



Neapolitan coffee brew chemical analysis in comparison to espresso, moka and American brews



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ABSTRACT

The aim of the present study was to characterize the chemical composition of Neapolitan coffee brew in comparison to espresso, American, and moka coffee brews. Despite the similarity of brewing principle of Neapolitan and American coffee-making techniques, i.e. percolation of hot water through ground coffee, the characteristics of Neapolitan coffee brew in terms of antioxidant activity, total phenolic compounds and total solids were more similar to moka coffee brew. Espresso and moka showed higher antioxidant activity, and espresso exhibited higher caffeine concentration, total phenolic compounds, and total solids with respect to other coffee brews studied. For the first time a characterization of the Neapolitan coffee aroma, a traditional Italian brewing procedure, was reported. A significant higher amount in hexanal, β -damascenone and some pyrazines was found in Neapolitan coffee aroma with respect to other procedures. These compounds could be considered as a distinctive characteristic of Neapolitan coffee aroma. Moka was characterized by higher guaiacol content with respect to other procedures, while espresso showed significantly higher levels in aldehydes and 2-furanmethanol acetate.

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1. Introduction

Coffee is one of the most appreciated beverages in the world and, generally, its aroma is considered as one of the most important attributes. Among coffee botanical species, the arabica one (*Coffea arabica*) has been reported as the most aromatic cultivar and it is commonly used for the production of superior quality coffee brews. Development of aroma compounds is greatly dependent upon roasting degree and in particular on time–temperature conditions (Baggenstoss, Poisson, Kaegi, Perren, & Escher, 2008), but the brewing method is also of crucial importance (Rocha, Maeztu, Barros, Cid, & Coimbra, 2003). So far about 800 volatile compounds have been reported in green and roasted beans and in coffee brews, mainly in filtered and espresso (Flament, 2002). The latter one has been described to be the most aromatic brew (Gloess et al., 2013; López-Galilea, Fournier, Cid, & Guichard, 2006; Rocha et al., 2003).

Coffee consumption has been related to many health benefits, due to its strong antioxidant activity and inhibition of lipid peroxidation (Napolitano, Fogliano, Tafuri, & Ritieni, 2007). Coffee also possesses protective effects against the risk of advanced liver disease and hepatocellular carcinoma, and coffee consumption protects the liver from damage caused by high-fat diet through different mechanisms (Vitaglione et al., 2010). Human trials considering the Italian consumer average coffee

intake (5 cups of espresso per day) found that coffee was able to significantly increase plasma glutathione concentration (Esposito et al., 2003). This effect has been attributed to diterpenes, particularly cafesterol, whereas several other biologically active substances are found in coffee, such as polyphenols and melanoidins (Ferruzzi, 2010). The concentration of these compounds is affected by the type and origin of ground coffee, its roasting degree (Sacchetti, Di Mattia, Pittia, & Mastrocola, 2009) and brewing procedure (Ludwig et al., 2012; Niseteo, Komes, Belščak-Cvitanović, Horžić, & Budeč, 2012).

Melanoidins are non-volatile, brown colored compounds in coffee beans and brews, produced by the Maillard reaction (MR). Their concentration in coffee brews increases with increasing roasting intensity and they play an important role on the total antioxidant activity (Borrelli, Visconti, Mennella, Anese, & Fogliano, 2002; Liu & Kitts, 2011; Perrone, Farah, & Donangelo, 2012; Vignoli, Caldeira Viegas, Gentil Bassoli, & De Toledo Benassi, 2013).

Different preparation methods are commonly used for coffee brew preparation, and their distribution varies worldwide depending on traditions, personal preferences, social behavior and many other factors. Although the most common coffee brewing technique is the filtered one, espresso coffee has gained popularity worldwide, while moka preparation method is almost unknown and restricted to a domestic level in southern European countries such as Italy and Spain (Pérez-Martínez, Caemmerer, De Peña, Cid, & Kroh, 2010). Different preparation techniques involve different polyphenol extraction, caffeine content, total solid content, antioxidant activity level and volatile profile

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that greatly varies among the different brewing methods (López-Galilea, De Peña, & Cid, 2007). Each brewing technique applies different water/ground coffee ratios, water temperature and extraction time, and different water pressures or final volumes (Petracco, 2001). In fact, a single serving volume, or “cup”, is enormously variable in different cultures, ranging from 15 mL of concentrated espresso in Sicily to over 250 mL of filtered coffee in the USA (Clarke & Vitzthum, 2001). The different brewing techniques are linked to local traditions and their names are usually given from their geographical origins of traditional use.

The Neapolitan coffee is a simple infusion method based on gravity, and hot water is allowed to percolate through a layer of medium-coarse ground coffee. The *macchinetta napoletana* (Neapolitan pot, also known as “flip drip pot”) has been used in Italian tradition since the first years of 1800 (Petracco, 2001). Although the antioxidant activity, caffeine, total phenolic compounds, and volatile composition have been widely studied, mainly in espresso and filtered coffee (Andueza et al., 2003; Gloess et al., 2013; López-Galilea et al., 2006, 2007; Maeztu et al., 2001; Sánchez-González, Jiménez-Escrig, & Saura-Calixto, 2005; Santini et al., 2011), no investigation reports data about the aroma of Neapolitan coffee brew.

Thus, the aim of the present paper was to characterize the chemical composition of Neapolitan coffee brew in comparison to espresso, American, and moka coffee brews.

2. Material and methods

2.1. Standards and coffee samples

Authentic reference chemical compounds were obtained from Sigma-Aldrich (Steinheim, Germany), Aldrich (Steinheim, Germany), and Fluka (Buchs, Switzerland). Acetaldehyde (99.5%), 2-methylpropanal (99%), 2-methylbutanal (95%), 3-methylbutanal (97%), hexanal (98%), 2-ethyl-6-methylpyrazine (95%), 2-ethyl-5-methylpyrazine (97%), 2-propylpyrazine (97%), 2-ethyl-3,5-dimethylpyrazine (47.5%), 2,5-dimethylfuran (99%), furfurylmethyl sulfide (97%), 2-furanmethanol acetate (99%), 2-furanmethanol (98%), guaiacol (98%), 4-ethylguaiacol (98%), 4-vinylguaiacol (98%), 2,3-pentanedione (97%), methanethiol (98%) and caffeine (98.9%) were obtained from Sigma-Aldrich. Butanal (99%) was obtained from Fluka, and β -damascenone (1%, ethanol) was obtained from Aldrich. A commercial sample of ground roasted Arabica coffee blend, packaged in protective atmosphere was provided by *Torraldo caffè* (Naples, Italy). The coffee sample consisted of a batch of Arabica 100% coffee, medium-high level of roasting. According to the information given by the industry, coffee beans were thermally treated for about 17 min at a maximum temperature of 227 °C, for the roasting process. The roasting degree indicated as Agstron Classification System was about 25 IR (dark roast), and the particle size (granulometry) was 0.35 mm. The samples were produced in February 2013, stored at room temperature and were used within two months from their production. The samples were stored in individual aluminum packages (7 g each), packed under Nitrogen protective atmosphere directly from the industry, to avoid any oxidation or deterioration of the product. Moreover, each package was open immediately before each extraction process or each replicate of the brewing step procedure.

