounds (called key odorants) are responsible for the coffee flavor (Grosch, 1998; Maeztu et al., 2001a; Rocha et al., 2003; Semmelroch & Grosch, 1995).

Methods for the characterization of coffee aroma: chemical and sensorial profile

One of the first studies to characterize coffee aroma was conducted by Holscher et al. (1990), who performed the first aroma extract dilution analysis (AEDA) of roasted coffee (Table 1) and identified the odor potency for each compound, termed the FD-factor (flavor dilution), using the gas chromatography-olfactometry (GCO) technique, in which trained testers provide a sensory evaluation of the eluate from the chromatographic column. They assign relative importance to the odor activity of an original sample and then a series of the same sample diluted with predetermined injection volumes; the final FD-factor is the ratio of concentrations between the largest and the smallest injection volumes still detectable by the tester. The AEDA technique is limited to odorants boiling higher than the solvent used. To overcome this problem, the change of sampling occurred and gas chromatography and olfactometric of headspace (GCO-H) technique was used. With this technique the same sample is injected using different headspace injection volumes; the FD-factor is calculated as previous reported (Holscher & Steinhart, 1992). In addition, the GCO-H apparatus was modified and the gas chromatographic column was connected to a mass spectrometer (GC-MS) to correctly identify each volatile compound (Semmelroch & Grosch, 1995). Comparing the results obtained on similar samples analyzed by Holscher & Steinhart (1992) and Blank et al. (1992), the value of FD-factors calculated by AEDA were different for the same compound. This could be due to the differences of sensitivity of the testers, but also to the differences in concentration in terms of yield of extraction.

These limitations revealed the need for a more accurate quantification of odorants in the sample. For this reason Semmelroch et al. (1995) introduced a new procedure, stable isotope dilution assay (SIDA), that provides high accuracy and sensitivity using the corresponding labeled internal standard. In this work, they also introduced odor activity value (OAV), the ratio between the concentration of the compound obtained by SIDA and its odor threshold in water. Unfortunately, this technique is very laborious for analyzing the over eight hundred volatile substances identified in ground coffee by GC-MS (Flament, 1991; Nijssen et al., 1996), and thus it was preferable to calculate OAV values for a selected number of compounds.

A complementary approach involves sensorial evaluation by trained assessors (panel test) to characterize a specific odorant and define its contribution to the overall coffee aroma. Starting from the results obtained by IDA, a model mixture smelling clearly coffee-like was prepared (Mayer et al., 2000). An omission test was performed to evaluate the contribution of each single component or class; assessors analyzed the complete model except for one or more constituents and stored the sensorial

Table 1. Potent odorants of roasted Arabica coffee from Colombia revealed by AEDA[a].

Odorant	Odor quality
3-Methyl-2-buten-1-thiol	Amine-like
2-Methyl-3-furanthiol	Meaty, boiled
2-Furfurylthiol	Roasty (coffee-like)
2-/3-Methylbutanoic acid	Sweaty
Methional	Boiled potato-like
Unknown	Fruity
Trimethylthiazole	Roasty, earthy
Trimethylpyrazine	Roasty, earthy
Unknown	Roasty, sulphury
3-Mercapto-3-methyl-1-butanol	Meaty (broth)
3-Mercapto-3-methylbutylformate	Catty, roasty
3-Isopropyl-2-methoxypyrazine	Earthy
5-Ethyl-2,4-dimethylthiazole	Earthy, roasty
2-Ethyl-3,5-dimethylpyrazine	Earthy, roasty
Phenylacetaldehyde	Honey-like
Unknown	Roasty, earthy
Linalool	Flowery
2,3-Diethyl-5-methylpyrazine	Earthy, roasty
2-Hydroxy-3,4-dimethyl-2-cyclopenten-1-one	Caramel-like
Guaiacol	Phenolic, burnt
4-Hydroxy-2,5-dimethyl-3(2H)-furanone (HDF)	Caramel-like
3-Isobutyl-2-methoxypyrazine	Earthy
Unknown	Roasty, earthy
5-Methyl-5(H)-cyclopenta[b]pyrazine	Roasty, sweet
(E)-2-Nonenal	Fatty
2(5)-Ethyl-4-hydroxy-5(2)-methyl-3(2H)-furanone	Caramel-like
3-Hydroxy-4,5-dimethyl-2(5H)-furanone (Sotolon)	Seasoning-like
4-Ethylguaiacol	Spicy
p-Anisaldehyde	Sweet, minty
5-Ethyl-3-hydroxy-4-methyl-2(5H)-furanone	Seasoning-like
4-Vinylguaiacol	Spicy
(E)-b-Damascenone	Honey-like, fruity
Unknown	Amine-like
Bis(2-methyl-3-furyl)disulphide	Meaty, sweet
Vanillin	Vanilla-like
Acetaldehyde	Fruity, pungent
Methanethiol	Cabbage-like
Propanal	Fruity
Methylpropanal	Malty
2-Methylbutanal	Malty
3-Methylbutanal	Malty
2,3-Butanedione	Buttery
2,3-Pentanedione	Buttery
Dimethyl trisulphide	Cabbage-like

[a]Holscher et al. (1990).

response to this action. When this sample was presented together with two complete models to testers, it was called triangle test.

