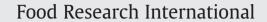
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# Roasting process affects differently the bioactive compounds and the antioxidant activity of arabica and robusta coffees



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#### ARTICLE INFO

Article history: Received 21 March 2013 Received in revised form 28 May 2013 Accepted 6 June 2013 Available online 12 June 2013

Keywords: Antioxidant Roasting degree Folin-Ciocalteau ABTS FRAP TEAC

#### ABSTRACT

The influence of different roasting degrees on the content of bioactive compounds and the antioxidant activity (AA) of arabica and robusta coffees was evaluated. AA was estimated by Folin–Ciocalteau, FRAP and ABTS methods. The results were analyzed by principal components analysis. While the levels of 5-CQA (5-caffeoylquinic acid), trigonelline, furfural and HMF (hydroxymethylfurfural) decreased with the degree of roasting, the level of melanoidins increased. Changes in the levels of the bioactive compounds were more intense that those observed for AA. PC 1 (principal component 1) was mainly correlated with the levels of, furfural, HMF, 5-CQA, trigonelline, and melanoidins. PC2 was mainly correlated with AA and caffeine content. Different compounds contribute to the AA of the coffee and the final result for AA is dependent on the balance of the compounds formed and degraded during the roasting process.

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#### 1. Introduction

Coffee consumption is mainly motivated by its pleasant flavor and aroma, the positive sensations it produces and its physiological effects. Coffee stands out amongst other beverages because of its antioxidant activity (AA): soluble and espresso coffees have been found to have greater AA than red wine or green tea (Pellegrini et al., 2003).

Coffee is a rich source of phenolic compounds, especially chlorogenic acids and their degradation products (caffeic, ferulic and coumaric acids). One of the chlorogenic acid isomers, 5-caffeoylquinic acid (5-CQA), has been cited as an efficient in vitro and ex vivo antioxidant (Xu, Hu, & Liu, 2012). However, only part of the antioxidant capacity of coffee is attributed to cinnamic acids. Other components with AA, such as caffeine and trigonelline, have been studied (Daglia et al., 2004; Esquivel & Jimenez, 2012; Leon-Carmona & Galano, 2011; Pérez-Hernández, Chávez-Quiroz, Medina-Juárez, & Meza, 2012).

Variations in the raw material and processing affect roasted coffee characteristics. The two species of coffee of greatest economic value are *Coffea arabica* and *Coffea canephora* (robusta). Brews originating from 100% arabica beans have superior sensory quality and are most acceptable to consumers than robusta ones. Daglia, Papetti, Gregotti, Bertè, and Gazzani (2000) studied brews of different coffee species and reported that robusta has greater antioxidant capacity than arabica coffee.

The coffee roasting degree is controlled by roasting time and temperature and is usually qualitatively assessed from color and classified as a light, medium or dark roast coffee (Somporn, Kamtuo, Theerakulpisut, & Siriamornpun, 2011). The roasting process causes changes in the chemical composition and biological activity of the coffee: while natural phenolic compounds may be lost, other antioxidant compounds are formed, such as Maillard reaction products (Wang, Oian, & Yao, 2011). Literature usually describe a decrease in the AA of the coffee beans as the roasting degree increases, which is mainly associated with the degradation of chlorogenic acids (Somporn et al., 2011). However, the roasting process produced melanoidins, reported as the compound responsible for the AA in the high molecular weight fractions isolated from roasted coffee (Daglia et al., 2000; Liu & Kitts, 2011; Perrone, Farah, & Donangelo, 2012). In addition, some volatile heterocyclic compounds produced during roasting have also been described as potential antioxidants (Yanagimoto, Ochi, Lee, & Shibamoto, 2004). Hydroxymethylfurfural, intermediate compound in Maillard reaction, presented AA similar to 2,6-dibutyl-4-methylphenol and α-tocopherol (Shinghara, Macku, & Shibamoto, 1998).

Several methods are used to characterize antioxidant capacity. However, there is no single universal method to measure AA accurately and quantitatively (Prior, Xianli, & Schaich, 2005). The various methods that have been used to evaluate the antioxidant potential of coffee include FRAP, ABTS and the determination of total phenolic

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compounds (Folin–Ciocalteau method) (Borreli, Visconti, Mennella, Anese, & Vincenzo, 2002; Sánchez-González, Jiménez-Escrig, & Saura-Calixto, 2005).

Despite the many studies addressing the AA of roasted coffee, little has been reported about the relationship between this biological activity and variations in the composition of the product in relation to the antioxidant compounds that are formed and/or destroyed in different phases of the roasting process. Another interesting consideration is that the methods used here for measuring the AA have different reaction mechanisms and, therefore, are able to evaluate the antioxidant capacity of different compounds. Hence, this study monitored the main potential antioxidant as 5-CQA, caffeine, trigonelline and Maillard reaction products (melanoidins, furfural, HMF) during the roasting process of arabica and robusta coffees, and estimates the correspondent antioxidant activity of the products by different methodologies. The highlight of the research is that the products were manufactured in an industrial pilot plant (with three repetitions of the process).