2.2. Coffee brew preparation

Several coffee-brewing procedures were compared and the following machines were used: American coffeemaker, Neapolitan pot, moka pot, and espresso machine. The ground coffee/brew ratio was chosen in accordance to the best indications found in literature and to the traditional practices based on Italian coffee-making tradition. The main difference to be underlined with respect to literature data consists on the amount of ground coffee used in moka and Neapolitan brews. For moka procedure we used a higher amount of coffee ground, which

was abundant in the filter, but it was not pressed. The process of extraction was repeated three times for each type of coffee brew. The preparation of the different coffee brews is reported as follows.

2.2.1. American coffee brew

This coffee brew consists of a glass resistant kettle and a special filter where ground coffee is added as desired by the consumer. The apparatus let the hot water percolate through the filter and coffee brew is collected in the kettle. American coffee brew, also called filtered coffee brew, was prepared from 25 g of ground-roasted coffee and a volume of 300 mL of distilled water. The obtained final volume of coffee brew was 230 mL and extraction took about 2 min (about 90 °C), by using a filter coffee machine Mr. Coffee model ARX23 (Sunbeam Products Inc., Boca Raton, FL, USA).

2.2.2. Neapolitan coffee brew

The *macchinetta napoletana* (also known as ‘flip drip pot’) is one of the simplest brewing methods based on infusion, and it was already known as an Italian tradition in the first years of 1800. It uses gravity for the percolation of hot water through a bed of medium-coarse ground coffee. The main difference between drip filter and Neapolitan extraction methods is that in the latter the ground coffee is immobilized between two filtering perforated plates, preventing the movement of the granules in the water (Petracco, 2001). In the Italian and particularly in the Neapolitan coffee-making tradition, the ground coffee/water ratio is higher with respect to that usually adopted. More specifically, the coffee powder is added in the coffee pot without pressing it but using a higher amount with respect to the pot capacity, and this could change the porosity and the internal pressure during the extraction procedure.

The Neapolitan coffee machine consists of a special coffeepot made of aluminum. In the lower part of the apparatus, a tank is filled with water, the filter is added and filled with ground coffee and the upper part is closed. A check valve existing in the coffeepot allows to verify when the water starts boiling. The coffeepot is rapidly overturned and the water is allowed to percolate through the filter, that consists only of a metallic punched chamber. Immediately after overturning it, the long coffeepot spout is traditionally covered by a homemade paper-cup, to avoid losing coffee aroma: this is called *cuppitiello* in the Neapolitan language. The coffee brew is finally collected in the lower part of the apparatus. Neapolitan coffee brew was prepared from 15.4 g of ground-roasted coffee and a volume of 145 mL of distilled water. The obtained final volume of coffee brew was about 75 mL and the extraction time was about 5 min. Water temperature was about 90 °C at the beginning of brewing process and raised about 60 °C when filtration finished. The coffeepot used was the ILSA Tz.1 (Torino, Italy).

2.2.3. Moka coffee brew

Moka is the most used coffee brew preparation technique in Italy at domestic level, and this coffee has been one of the most consumed also in other countries. Pressure is applied to the water by simply boiling it in an autoclave-type aluminum or steel kettle on an open flame, and forcing it through an immersed pipe across the coffee cake formed in a strainer basket. The beverage is conveyed through appropriate tubing into an upper vessel, screwed and sealed by a rubber gasket to the base kettle. Contact time mainly depends on the cake hydraulic resistance, which in turn hangs on three factors: the amount of ground coffee used, its particle size distribution (grinding fineness) and the tamping force exerted on it, whether deliberately or just by forcing down a heap of coffee while fastening the top part (Petracco, 2001). The apparatus consists of a metallic tank base used as a water boiler and a metallic filter where ground coffee is put. The upper part of the device is a cylindrical cooler, tightly screwed onto the base, where the coffee drink is quickly cooled and then collected before the use. Boiling water is forced and then it filters through the coffee grounds into the upper section of the coffeepot where the coffee is collected. The moka coffee brew was prepared from 11.3 g of ground-roasted coffee and a

volume of 80 mL of distilled water by a moka machine model Dama ST/C5 (Bialetti Industrie SpA, Coccaglio, BS, Italy). Also in this preparation, like the *Neapolitan coffee*, the coffee powder is added in the coffee pot without pressing in an amount higher with respect to the pot capacity. The obtained final volume of coffee brew was 62 mL and extraction took about 3 min (above 100 °C). For moka and Neapolitan preparations, the flame of gas cooker was maintained very low to reduce the coffee burning, as this has been largely considered an important parameter for a “good Italian coffee” production.

2.2.4. Espresso coffee brew

Espresso is a preparation technique based on pressure induced percolation of a limited amount of hot water through a ground coffee cake, where the energy of water pressure is spent within the cake itself. Espresso coffee is prepared with a special machine that uses hot water and high pressure for a short time (25 s) to produce a “short” coffee brew (25 mL) with a distinctive cream layer on top (about 2 mL). The espresso coffee brews were prepared from 7 g of ground-roasted coffee, using an Espresso machine model Pinocchio C (Spinel s.r.l., Parabita, LE, Italy). The specifics of the machine and the brewing procedure were chosen in accordance to those reported by Caprioli et al. (2012). The thermostat was set by the producer at 95 °C and the actual temperature of water measured during extraction was about 93 °C. The pump pressure was set at 15 bar, and the outlet pressure measured was about 9.5 bar.

2.3. Determination of pH and total solids

After the brewing process, samples were rapidly cooled at 20 °C, and the pH was measured using a pH-meter. Total solids were determined by oven drying 10 mL of different coffee brews to a constant weight, for 24 h at 100 °C. The analyses were performed in triplicate for each brewing procedure.

2.4. Total phenolic compounds

Total phenolic compounds were measured using the Folin–Ciocalteu reagent according to the method described by Bravo, Monente, Juárez, De Peña, and Cid (2013) for coffee brews analysis. After dilution (3:10 v/v), the Folin–Ciocalteu reagent was added to start the reaction and absorbance was taken after 2 min at 765 nm using a spectrophotometer UV-1601 (Shimadzu, Kyoto, Japan). Gallic acid was used as a standard for the calibration curve. The analyses were performed in triplicate for each brewing procedure.