Boiled coffee brew aroma profile

The AEDA technique introduced by Holscher et al. (1990) (Table 1) leading to the identification of 21 potent odorants in *C. arabica* roasted coffee and their corresponding FD-factors was next applied to brewed coffee. Moving from ground coffee to brew coffee, the caramel-like, buttery and phenolic notes became more intense. AEDA showed that this change in the flavor profile is not caused by the formation of new odorants, but by a shift in the concentrations (Blank et al., 1992; Grosch, 1998). This aspect was further investigated by Semmelroch & Grosch (1996) who used stable isotope dilution assays on *C. arabica* brewed coffee to quantify the extraction yields of seventeen potent odorants that had been identified in previous articles (Table 2) (Blank et al., 1992; Semmelroch & Grosch, 1995). As expected, the polar odorants are preferentially extracted by hot water, leading to yields higher than 70% for thiol **3**, pyrazine **4**, furanones (**9**–**12**),

Table 2. Extraction yield[a] of odorants in the preparation of a filtered coffee beverage[b] from ground Arabica coffee by SIDA.

Odorant	Yield[c] (%)	Yield[d] (%)
2-Furfurylthiol (**1**)	33	19
Methional (**2**)	45	74
3-Mercapto-3-methylbutylformate (**3**)	78	81
2-Ethyl-3,5-dimethylpyrazine (**4**)	74	79
2-Ethenyl-3,5-dimethylpyrazine (**5**)	n.d.	35
2,3-Diethyl-5-methylpyrazine (**6**)	62	67
2-Ethenyl-3-ethyl-5-methylpyrazine (**7**)	n.d.	25
3-Isobutyl-2-methoxypyrazine (**8**)	22	23
4-Hydroxy-2,5-dimethyl-3(2H)-furanone (**9**)	77	95
2(5)-Ethyl-4-hydroxy-5(2)-methyl-3(2H)-furanone (**10**)	90	93
3-Hydroxy-4,5-dimethyl-2(5H)-furanone (**11**)	97	78
5-Ethyl-3-hydroxy-4-methyl-2(5H)-furanone (**12**)	100	n.d.
Guaiacol (**13**)	75	65
4-Ethylguaiacol (**14**)	58	49
4-Vinylguaiacol (**15**)	47	30
Vanillin (**16**)	85	95
(E)-β-Damascenone (**17**)	12	11
Acetaldehyde (**18**)	n.d.	73
2,3-Butanedione (**19**)	100	79
2,3-Pentanedione (**20**)	73	85
Methylpropanal (**21**)	n.d.	59
2-Methylbutanal (**22**)	n.d.	62
3-Methylbutanal (**23**)	n.d.	62
2-Methyl-3-furanthiol (**24**)	n.d.	34
3-Methyl-2-buten-1-thiol (**25**)	n.d.	85
Methanethiol (**26**)	n.d.	72

[a]The yields were calculated by comparison of the concentration values in the brewed coffee with those of the powdered coffee.
[b]The coffee beverage was prepared by pouring hot water (1.1 l, ca. 95 °C) on the medium roasted, ground Arabica coffee from Colombia (54 g) in a filter, yielding 1 l of brewed coffee.
[c]Semmelroch & Grosch (1996).
[d]Mayer et al. (2000).

guaiacol (**13**), vanillin (**16**) and the diones **19** and **20**. On the other hand, yields <25% were obtained for pyrazine **8** and for β-damascenone (**17**). The extraction yield of the other odorants, e.g. 2-furfurylthiol (**1**), methional (**2**), 4-ethyl- (**14**) and 4-vinylguaiacol (**15**) and pyrazine **6** lay between 30 and 70%. The results for brewed Robusta coffee were similar.

On the basis of the quantitative data obtained for the odorants in the brewed coffees, models were formulated for both blends. The flavor models were clearly coffee-like and reproduced the differences in the odor profiles of the two original brews, but were not completely similar to the real samples. In particular, in both models, the intensity of the earthy/musty odor notes was particularly low.

Another series of similar experiments was carried out by Mayer et al. (2000) in order to identify odorants that contribute to the aroma of brewed coffee. In this case, they achieved this aim by increasing the number of odorants quantified by SIDA (25 compounds, Table 2); specifically, they added, among others, two pyrazines (**5** and **7**) associated with earthy-musty flavor. In addition, a triangle test was assessed, consisting of a model containing the complete set of 24 odorants (pyrazine **7** was compensated with a corresponding increasing in the concentration of pyrazine **5**) was compared with models missing one or more odorants. These experiments indicated that the brew aroma was mainly caused by some group of molecules such as alkylpyrazines, furanones and phenols, and by single substances such as 2-furfurylthiol, methional and 3-mercapto-3-methylbutyl formate. The overall aroma was successfully mimicked using 24 odorants in the same concentrations as in the brew, thus achieving a

similarity index of 2.0 on a scale ranging from 0 (not detectable) to 3 (strong).

Later, Sanz et al. (2002b) used parallel AEDA analysis and sensorial evaluation to investigate the correspondence between the concentration of thiols and roasty-sulfury note in brewed coffee, comparing the aroma profile of freshly prepared filtered coffee brew (FC) to that of an instant coffee beverage (IC) supplied by the same manufacturer. The panel test discovered a clear difference in the aromas of the two beverages at 60 °C. In particular, the sweetish-caramel odor was higher in IC, while the roasty-sulfury note was more intense in FC. AEDA revealed that IC had a lower concentration in thiols than FC and this observation was used to explain the predominant caramel-like note in IC. It is probably due to the irreversible binding of thiols to the coffee melanoidins (Hofmann et al., 2001) during the IC manufacturing process.

Aroma of EC

A number of articles have been written about the aroma of ground roasted coffee and coffee brews. However, only a few works about EC aroma have been produced.

The particular aroma of EC can be attributed to the presence of surface foam, which traps the volatilized aromas and doses their emission into the atmosphere (Illy & Viani, 1995a, b). Since the foam plays an important role in sensory flavor perception of EC, sensory descriptive analysis conducted with a panel of judges, might prove the most suitable method to describe the real aroma profile of EC.

In addition, recent developments in multivariate statistical methods offer promising tool for relating instrumental and sensory flavor results. For examples, Maeztu et al. (2001a) used multivariate statistical methods to correlate key odorants and flavors in different ECs. From these studies, it is confirmed that, among the sulfur compounds identified, methanethiol is responsible for the freshness aroma of EC, as previously reported (Holscher & Steinhart, 1992). Among the aldehydes, acetaldehyde and propanal showed a very low correlation with fruity flavor but, as reported by Mayer et al. (2000), this contribution can be increased when methanethiol is present, playing a synergistic effect. 2-Methylpropanal, 2-methylbutanal and 3-methylbutanal, which are the Strecker degradation products of valine, isoleucine, and leucine, were proposed as responsible for malty flavor in brewed coffee (Semmelroch & Grosch, 1995, 1996). In the work of Maeztu et al. (2001b), no correlation between malty flavor and Strecker aldehydes was found, possibly because of masking by other more potent odorants in the EC samples. On the other hand, a highly significant correlation between fermented flavor and 2-methylbutanal was found, as confirmed by Holscher & Steinhart (1992).

Among ketones, Blank et al. (1991) and Maeztu et al. (2001b) associated diones **19** and **20** (Table 2) with buttery flavor. From a quantitative point of view, during EC percolation, the Strecker aldehydes were more efficiently extracted than diones, in contrast to the findings of Semmelroch & Grosch (1996) in coffee brew, causing the EC to have a stronger aroma than the latter. Instead, the pyrazines have been associated with roasty and earthy/musty flavors in ground roast coffee and coffee brew (Blank et al., 1991; Holscher et al., 1990). Also in EC samples, 2-ethyl-3,5-dimethylpyrazine, 2-ethylpyrazine and 2-ethyl-6-methylpyrazine have been correlated with woody/papery, roasty/burnt and earthy/musty flavors (Maeztu et al., 2001b).

Guaiacol, a phenolic compound, is responsible for phenolic and spicy aromas and phenolic and burnt flavors in ground roast coffee and coffee brew (Blank et al., 1991; Semmelroch & Grosch, 1996). Instead, in EC samples, a highly significant correlation was found only between this compound and spicy flavor.