2.5. Antioxidant activity by ABTS⁺ method

The ABTS antioxidant capacity was performed according to the method reported by Bravo et al. (2013). The only modification was the use of ABTS⁺ radical prepared in aqueous solution instead of ethanol one as reported by Del Castillo, Ames, and Gordon (2002). This modification was made to avoid precipitation of coffee components that would have occurred in the ethanol environment. In fact, ABTS⁺ has been reported to possess higher efficiency in aqueous solution with respect to ethanol solution for coffee brew analysis, due to the higher solubility in water of some coffee components showing high antioxidant activity (Del Castillo et al., 2002). Each coffee brew was diluted (3:100 v/v) with demineralized water and an aliquot of 100 µL was added to 2 mL of radical cation ABTS solution (ABTS^{•+}). After exactly 6 min of dark storage, absorbance was measured at 734 nm using a spectrophotometer UV-1601 (Shimadzu, Kyoto, Japan). The antioxidant capacity was expressed as micromoles of Trolox per mL coffee brew (µmol Trolox mL⁻¹). The analyses were performed in triplicate for each brewing procedure.

2.6. Caffeine quantification by HPLC

Quantification of caffeine was performed by HPLC in accordance with the method reported by Niseteo et al. (2012) for coffee brews. The samples were filtered through a 0.45 µm filter (Nylon Membranes, Phenomenex, Torrance, CA, USA) and an HPLC Agilent Series 1100 was used (Agilent Technologies, Palo Alto, CA, USA) with a Photodiode Array Detector with reversed-phase column Phenomenex C18 RP (250 × 4.6 mm, 4 µm i.d.) (Phenomenex, Torrance, CA, USA). The solvents consisted of 3% formic acid (solvent A) and HPLC grade methanol (solvent B) at a flow rate of 1 mL min⁻¹. The elution was chosen according to that previously reported in literature (Niseteo et al., 2012). Chromatograms were recorded at 278 nm wavelength. Caffeine identification and calibration were performed by comparing the retention time and spectral data obtained using the pure compound. ChemStation Software version A.09 (Agilent Technologies, Palo Alto, CA, USA) was used for data acquisition and treatment. The analyses were performed in triplicate for each brewing procedure.

2.7. Analysis of volatile compounds by SPME-GC/MS

Volatile compounds were analyzed by solid-phase micro-extraction gas-chromatography coupled with mass spectrometry (SPME-GC/MS). A SPME device (Supelco Co., Bellefonte, USA) was equipped with a fiber coated by divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) 50/30 µm thickness 1 cm length coating phase. The same type of fiber was reported to be effective and highly efficient for coffee aroma analysis (Akiyama et al., 2007; López-Galilea et al., 2006). The fiber was conditioned at 250 °C for 3 h in a GC injection port prior to the analysis in order to avoid the release of extraneous compounds. Within 2 min after coffee brewing, 10 mL coffee brew was put in a 15 mL vial, immediately capped with a PTFE-silicon septum and the vial was put on a Trade Raypa magnetic stirrer (Analitica De Mori, Italia), and the fiber was inserted in the sample headspace for sampling volatile compounds at 50 °C for 2 min. The exposure time and the condition for analysis were chosen according to Akiyama et al. (2007). A Shimadzu GC-MS QP5050A (Kyoto, Japan) and a Supelcowax-10 fused capillary column 60 m × 0.32 mm i.d., 0.5 µm film thickness (Supelco Co., Bellefonte, USA) were used. To avoid contamination, a blank test was performed before each analysis at the same chromatographic conditions of the sample analyses. The identification of compounds was confirmed by using pure standards and comparison of their retention indices and mass spectra. When reference compounds were not available, a tentative identification was given on the basis of the mass spectra stored in NIST libraries. GC-MS analysis in selective ion monitoring (SIM) was applied to quantify the volatile compounds. Indication of the employed ions and their peak areas normalized by the total area was reported in Table 1. The results were indicated as a percentage of total peak area. Data were processed using the software Lab Solutions (GCMS Solution version 1.20, Shimadzu, Kyoto, Japan). The analysis of volatile compounds was performed in triplicate.

2.8. Statistical analysis

Significant differences between coffee brewing techniques were determined for each coffee chemical component by one-way ANOVA. Tukey's test was used to discriminate among the means of the variables. Differences of $p < 0.05$ were considered significant. Principal component analysis (PCA) was performed on the antioxidant activity (mmol Trolox L⁻¹), caffeine concentration (mg mL⁻¹), total phenolic compounds (mmol mL⁻¹), total solids (mg mL⁻¹), pH, and peak area (%) for the volatile compounds to observe the main differences among different coffee brews. All chemical attributes were included in the PCA, which was calculated based on the Pearson correlation matrix. Data elaboration was carried out using XLStat (version 2009.3.02), an

Table 1

Chemical standards, odor descriptors and MS fragments used for quantitative analysis.

Compound	Odor descriptor ^a	Ion fragments ^b (m/z)
<i>Aldehydes</i>		
Acetaldehyde	Fruity ^{I,II,VIII} , pungent ^{II,III,VIII} , green ^{VIII} , ethereal ^{VIII}	43
2-Methylpropanal	Malty ^I , banana ^{IV,VIII} , toasted ^{III} , fruity ^{III,VIII} , pungent ^{III,VIII}	41–72
Butanal	Chocolate ^V , caramel ^V , fruity ^{VIII} , green-fresh ^{VIII}	44–72–57
2-Methylbutanal	Malty ^{I,II,VIII} , buttery ^{III} , oily ^{III} , fruity ^{IV,V,VIII} , roasted cocoa ^{IV,VIII} , chocolate-like ^V , fermented ^{VIII}	57–44
3-Methylbutanal	Malty ^{I,II} , buttery ^{III} , oily ^{III} , peach ^{IV,VIII} , chocolate ^{IV,VIII} , burned ^{IV} , acrid-pungent ^{VIII} , fruity ^{VIII}	57–44
Hexanal	Green ^{III,VI} , grassy ^{III,VII,VIII} , fruity ^{IV,VIII} , leaf-like ^{VI} , fatty-green ^{VII,VIII}	56
<i>Pyrazines</i>		
2-Ethyl-6-methylpyrazine	Flowery ^V , fruity ^V , hazelnut-like ^{VIII}	121–122
2-Ethyl-5-methylpyrazine	Coffee-like ^{VIII}	121–122
2-Propylpyrazine	Green ^{VIII} , vegetable ^{VIII}	94–122
2,6-Diethylpyrazine	Pyrazine ^V , potato-like ^V , hazelnut-like ^{VIII}	135–136
2-Ethyl-3,5-dimethylpyrazine	Earthy ^{I,IV,VIII} , roasty ^{I,III,VIII} , burnt ^{III} , meaty ^{III} , green ^{III} , nutty ^{III} , potato-like ^V , almond ^{IV} , nuts ^{IV}	135–136
2-Methyl-3-trans-propenylpyrazine	Roasty ^V , green ^{VIII} , nitrobenzene-like ^{VIII}	119–134
<i>Furans</i>		
2,5-Dimethylfuran	Ethereal ^{VIII}	96–95–81
Furfuryl methyl ether	Herbal ^V , potato-like ^V , mustard ^{VIII} , nutty ^{VIII} , ricy ^{VIII}	81–112–53
Furfurylmethyl sulfide	Sulfur ^V , garlic ^{IV,VIII} , toasty ^{IV}	81–128
2-Furanmethanol acetate	Ethereal-floral ^{VIII} , herbal-spicy ^{VIII}	81–98–140
2-Furanmethanol	Caramellic ^{VIII} , warm-oily ^{VIII} , burnt ^{VIII} , smoked ^{VIII}	98–97
<i>Phenolic compounds</i>		
Guaiacol	Phenolic ^{I,II,VIII} , burnt ^{I,II,VIII} , smoky ^{VI,VIII} , spicy ^{VII,VIII} , harsh ^{VII} , earthy ^{VII}	109–81–124
4-Ethylguaiacol	Spicy ^{I,II,III,VIII} , phenolic ^{II} , smoky ^{VIII} , roasted ^{VIII}	137–152–122
4-Vinylguaiacol	Spicy ^{I,II,III,VIII} , phenolic ^{II} , eugenol-like ^{III} , clove-like ^{VIII} , smoky ^{VIII} , sweet ^{VIII}	150–135–107
<i>Ketones</i>		
2,3-Pentanedione	Buttery ^{I,II,III,IV,V,VIII} , oily ^{III,IV,VIII} , caramel-like ^V	43–57
β-Damascenone	Honey-like ^{I,II,VI,VIII} , fruity ^{I,II,IV,VI,VII,VIII} , sweet ^{VII,VIII} , woody ^{VIII} , tea-like ^{VIII}	69–190–105
<i>Sulfur compounds</i>		
Methanethiol	Cabbage-like ^{I,II,VIII} , putrid ^{II} , sulphurous ^{III} , gasoline ^{III} , garlic ^{III} , rotten eggs ^{III} , meat ^{III} , cheesy ^{III}	47–48
<i>Pyrroles</i>		
1-Methyl-(1H-pyrrol-2-yl)-1-ethanone	Roselike ^V , nutty ^{VIII} , floreal ^{VIII} , smoky ^{VIII}	98–97

^a The odor descriptors were indicated as reported in literature.^I Grosch, 1998.^{II} Semmelroch & Grosch, 1995.^{III} D'Acampora Zellner, Dugo, Dugo, & Mondello, 2008.^{IV} do Nascimento, de Aquino, do Nascimento, Chang, & de Moraes, 2007.^V López-Galilea et al., 2006.^{VI} Mayer & Grosch, 2001.^{VII} Piccone, Lonzarich, Navarini, Fusella, & Pittia, 2012.^{VIII} Flament, 2002.^b Bold numbers indicate quantifier ions.

add-in software package for Microsoft Excel (Addinsoft Corp., Paris, France).

3. Results and discussion

3.1. pH, solids, total phenolic compounds, antioxidant activity and caffeine

The pH values of Arabica coffee brews by different techniques varied from 5.52 (Neapolitan coffee) to 6.01 (American coffee), as reported in Table 2A. Besides Neapolitan and American coffee brews are both based on hot water percolation and long brewing time with respect to moka and espresso, the results obtained about their acidity were quite unexpected, and it could be probably explained by their total solid content. In fact, the total solid concentration, in which are considered the aliphatic carboxylic acids mainly responsible of the coffee acidity (Clarke & Vitzthum, 2001), significantly varied among coffee brews. In particular, espresso coffee showed the highest extraction yield (73.66 mg mL⁻¹), followed by moka and Neapolitan brews (56.47 mg mL⁻¹ and 48.97 mg mL⁻¹, respectively), that did not differ. The lowest value was obtained for American brew (12.20 mg mL⁻¹). In general, the total solid concentration has been reported to influence the sensory property of coffee brew described as “body” (Gloess et al., 2013) and it seems to depend upon the coffee/water ratio (Andueza, Vila, Peña,

& Cid, 2007) and the brewing procedure applied (López-Galilea et al., 2007). In fact, at higher amounts of ground coffee used, as it occurs for the Neapolitan coffee brew, higher total solid content was measured. Moreover, higher temperature and pressure promote higher extraction yields and rates, as occurred for espresso and moka with respect to filtered coffee brews. López-Galilea et al. (2007) reported higher concentration for total solids, and it was attributed to the higher pressure applied. Our results were in accordance with literature, in fact, a pressure of ~10 bar is generally the outlet pressure in the espresso machine, followed by moka which uses a pressure of about 1.5 bar and by the infusion methods (American and Neapolitan), in which water brews at about atmospheric pressure. This effect could also partially explain the extraction efficiency of the different brewing procedures (Table 2B). In fact, in the case of American brew, by considering the antioxidant activity on the dry basis (total coffee solids), it resulted in higher level respect to other procedures, whereas Neapolitan coffee resulted to be the lowest one (data not shown). The extraction efficiency can be defined as the ratio between the mass of the coffee material that passes into the cup and the total ground coffee used (Clarke & Vitzthum, 2001). Nevertheless, the moka coffee brew gave rise to the highest extraction of total solids (309.85 mg g⁻¹ ground coffee) followed by espresso (259.72 mg g⁻¹ ground coffee), Neapolitan (241.65 mg g⁻¹ ground coffee) and American coffee brew

Table 2
pH, temperature, total solids, total phenolics evaluated by Folin–Ciocalteu method, antioxidant activity evaluated by ABTS, and caffeine content of different coffee brews (A). Coffee extraction, considering the brewed coffee obtained with respect to the amount of ground coffee used (see Section 2.2) (B). Values expressed “per cup” were calculated considering one coffee cup equal to a volume of 125 mL (American coffee), 40 mL (Moka and Neapolitan coffee) and 25 mL (Espresso) (C).