Moreover, Rocha et al. (2003) compared the aroma profile of EC and plunger (cafetiere) coffees prepared from different blends (Arabica, Robusta Natural blend, Robusta Torrefacto), using the headspace solid-phase microextraction (HS-SPME) as sampling technique. HS-SPME/GC-MS analyses allowed the identification of 37 compounds: four aldehydes, two ketones, 11 furans, 10 pyrazines, two pyridines, three phenolic compounds, two indoles, one lactone, one ester and one benzothiazine. The volatile composition was related more to the botanical species (*C. arabica* or *C. canephora*) than to the method of preparation of the sample (EC or plunger) (Rocha et al., 2003). They found that the chromatographic areas obtained for EC volatiles were higher than those obtained for plunger coffee volatiles. Additionally, they used PCA to study the main sources of variability between the different coffees and to establish relationships between the botanical varieties, blending technologies, brews modes of preparation and volatile components. The study identified pyridine as the characteristic component of plunger coffee, whilst 2-methylfuran is the characteristic component of the ECs.

EC quality is related to the coffee blend, but also to all the parameters set on the espresso machine: temperature, pressure and composition of water, amount and granulometry of coffee powder used, and time of percolation. Andueza et al. (2003) sought to correlate the final quality of EC and the extraction temperature used in preparing it. They investigated the effects of water temperature (88, 92, 96 and 98 °C) on the final quality of three types of EC (Arabica, Robusta Natural blend and Robusta Torrefacto blend), in order to select the optimal temperature, keeping constant all the other parameters, and pressure always 9 bar. They found that volatile compounds (analyzed by HS/GC-MS) and sensory flavor profiles were the most relevant parameters for selecting the best water temperature. The results revealed that 92 °C was the optimal water temperature for all blends examined.

Caprioli et al. (2012) investigated how EC aroma is influenced by both temperature (88, 92, 98 °C) and pressure (7, 9 and 11 bar), using a semi-quantitative HS-SPME–GC/MS technique. In addition to the nine combinations of temperature and pressure, they focused on the presence and the quantitative trend of 12 volatiles. Of the latter, 10 were the ''key odorants'' identified by Maeztu et al. (2001b) (six of which gave a positive contribution, the remaining four defined as negative ''key odorants''), while the remaining two compounds did not affect coffee flavor, but showed the highest peak area among aroma constituents in EC samples. At the same time, all coffee samples were evaluated by panel test, which indicated that the sum of positive and negative key odorants showed a similar trend. At 9 bar, the intensity of aroma was higher than at other pressure conditions; regarding water temperature, at 9 bar the ratio of positive and negative key odorants was maximum at 92 °C. From a sensorial point of view, the global positive odorants (GOP) and the global negative odorants (GON) were evaluated. They are two hedonistic index that indicate the olfactive intensity, respectively, positive and negative, released from the EC and they were evaluated by panelists using a scale between the expressions ''very bad'' (0) and ''very good'' (10); the results are the mean of panelist judgments. GOP trend given by panelists was quite similar to the chemical profile. On the contrary, the trend of GON was different and almost mirrored that of GOP (Figure 1) and analytical data.

The results suggested that positive odorants mask negative ones, from a sensorial point of view; for this reason, panelists did not perceive the increase of negative notes observed in the instrumental analysis. The best sensorial conditions were at 9 bar and 88 or 92 °C. Combining these results with the chemical ones

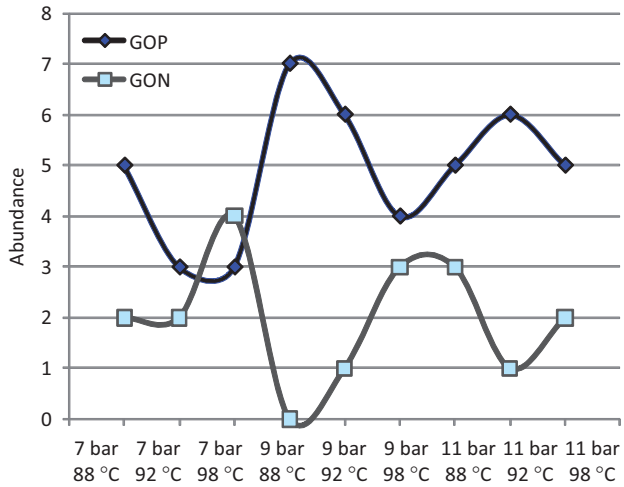

Figure 1. Hedonistic index of GOP and GON obtained from judges in the panel test (Caprioli et al., 2012).

confirmed the setting of 9 bar and 92 °C as the best setting in the EC machines, in line with Andueza et al. (2003).