	American	Neapolitan	Moka	Espresso
(A) Concentration				
pH (20 ± 1 °C)	6.01 ± 0.09 a	5.52 ± 0.12 c	5.71 ± 0.15 bc	5.87 ± 0.02 ab
T (°C)	66.40 ± 0.65 bc	61.00 ± 1.50 c	80.23 ± 3.75 a	68.00 ± 1.50 b
Total solids (mg mL ⁻¹)	12.20 ± 0.91 c	48.97 ± 4.01 b	56.47 ± 7.05 b	73.66 ± 8.90 a
Total phenolics (mmol mL ⁻¹ gallic acid)	14.08 ± 0.58 c	36.56 ± 1.55 b	35.43 ± 2.55 b	46.35 ± 3.81 a
Caffeine (mg mL ⁻¹)	1.39 ± 0.30 b	1.30 ± 0.18 b	1.68 ± 0.20 b	2.44 ± 0.24 a
ABTS (mmol L ⁻¹ Trolox)	22.88 ± 1.06 c	47.94 ± 13.79 b	71.89 ± 6.10 a	81.50 ± 5.74 a
(B) Extraction efficiency				
Total solids (mg g ⁻¹ ground coffee)	112.27 ± 8.35 c	241.65 ± 19.80 b	309.85 ± 38.69 a	259.72 ± 31.40 b
Total phenolics (mg gallic acid g ⁻¹ ground coffee)	22.03 ± 0.91 c	34.13 ± 1.45 a	29.74 ± 2.14 b	27.81 ± 2.28 b
Caffeine (mg g ⁻¹ ground coffee)	12.75 ± 2.73 a	6.33 ± 0.88 b	9.22 ± 1.10 ab	8.60 ± 0.84 ab
ABTS (mmol Trolox g ⁻¹ ground coffee)	0.21 ± 0.01 c	0.24 ± 0.07 c	0.39 ± 0.03 a	0.29 ± 0.02 b
(C) Intake per cup				
Total solids (mg)	1525.36 ± 113.41 c	1958.67 ± 160.51 b	2258.89 ± 282.05 a	1841.42 ± 222.62 b
Total phenolics (mg gallic acid)	299.38 ± 12.36 a	248.78 ± 7.91 b	241.09 ± 17.35 b	197.14 ± 16.20 c
Caffeine (mg)	173.25 ± 37.13 a	52.00 ± 7.25 b	67.18 ± 8.00 b	60.95 ± 5.94 b
ABTS (mmol Trolox)	2.86 ± 0.13 a	1.92 ± 0.55 b	2.87 ± 0.24 a	2.04 ± 0.14 b

All values are shown as means $\pm$ standard deviation ($n = 9$). Numbers followed by different letters on the same line are significantly different ($p < 0.05$).

(112.27 mg g⁻¹ ground coffee). This result could be explained as an effect of both the water pressure and temperature, but also attributed to the brewing time, because longer brewing time implies longer contact time between the coffee and water, thus allowing a higher extraction of some compounds (Gloess et al., 2013). The same trend was obtained for total polyphenols and caffeine concentrations (Table 2A). The concentration of total phenolic compounds resulted higher in espresso technique, while moka and Neapolitan showed a lower extraction. The lower level of total phenolic compounds resulted for American coffee, which gave rise to less than half the value obtained from other brewing techniques. This result was not in accordance with previously published papers (Gloess et al., 2013; Pérez-Martínez et al., 2010), but this difference could be due to different water/ground coffee ratios and the final volume obtained. Concerning the extraction efficiency, Neapolitan coffee brew showed the highest level of total phenolic compounds with respect to all other techniques considered (Table 2B). This result was explained by the higher contact time during brewing process, in partial agreement with previous papers (Ludwig et al., 2012). The American technique resulted to be the less efficient among the four studied brewing methods.

The caffeine concentration in the brewing techniques analyzed ranged from 1.30 mg mL⁻¹ (Neapolitan) to 2.44 mg mL⁻¹ (espresso). No significant differences were obtained among Neapolitan (1.30 mg mL⁻¹), American (1.39 mg mL⁻¹) and moka (1.68 mg mL⁻¹) coffee brews. These findings were similar to those reported by Santini et al. (2011) for different coffee beverages. The higher caffeine concentration in espresso coffee brew could be explained by the very low volume (25 mL) and the higher pressure in espresso with respect to other extraction techniques (Santini et al., 2011).

Despite the low caffeine concentration in American coffee brew, this brewing procedure allowed the highest caffeine extraction efficiency (12.75 mg g⁻¹ ground coffee), considering the amount of caffeine extracted with respect to the coffee powder used. The caffeine yield for American brew was almost double with respect to the Neapolitan brew, besides the similarities of these two techniques in the type of extraction. This difference could be explained by the higher temperature of American coffee also after brewing procedure because of the coffee machine hotplate, while Neapolitan coffee pot is rapidly cooled immediately before the percolation process. Considering that caffeine is hydrosoluble, the highest caffeine extraction efficiency for American brew could be related to the time of brew preparation, or due to the time of contact between coffee and hot plate.

Some coffee compounds such as caffeine or phenolics as chlorogenic acids, hydroxycinnamic acids or compounds produced from Maillard reaction (MR) such as melanoidins have been identified as antioxidants and have benefit effects. Antioxidant activity evaluated by the ABTS⁺ method resulted significantly different among different brewing procedures. The lower antioxidant activity was obtained for American coffee, while Neapolitan coffee resulted in a double value for antioxidant activity with respect to the first one. Antioxidant activity for moka and espresso was more than three times higher with respect to the American brew, as showed in Table 2A. This result was partially attributed to the dilution effect of the brewing techniques, whereas one has to consider that we did not perform a complete characterization of all the coffee components which could have influenced its antioxidant activity. Generally, the results for antioxidant activity reflected those obtained for total phenolic compounds, except for moka coffee. In fact, a lower amount of phenolic compounds was found in moka with respect to espresso coffee brew and the level was similar to Neapolitan coffee brew. This result was explained by the probably higher formation of MRP due to higher extraction temperatures and time in moka pot (Sacchetti et al., 2009). In fact, as it is well known, the ABTS⁺ radical reacts with any hydroxylated aromatic compound, based on electron-transfer redox reaction, and for this reason one cannot distinguish an antioxidant activity due to phenolic and non-phenolic compounds such as MRPs. The quantification of the melanoidins in the coffee brews would be necessary to fully explain the changes in antioxidant activity of coffee brews. Therefore, Neapolitan coffee brew showed an intermediate antioxidant activity, although the total polyphenol content was similar to that of moka brew. It is important to highlight that the roasting process has a crucial effect on the antioxidant activity of coffee brews, and increases up to 25% of the antioxidant activity was reported related to the formation of new products from Maillard's reaction, particularly melanoidins (Napolitano et al., 2007). Pérez-Martínez et al. (2010) reported that, besides the melanoidin compounds, higher antioxidant activity in moka coffee was due to the chlorogenic acids, i.e. caffeoylquinic acid isomers. Moreover, Vignoli et al. (2013) found a correlation between caffeine concentration and antioxidant activity, both in Robusta and Arabica coffee. The same authors gave a wide discussion on the possible factors affecting the concentration of coffee bioactive compounds and antioxidant activity. Thus, our results could be explained by the different operative conditions such as the flame intensity applied to the moka pot. In fact, higher temperatures in the moka pot (as it is in contact with the flame until all the water passes in the upper part) could break the covalent bond between chlorogenic acids

and polyphenol compounds during coffee brewing as it occurs during coffee bean roasting (Perrone et al., 2012).

The pH could also affect the antioxidant activity, as the hydrogen-donor capacity of the antioxidant compounds is higher when the acidity is slightly higher (Pérez-Martínez et al., 2010), whereas it seems to depend on the type of coffee brew, i.e. in the case of “strong” extraction technique such as moka and espresso the effect is different with respect to the techniques such as plunger and American brews. The slight but significantly lower pH value found in Neapolitan coffee with respect to moka could partially explain the significant lower antioxidant activity found in the first one, although its total phenolic content was similar to those found in moka brew. The difference between Neapolitan and American coffee brew was partially explained by the different ground coffee/water ratio which differentiates the two coffee preparation techniques, as it has been reported for espresso coffee (Andueza et al., 2007).

In relation to the intake of coffee brew, some considerations could be drawn. The usual amount of coffee cup is enormously variable in different cultures and traditions, ranging from 15 mL of concentrated espresso to over 250 mL of filtered coffee. There is also a high variation according to the number of coffees usually consumed in a day. Therefore, considering the typical volume of each coffee beverage (25 mL for espresso; 40 mL for moka and Neapolitan coffee; 125 mL for American coffee), the highest antioxidant intake was obtained from moka (2.87 mmol Trolox) and American coffee (2.86 mmol Trolox), while the lowest value was obtained for Neapolitan brew (1.92 mmol Trolox), as shown in Table 2C.

The highest intake of total phenolic compounds could be obtained by American brew, while both Neapolitan and moka coffees showed intermediate values and were not significantly different. Due to the volume of an espresso coffee cup, the intake of phenolic compounds was significantly lower with respect to the other brewing techniques, while their concentration resulted higher.

The highest value of caffeine intake was reached for American brew, which resulted in 173 mg caffeine per cup. No significant differences were obtained among Neapolitan, moka and espresso coffee brews (Table 2C). The higher caffeine concentration in espresso is balanced by the limited volume of a serving cup, which results in a more similar caffeine intake in comparison to Neapolitan and moka brews. On the contrary, caffeine intake in American coffee brew was about three times higher with respect to the other coffee brews, whereas the caffeine concentration in the first one was the lowest among all the coffee brews analyzed. The antioxidant activity and caffeine intake showed a similar trend to that reported by Santini et al. (2011) for different coffee beverages.

3.2. Analysis of volatile compounds

A total of 24 volatile compounds were monitored and quantified in the headspace of Arabica coffee brews obtained by different preparation methods (Table 3). Despite the large number of volatile compounds reported for coffee brews, few of them are considered key odorants of coffee aroma, which are generally found at higher levels with respect to

Table 3
Headspace concentration of volatile compounds in different coffee brews.

Compound	Peak area ^a (%)			
	American	Neapolitan	Moka	Espresso
<i>Aldehydes</i>				
Acetaldehyde	0.124 ± 0.028 ab	0.078 ± 0.017 a	0.080 ± 0.011 a	0.170 ± 0.024 b
2-Methylpropanal	0.590 ± 0.143 b	0.310 ± 0.057 a	0.277 ± 0.050 a	0.652 ± 0.101 b
Butanal	0.076 ± 0.017 ab	0.046 ± 0.009 a	0.043 ± 0.008 a	0.082 ± 0.015 b
2-Methylbutanal	1.673 ± 0.245 ab	1.224 ± 0.058 ab	1.075 ± 0.191 a	1.799 ± 0.349 b
3-Methylbutanal	1.454 ± 0.245 b	0.958 ± 0.027 ab	0.813 ± 0.151 a	1.297 ± 0.214 ab
Hexanal	0.066 ± 0.280 b	0.076 ± 0.010 b	0.030 ± 0.002 a	0.045 ± 0.010 ab
Total	3.983 ± 0.726 b	2.692 ± 0.178 ab	2.318 ± 0.412 a	4.046 ± 0.712 b
<i>Pyrazines</i>				
2-Ethyl-6-methylpyrazine	4.941 ± 0.055 ab	4.888 ± 0.159 ab	5.240 ± 0.283 b	4.677 ± 0.221 a
2-Ethyl-5-methylpyrazine	2.885 ± 0.346 a	3.082 ± 0.107 a	3.294 ± 0.152 a	2.897 ± 0.131 a
2-Propylpyrazine	0.466 ± 0.047 a	0.520 ± 0.026 a	0.504 ± 0.026 a	0.481 ± 0.030 a
2,6-Diethylpyrazine	0.879 ± 0.110 a	1.008 ± 0.022 a	0.942 ± 0.126 a	0.860 ± 0.074 a
2-Ethyl-3,5-dimethylpyrazine	2.540 ± 0.055 ab	2.685 ± 0.156 ab	2.851 ± 0.203 b	2.304 ± 0.235 a
2-Methyl-3-trans-propenylpyrazine	0.357 ± 0.038 a	0.408 ± 0.047 ab	0.498 ± 0.010 b	0.383 ± 0.064 ab
Total	12.068 ± 0.652 ab	12.592 ± 0.517 ab	13.328 ± 0.801 b	11.602 ± 0.755 a
<i>Furans</i>				
2,5-Dimethylfuran	0.412 ± 0.092 b	0.210 ± 0.016 a	0.158 ± 0.034 a	0.312 ± 0.060 ab
Furfuryl methyl ether	2.015 ± 0.238 b	1.069 ± 0.269 a	1.026 ± 0.172 a	1.408 ± 0.242 ab
Furfurylmethyl sulfide	8.479 ± 1.290 a	8.675 ± 0.859 a	6.015 ± 0.768 a	7.472 ± 1.467 a
2-Furanmethanol acetate	34.382 ± 3.932 ab	30.752 ± 1.069 ab	29.384 ± 1.385 a	37.347 ± 4.031 b
2-Furanmethanol	15.573 ± 2.940 a	15.890 ± 2.847 a	19.522 ± 2.463 a	17.697 ± 3.670 a
Total	60.862 ± 8.492 ab	56.596 ± 5.061 a	56.106 ± 4.821 a	64.237 ± 9.470 b
<i>Phenolic compounds</i>				
Guaiacol	8.427 ± 1.644 a	8.677 ± 1.299 ab	11.844 ± 0.318 b	9.118 ± 1.194 ab
4-Ethylguaiacol	7.164 ± 1.846 a	6.545 ± 1.646 a	8.046 ± 0.731 a	4.850 ± 0.880 a
4-Vinylguaiacol	4.384 ± 1.197 a	4.047 ± 1.001 a	5.332 ± 0.764 a	3.241 ± 0.548 a
Total	19.975 ± 4.687 ab	19.269 ± 3.947 a	25.221 ± 1.812 b	17.209 ± 2.622 a
<i>Ketones</i>				
2,3-Pentanedione	1.106 ± 0.171 b	0.631 ± 0.116 a	0.624 ± 0.124 a	0.830 ± 0.082 ab
β-Damascenone	0.098 ± 0.019 ab	0.121 ± 0.028 b	0.051 ± 0.010 a	0.061 ± 0.006 a
Total	1.204 ± 0.191 b	0.752 ± 0.144 a	0.675 ± 0.134 a	0.891 ± 0.089 ab
<i>Sulfur compounds</i>				
Methanethiol	0.095 ± 0.005 ab	0.087 ± 0.014 a	0.104 ± 0.014 ab	0.131 ± 0.021 b
<i>Pyrroles</i>				
1-Methyl-(1H-pyrrol-2-yl)-1-ethanone	1.853 ± 0.194 a	2.083 ± 0.254 a	2.236 ± 0.073 a	1.884 ± 0.069 a