Influence of espresso and brew coffee preparation on the content of caffeine and chlorogenic acids

The health benefits of coffee beverages are strictly related to the presence and amount of bioactive compounds, factors in which extraction process plays a crucial role (Peters, 1991; Petracco, 2001, 2005). Finding coherent data in literature about this process is far from simple, mainly due to an unstandardized method of coffee preparation, especially for boiled brew. For example, the quantity of ground coffee and the degree to which it has been roasted, the extraction time, and the volume of water used are not constant and not always reported completely. In addition, the results are reported using different unit of measurement: w/w, w/v, w/dose, and w/cup. This situation makes it difficult to correlate date from different studies, especially between the two different preparation techniques (boiled brew coffee and EC) when they are not in the same study.

An overview on caffeine in coffee

Caffeine (1,3,7-trimethylxanthine) has surely been for many years the world's most widely consumed drug, with its main source found in coffee (Ellenhorn & Barceloux, 1988), in which it is one of the most abundant bioactive compounds. For these reasons, its metabolism is widely reported in the literature (Baselt, 2002; Ellenhorn & Barceloux, 1988). Caffeine produces central nervous system stimulation and has been found to positively influence human performance. Although there are beneficial effects from caffeine ingestion, there may also be potentially harmful dose-dependent effects. There has been considerable study of the effects of caffeine on the cardiovascular system (McCusker et al., 2003). Moreover, Ludwig et al. (2012) reported high correlations between the antioxidant capacity of coffee beverages and caffeine, suggesting that caffeine might be also a good contributor to the antioxidant capacity of coffee brews or their ability to reduce the presence of free radicals in the body. Usually, it is detected together with other two bioactive compounds, i.e. trigonelline and nicotinic acid.

An overview of chlorogenic acids (CGAs) in coffee

Other important bioactive species found in high concentration in coffee are chemicals of the chlorogenic acids family. When beans are roasted these secondary metabolites are degraded into phenolic compounds, responsible for coffee bitterness (Campa et al., 2005). GCA is an ester formed between caffeic acid and quinic acid: previous findings reported that these phenolic compounds can act as antioxidant, antitumor, antimutagenic and anticarcinogenic agents (Cetto & Wiedenfeld, 2001; Moseira et al., 2000). Caffeoylquinic acid derivatives, such as 3-*O*-caffeoylquinic acid (3-CQA), 5-*O*-caffeoylquinic acid (5-CQA) and 3,5-di-*O*-caffeoylquinic acid (3,5-diCQA) are natural phenolic compounds that have been isolated from a variety of traditional medicinal plants and present a broad spectrum of pharmacological properties, including antioxidant, hepatoprotectant, antibacterial, antihistaminic and other biological effects (Basnet et al., 1996).

Moreover, it has been demonstrated that caffeoylquinic acid derivatives also exert neuroprotective effects (Hur et al., 2001; Soh et al., 2003). In detail, it is reported that 3,5-diCQA exhibited neuroprotective properties against neuronal cell death; this can be useful for brain protection, as well as in the treatment of neurodegenerative diseases such as Alzheimer's disease, Parkinson's disease and ischemia (Kim et al., 2005).

The acidity and sourness of coffee brews (together with aroma and bitterness) have always been recognized as important attributes of their sensory quality (Ginz et al., 2000). The main acids in green coffee beans are citric, malic, chlorogenic and quinic. During the roasting process the first three acids decrease while quinic acid increases, as a result of the degradation of chlorogenic acids (Balzer, 2001).

The roasting process affects CGA content of the final coffee product. In fact, a study on green coffee (Trugo & Macrae, 1984) reported the degradation of CGA during the roasting process, and received subsequent confirmation in findings that CGA transforms to the corresponding lactones, especially when light/medium roasting conditions are applied (Farah et al., 2005).

Campa et al. (2005) investigated the relationship between caffeine and chlorogenic acid in wild Coffea species. According to their results, caffeine content (dry matter basis of green coffee bean) varies markedly between species and within species. *C. canephora* var. robusta (Robusta coffee), *C. brevipes* and *C. stenophylla* are the coffee species with the highest caffeine content, while *C. pseudozanguebariae* and *C. humblotiana* are almost caffeine-free. Moreover, they found a similar trend between caffeine and CGA content. Comparing the two most widely cultivated and studied species (*C. arabica* and *C. canephora* var. robusta), it is reported that Robusta coffees are richer in caffeine and CQAs than Arabica ones (Belitz et al., 2009; Farah et al., 2005; Ludwig et al., 2012).