^a All values are shown as means ± standard deviation (n = 3). Values followed by different letters on the same line are significantly different (p < 0.05).

their odor thresholds (Caprioli et al., 2012; Rocha et al., 2003; Semmelroch & Grosch, 1996). These volatile compounds are mainly formed during roasting coffee beans. In terms of the chemical classes considered in our study, furans were the most abundant volatile compounds in all the coffee brews, followed by total phenolic compounds, pyrazines, aldehydes and ketones. One of the main variables influencing the volatiles extraction from ground coffee and final quality of coffee brew is the preparation method, including water temperature, ground coffee, and final volume (Gloess et al., 2013).

Furans and pyrans have been described as Maillard-reaction products arising from thermal degradation of D-glucose and sugar polymers or from thermal oxidation of lipids and thiamine degradation or breakdown of nucleotides (Flament, 2002). These molecules are described as the main responsible components for the typical aroma of coffee brew (Flament, 2002). Furans which do not contain sulfur are generally associated with nutty, caramel, smoke, floral, and ethereal odor, while those containing sulfur are responsible of sulfur, garlic, or toasty odor note (Table 1). Espresso coffee showed higher content in furans with respect to Neapolitan and moka coffee while they were similar to American coffee. The main differences were attributed to 2-furanmethanol acetate, 2,5-dimethylfuran and furfuryl methyl ether. The former compound was found in higher level in espresso while American brew showed higher values for the latter two compounds. On the contrary, 2-furanmethanol and furfurylmethyl sulfide did not show significant differences among the coffee brews analyzed.

Phenolic compounds were described as essential contributors to the typical quality of coffee flavor (Flament, 2002), with smoky-like odor (Table 1). The main difference for phenolic compounds was obtained for guaiacol content, which was higher in Moka coffee brew. Guaiacol is formed by a thermal degradation of ferulic acid, and its level increases with roasting (Flament, 2002). Therefore, the increase in guaiacol seems to be higher when higher extraction temperatures are applied (Clarke & Vitzthum, 2001; Flament, 2002). As in our experiments one batch of Arabica coffee blend was used, the differences found in the amounts of guaiacol in moka coffee could be only attributed to the higher temperature reached in the Moka pot, being this latter in contact with the flame until all the water passes in the upper part.

Pyrazines are formed by complex interactions between α -amino acids and carbohydrates. Among them, the alkylpyrazines have a key role in the aroma of coffee brew (Flament, 2002) exhibiting a hazelnut-like and coffee-like odor (Table 1). Among this class of compounds, only 2-ethyl-6-methylpyrazine, 2-ethyl-3,5-dimethylpyrazine and 2-methyl-3-*trans*-propenylpyrazine were found at higher levels in moka coffee, while in espresso they showed significantly lower concentrations. Andueza et al. (2003) reported that the pyrazine concentration was significantly higher when espresso coffee brew from Arabica coffee was obtained using water temperature ≥ 96 °C. Thus, higher water temperature used for the extraction of coffee during its brewing could also cause the formation of higher amounts of some pyrazines in the headspace of moka coffee, as described for guaiacol.

Aldehydes are formed by the oxidative degradation of amino acids during their interactions with sugars at high temperatures or polyphenols in the presence of polyphenol oxidase. Some aldehydes, as hexanal, are known as autooxidation products of unsaturated fatty acids via breakdown of hydroperoxide intermediates and they participate in the staling of roasted coffee in oxygen exposure (Flament, 2002). Therefore, considering that green coffee beans contain lipids and proteins, their contribution to aroma of coffee brew is not surprising. In fact, acetaldehyde, together with propanal, has been reported as responsible of fruity and green odor in coffee brew (Flament, 2002). 2-Methylpropanal, 2-methylbutanal and 3-methylbutanal have been reported as responsible of the chocolate and malty odor in coffee brew (Semmelroch & Grosch, 1996), whereas hexanal has been described as the main responsible for green note (Flament, 2002). Among the analyzed coffees, moka showed a lower content in total aldehydes.

The concentration of 2,3-pentanedione in American coffee brew was significantly higher with respect to other brewing techniques, while β -damascenone was higher in Neapolitan coffee brew. 2,3-Pentanedione is described as the main volatile compound formed by thermal degradation of furaneol, while β -damascenone is synthesized from carotenoids, which are responsible for the buttery and fruity odors, respectively. Our results were in general accordance with those reported in literature. In fact, López-Galilea et al. (2006) reported that ketones were more abundant in filtered coffee brew with respect to an espresso one.

Methanethiol is a mercaptan biosynthesizes from methionine pyrolysis and gives intense cabbage-like cheese garlic and sulfur odor (Flament, 2002). It was found in lower level in Neapolitan coffee brew while the higher concentration was obtained in espresso, probably due to the higher extraction pressure in the espresso machine.

Pyrroles are described as furan degradation products and amino acid derivatives, but they also derive from thermal degradation of Amadori intermediates (Flament, 2002). The most abundant pyrrole, 1-methyl-(1H-pyrrol-2-yl)-1-ethanone seems not to be affected by the preparation technique.