Caffeine and coffee preparation techniques

McCusker et al. (2003) evaluated the caffeine content of caffeinated and decaffeinated EC and coffee brew purchased ready-to-drink from coffee shops. Caffeine was isolated from the coffee beverages by liquid-liquid extraction and analyzed by gas chromatography with nitrogen-phosphorus detection (GC-NPD). In this study, seven coffees sold as decaffeinated were found to have low caffeine concentrations (<17.7 mg/dose). There was a wide range in caffeine content in regular coffees (58–259 mg), mainly due to the large difference in volume of the coffees sold (30–473 ml). Considering the caffeine dose (in milligram), caffeinated EC were lower in caffeine content than caffeinated brewed coffees, but also EC volumes are smaller than regularly brewed coffees. In fact, in terms of caffeine concentration, the results were opposite; EC displayed higher caffeine concentration than brewed coffees. Fujioka & Shibamoto (2008) analyzed the differences in caffeine content between seven regular and five decaffeinated coffees and found that the caffeine content in the

Table 3. Caffeine content in brewed coffee from different types (robusta versus arabica) and different geographic origins (Rodrigues et al., 2007).

Type	Sample identification	Origin	Roast	Caffeine (mg/l)
Robusta	I A	India	Medium	314
Robusta	I B	India	Medium	413
Robusta	I C	India	Medium	373
Robusta	I D m	India	Medium	739
Robusta	I D l	India	Light	762
Robusta	I D d	India	Dark	421
Robusta	V	Vietnam	Medium	510
Robusta	C 1	Cameroon	Medium	327
Robusta	C 2	Cameroon	Medium	394
Robusta	C i	Cote D'Ivoire	Medium	646
Arabica	K	Kenya	Medium	190
Arabica	H 1	Honduras	Medium	214
Arabica	H 2	Honduras	Medium	174
Arabica	Z 1l	Zambia	Light	303
Arabica	Z 1d	Zambia	Dark	322
Arabica	Z 2	Zambia	Medium	253
Arabica	Z 3	Zambia	Medium	456
Arabica	B	Brazil	Medium	266
Arabica	T	UR Tanzania	Medium	310
Arabica	Co	Colombia	Medium	279

regular coffees ranged from 10.9 to 16.5 mg/g while that of decaffeinated coffees was from 0.34 to 0.47 mg/g.

Rodrigues et al. (2007) applied solid-phase extraction (SPE) to brewed coffee in order to determine the organic acids and caffeine content using reversed-phase (RP)-HPLC-UV. The method was tested in several coffee beverages prepared from different types of roasted coffees (Arabica and Robusta) from 10 different geographic origins and, in some cases, roasted in different conditions (Table 3). They found that Robusta coffee contained higher levels of caffeine (ranging from 314 to 762 mg/l) than Arabica (ranging from 174 to 310 mg/l). These findings were in agreement with Ludwig et al. (2012) who quantified caffeine in both espresso and brew coffees and their time fractions using Vietnam (*C. canephora* var. robusta) and Guatemala (*C. arabica*) coffees. Caffeine concentration was significantly higher in the Vietnam espresso and coffee brews and their fractions, than in Guatemala ones. Another finding that can be extrapolated from their results is that in both blends analyzed, EC coffee has higher concentration levels (mg/100 ml) of caffeine than coffee brew. However, considering the different volumes (46–47 ml for EC in 24 s of extraction and 520–532 ml for brew coffee in 375 s of extraction), the quantity of caffeine in a cup of brew coffee was around five times higher than in a cup of EC in both blends.

Recently, Caprioli et al. (2014) quantified caffeine content in EC prepared with two different espresso machines, working with different pressure and temperature curves and two different blends, *C. arabica* and *C. canephora* var. robusta. Pressure curve values increased up to a maximum of 9 bar for the Aurelia EC machine (A) and 8 bar for the Leva EC machine (B). After that, the pressure curve in machine A, equipped with an electric pump, was constant during the extraction time, while in machine B the pressure decreased until it reached a final minimum value of 2 bar. The temperature curve values increased in the first seconds of extraction up to a maximum of 93 °C for machine A and 101 °C for machine B. Due to the differences in construction, the temperature value remained constant in machine A, while in machine B the temperature dropped ~10 °C during extraction. Caprioli et al. (2014) examined the caffeine content in a cup of espresso (prepared according to the criteria for a Certified Italian Espresso, with 25 s of extraction). The caffeine content in Robusta EC prepared using machine B was lower than that prepared using machine A at optimum settings (92 °C and 9 bar). This observation was in line with the fact that machine B uses low pressure and high temperature, and that when machine A is operated at these conditions (98 °C and 7 bar) it also has low extraction efficiency. On the contrary, using Arabica blend, machine B yielded a higher content of caffeine than machine A. In general, it was demonstrated that a key role is played by temperature with respect of water pressure, so that Robusta has a high extraction efficiency at low temperature (88–92 °C) while Arabica does so at high temperature (92–98 °C).

In summary, while the reports in the literature are not homogeneous in terms of values and unit of measurement, the common finding is that Robusta contains a higher amount of caffeine than Arabica (Belitz et al., 2009, Caprioli et al., 2014).

CGAs content in the different types of coffee

A complete screening of CGA content in brewed coffee was also conducted in the Fujioka & Shibamoto (2008) study noted above, revealing three caffeolylquinic acids (3-CQA, 4-CQA and 5-CQA), three feruloylquinic acids (3-FQA, 4-FQA and 5-FQA) and three dicaffeoylquinic acids (3,4-diCQA, 3,5-diCQA and 4,5-diCQA). The total CGAs ranged from 5.26 to 17.1 mg/g in regular coffees and from 2.10 to 16.1 mg/g in decaffeinated coffees. Among CGAs, 5-CQA was present at the highest level, ranging from 2.13 to 7.06 mg/g coffee, and comprising 36–42% and 37–39% of the total CGA in the regular and decaffeinated coffees. CGA isomer contents were 5-CQA > 4-CQA > 3-CQA > 5-FQA > 4-FQA > 3-FQA > 3,4-diCQA > 4,5-diCQA > 3,5-diCQA, in decreasing order. This order, in terms of relative concentration between CGAs, is a common finding in the literature for roasted coffee (Perrone et al., 2008), as well as for EC and coffee brew (Alves et al., 2010; Ludwig et al., 2012).

The effect of brewing time and preparation methods on the amount of these antioxidants in coffee was reported by Ludwig et al. (2012) on Vietnam (*C. canephora* var. robusta) and Guatemala coffee (*C. arabica*). Data are reported in Figure 2. They found lower amounts of caffeoylquinic acids in the Vietnam coffee (*C. canephora* var. robusta) than in the Guatemala kind (*C. arabica*) in line with the results of Vignoli et al. (2011) on the amount of 5-CQA, even if these results contradict the common finding of Robusta as the blend with the highest CGA content (Farah et al., 2005). Fractions obtained from espresso of both coffees showed that the amount of all three CQA isomers (3-, 4- and 5-CQA) decreased sharply with extraction time. F1 (0–8 s) accounted for ~70%, F2 (8–16 s) for 17% and F3 (16–24 s) for <14% of the total CQA amounts found in an ECs. Instead, in filtered coffee, the extraction time had a different effect on the content of caffeoylquinic acids. In Guatemala (*C. arabica*) filtered coffee, extraction of CQAs and diCQAs showed a U-shaped profile with the highest concentration in F1 (0–75 s) and F5 (300–375 s) and the lowest in F3 (150–225 s), similar to that observed in antioxidant capacity tests. Thus, in filtered coffees there appears to be a correlation between CGAs and antioxidant capacity. However, in Vietnam (*C. canephora* var. robusta) filtered coffee, the U-shaped extraction of caffeoylquinic acids started after 75 s and F1 exhibited the significantly lowest concentration in caffeoylquinic acids. The extraction percentages of CQAs were similar to those of diCQAs in each coffee fraction as the filter brewing process in contrast to those obtained with the espresso method, in line with the results of Caprioli et al. (2013). Moreover, when the concentration of antioxidants is calculated per gram of coffee, taking into account the different fraction volumes, higher extraction of these phenolic compounds per gram

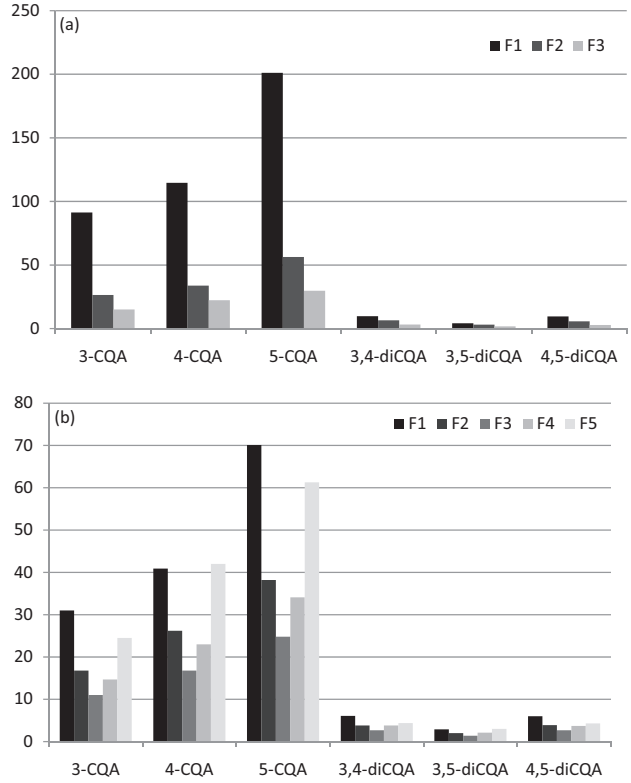

Figure 2. Chlorogenic acids in EC (a) (F1 = 0–8 s, F2 = 8–16 s, F3 = 16–24 s) and brew coffee (b) (F1 = 0–75 s, F2 = 75–150 s, F3 = 150–225 s, F4 = 225–300 s, F5 = 300–375 s) and fractions from Guatemala blend (Ludwig et al., 2012).