Principal component analysis (PCA) was performed in all the analytical data to examine differences between aroma compounds and chemical composition of different coffee brews (Fig. 1). For volatile compounds, only those that presented a significant difference among coffee brews according to the Tukey's test were considered (Table 3). The different brews were clearly distinguished by PCA and 87.25% of the total variance was explained, thus indicating that each coffee brew possesses some chemical peculiarities. Guaiacol, 2-ethyl-6-methylpyrazine, 2-methyl-3-*trans*-propenylpyrazine, and 2-ethyl-3,5-dimethylpyrazine were well correlated with moka coffee. Acetaldehyde, methanethiol, 2-furanmethanol acetate, butanal and 2-methylpropanal characterized espresso coffee. Both coffee brews were characterized by higher level of total phenolic compounds, total solid, and antioxidant activity, while espresso was also better correlated to the caffeine content.

Pyrazines and guaiacol, correlated with higher processing temperatures (Flament, 2002; Sanz, Maeztu, Zapelena, Bello, & Cid, 2002), have been described in literature with sensory notes of smoky, nutty, hazelnut-like, and roasty notes. In addition, it is possible that these compounds, as previously reported for some other volatile compounds, may exhibit antioxidant activity, thus explaining the reason of the higher antioxidant activity found in moka brew besides its low level of total phenolic content (Table 2A).

Methanethiol is a characteristic coffee aroma volatile compound, even if it has been described with unpleasant odor. It is generally related to coffee freshness because it rapidly degraded during coffee brew oxidation (Marin, Požrl, Zlatić, & Plestenjak, 2008). The higher level of methanethiol in espresso coffee could be due to its rapid brewing time of about 25 s with respect to other techniques, in which the brewing time ranges from 2 to 5 min.

β -Damascenone and hexanal correlated well with American and Neapolitan coffee brews, resulting from literature data in fruity and green notes for these coffees. The formation of these compounds increases as it is affected by carotenoid degradation and lipid oxidation (Flament, 2002). Thus, coffee brewing techniques that imply longer preparation times lead to the formation of higher amount of these compounds indicating a high susceptibility to oxidation and degradation during coffee brewing (Clarke & Vitzthum, 2001). Therefore, the higher hexanal content in American and Neapolitan coffee brews could be explained by the considerable higher brewing time and by a higher oxygen exposure of the ground coffee than other techniques. In fact, espresso coffee brewed in about 25 s and moka needed about 3 min, but by using the latter technique, the coffee beverage is rapidly cooled in the upper part of the machine while brewing, thus reducing the formation of lipid oxidation products such as hexanal. López-Galilea et al. (2006) reported no significant changes for hexanal due to brewing techniques, but the authors only considered filter (American) and espresso techniques. Our results were in agreement with literature for these

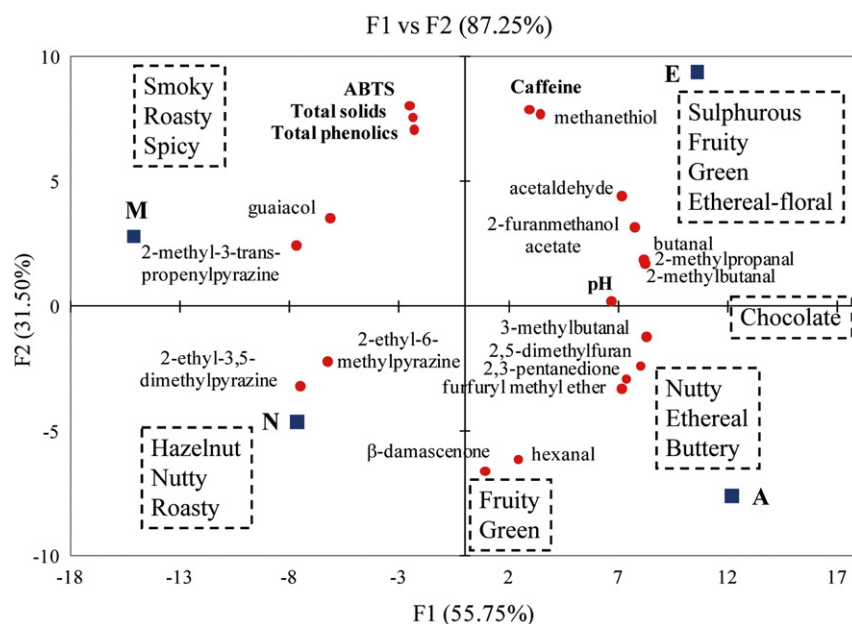


Fig. 1. Principal component analysis (PCA) of volatile compounds, caffeine, total phenolic compounds, total solid, ABTS and pH of coffee brews. The sensory descriptors reported for the volatile compounds are from literature data (see Table 1).

two techniques, but we found significant differences for moka with respect to American and Neapolitan brews (Table 3).

Furfuryl methyl ether, 2,3-pentanedione, and 2,5-dimethylfuran were also correlated to the American coffee brew, thus giving buttery, nutty, ethereal, fruity, and green odors, because these compounds have been reported in literature to give these odor descriptions. Despite the similarities of the brewing techniques for American and Neapolitan, the latter one resulted much more similar to moka but with lower smoky notes and more fruity, sweet, and green notes with respect to the last one. In addition, the Neapolitan coffee showed an intermediate content of total solid, total phenolic compounds, and antioxidant activity with respect to American and moka, and lower caffeine level.

4. Conclusions

A characterization of the Neapolitan coffee brew was given in comparison to other coffee brews and a semi-quantification of the main volatile compounds was performed. It was shown that, despite the similarity of brewing principle of American coffee-making technique, the Neapolitan coffee was nearer to moka in terms of antioxidant activity, polyphenol content, and total solids. In terms of volatile compounds, Neapolitan and moka coffee brews showed the lowest content in aldehydes with respect to espresso brew. Moka was correlated by guaiacol and pyrazines, while Neapolitan and American by hexanal and β-damascenone. Pyrazines were also well correlated to Neapolitan coffee brew. The difference between Neapolitan and American coffee brew could be mainly due to the different ground coffee/water ratio that differentiates the two coffee preparation techniques while those between filtered and no-filtered coffee (moka and espresso) could be explained by the different water temperature and pressure. The brewing time seems to influence the hexanal and methanethiol level in coffee brews. Unexpected and interesting results were obtained for Neapolitan coffee brew in terms of chemical composition and particularly volatile compounds, which offer new insights into the coffee preparation techniques, opening the way to the valorization of this brewing procedure.

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