of coffee was obtained in filter coffee brews than in espresso ones, in agreement with Perez-Martinez et al. (2010).

This may be due to the differences between espresso and filter coffee makers. Although the high water pressure applied in EC makers favors the extraction process, the short time of contact between water and coffee grounds, the high coffee/water ratio and the limited space in the coffee cake do not allow equilibrium to be reached (Petracco, 2005). In contrast, in the filter coffee maker extraction chamber, the water stays in contact with the coffee for a longer time and there is more turbulence. Time and turbulence are two factors which enable extraction of additional compounds, including both CQAs and diCQAs, free and bound with melanoidins, as the water as not become so saturated with dissolved material as in the espresso method. In fact, turbulences are viewed as the third most important factor in filter coffee brewing, after time and temperature (Lingle, 1996). Less turbulence during sequential coffee percolation could also be the reason why Blumberg et al. (2010) found that monoCQA and CQAs extraction behaviors were more similar to the results on EC fractions found by Ludwig et al. (2012), i.e. higher extraction in the first fractions and slower release of dicaffeoyl quinides. Other factors that influence the extraction of antioxidants in coffee are brewing time and water pressure. Higher water pressure increases antioxidant extraction speed, as seen in the first fraction of EC. Nevertheless, the parameters of turbulence and longer contact time that are typical of a filter coffeemaker should be considered in order to increase extraction efficiency, mainly in less polar antioxidant compounds such as diCQA.

Recently, Caprioli et al. (2013) quantified the three most concentrated chlorogenic acids, 3-CQA, 5-CQA and 3,5-diCQA, in time portions of ECs, with two EC machine (Aurelia machine A and Leva machine B) in the same conditions previously described for caffeine. The amount of these chlorogenic acids (milligram) in a cup of EC ranged from 24.7 to 39 mg, 9.9 to 13.9 mg and 2.3 to 4.4 mg for 5-CQA, 3-CQA and 3,5-diCQA, respectively. The highest levels of 5-CQA and 3-CQA were found in Arabica coffee prepared with EC machine A, 1.56 and 0.56 mg/ml respectively. On the contrary, the highest concentration of 3,5-di-CQA was found in the Robusta coffee sample prepared with EC machine A (0.18 mg/ml). The best extraction performance from the two blends was obtained with EC machine A, leading to a concentration of 2.22 and 2.12 mg/ml and a content of 55.6 and 53.1 mg when processing Arabica and Robusta blends, respectively. On the contrary, coffees made with EC machine B displayed a lower concentration and a lower content of total CGA compounds, with a concentration of 1.73 and 1.52 mg/ml and a content of 43.3 and 38.1 mg, for Arabica and Robusta, respectively. In conclusion, the higher and constant water pressure afforded by the EC machine offers better extraction of these antioxidant species, supporting the theory of Petracco (2005) and Ludwig et al. (2012).

Conclusion

Coffee is one of the most consumed and studied beverage in the word. It is well-known that factors such as the variety and blend of coffee beans, the degree of roasting and the grinding process affect coffee composition and quality. However, also the brewing process influences the sensorial and beneficial properties of coffee.

From the sensorial point of view, the volatile fraction plays a crucial role. The comparison between the results from the brew and EC reveals that the chromatographic areas obtained for EC volatiles were higher than those obtained for brew coffee volatiles.

Moreover, the content of bioactive compounds is strongly affected by the extraction mechanism. On the one hand, the EC maker has the positive effect of high water pressure, while on the other, in the filter coffeemaker, the longer time and turbulence in the extraction chamber enhance the recovery of bioactive compounds from ground coffee. Quantification studies of caffeine and CQAs highlight that brewed coffee have a higher content of these species than EC, mainly due the higher final volume. In addition, the particular technical characteristics of the different EC machines affect the extraction mechanism and, consequently, the final quality of ECs.

Acknowledgements

The authors would like to thank Sheila Beatty for her editing of the English usage in this article.

Declaration of interest

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of this article. This article does not contain any studies with human or animal subjects.

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