#### 2. Materials and methods

#### 2.1. Material

#### 2.1.1. Samples and treatments

The samples were provided by Companhia Iguaçu de Café Solúvel (Cornélio Procópio, Paraná State, Brazil) using different raw materials and roasting degrees. C. arabica (A) and C. canephora (R) beans were roasted in a Raiar pilot roaster (São Paulo, Brazil), with the processing time varying from 7 to 10 min and temperatures varying from 215 to 225 °C. Three repetitions of the roasting process were produced. For each coffee species, 12 types of roasted coffees (with 3 repetitions, 36 samples) were produced ranging in color from 80 IR (light roast) to 25 IR (dark roast), with an interval of 5 IR between them. The color evaluation system, based on the index of reflectance (IR), uses standard disks to compare and to assign the coffee color during the roasting process, similar to the Agtron Classification System. The samples were subsequently ground to a granulometric size of 0.35 mm. The color of the roasted coffees was also characterized by the CIELAB system (lightness L\*, and hue, h°) using a Byk Gardner GmbH colorimeter (Berlin, Germany), with 45/0 geometry and D65 illuminant (Table 1).

The extracts for AA and HPLC analysis were obtained by preparing coffee extracts in 50 mL of water at 95 °C, stirring for 5 min and then filtering with a Whatman filter paper no. 4. The concentration used was specific for each methodology. All samples were prepared in duplicate and the measurements were made in triplicate. Aliquots of each extract were lyophilized and the solid concentrations were determined. All results were expressed considering the level of soluble

#### Table 1

Values of lightness  $(L^\ast)$  and hue  $(h^\circ)$  corresponding to the IR colors for roasted and ground coffees of the arabica and robusta species.

	Robusta		Arabica	
IR	L*	h°	L*	h°
25	$14 \pm 1$	$53 \pm 2$	$12 \pm 1$	$50\pm3$
30	$16 \pm 1$	$54 \pm 2$	$20 \pm 2$	$52 \pm 2$
35	$19 \pm 1$	$55 \pm 1$	$16 \pm 1$	$53 \pm 1$
40	$21 \pm 1$	$57 \pm 1$	$20 \pm 2$	$58 \pm 0$
45	$22 \pm 1$	$57 \pm 1$	$21 \pm 1$	$55 \pm 1$
50	$24 \pm 1$	$58 \pm 0$	$25 \pm 2$	$57 \pm 2$
55	$25 \pm 1$	$59 \pm 2$	$24 \pm 1$	$58 \pm 0$
60	$27 \pm 1$	$62 \pm 1$	$27 \pm 1$	$60 \pm 1$
65	$31 \pm 1$	$62 \pm 1$	$28 \pm 1$	$61 \pm 1$
70	$32 \pm 3$	$63 \pm 1$	$30 \pm 0$	$61 \pm 0$
75	$33 \pm 1$	$63 \pm 0$	$30 \pm 1$	$62 \pm 0$
80	$33 \pm 1$	$63 \pm 1$	$31 \pm 2$	$62 \pm 1$

Mean and standard deviation of 9 values (3 repetitions of the process, triplicate analysis).

solids in order to simulate the effect in coffee brews and to allow the comparison with other products as instant coffees.

#### 2.1.2. Reagents and equipment

5-O-caffeoylquinic acid (5-O-CQA), caffeine and gallic acid (HPLC grade) were purchased from Sigma Aldrich (St. Louis, USA). ABTS (2,2-azinobis-3 ethyl benzothiazoline-6-sulphonic acid) and DPPH (2,2-diphenyl-1-picrylhydrazyl) were obtained from Sigma Chemical CO. (St. Louis, USA). Trolox (6-hydroxy-2,5,7,8,-tetramethylchromane-2-carboxylic acid) and TPTZ (2,4,6-tri(2-pyridyl)-S-triazine) were obtained from Fluka/Sigma-Aldrich (Vallensbaek Strand, Denmark). Folin–Ciocalteau reagent, acetic acid (HPLC grade) and acetonitrile (HPLC grade) were purchased from Merck (Darmstadt, Germany).

Melanoidins were separated by dialysis using 12–14 kDa cutoff membranes (Spectra/Por, Irving, USA).

AA measurements were taken in a UV–Vis–UV mini-1240 spectrophotometer (Shimadzu, Kyoto, Japan) and bioactive compounds were determined by HPLC. The HPLC apparatus consisted of a Dionex LC (Idstein, Germany) equipped with a P680 gradient pump, TCC-100 column oven, automated sample injector (model ASI-100) and photodiode array detector (model PDA-100). The system is operated by a computer using Chromeleon version 6.6 software.

#### 2.2. Methodology

#### 2.2.1. Evaluation of antioxidant activity

2.2.1.1. ABTS methodology (TEAC). The methodology for evaluating the antioxidant capacity of the coffee extracts with regard to the ABTS+ free radical followed Vignoli, Bassoli, and Benassi (2012). The samples were prepared at a concentration of 15 mg/mL, resulting in a filtrate with a concentration of 4.33 mg/mL of soluble solids. Briefly ABTS radical cations (ABTS<sup>+•</sup>) were produced by reacting 7 mM of ABTS stock solution with 2.45 mM of potassium persulfate. The mixture stood in a dark flask at room temperature for 12-16 h before use. The ABTS<sup>+•</sup> solution was then diluted with phosphate buffered saline (pH 7.4) to an absorbance of 0.70  $\pm$  0.2 at 730 nm. 10  $\mu$ L of the sample or Trolox standard was added to 4 mL of the diluted ABTS<sup>+•</sup> solution and readings were taken at 730 nm after a reaction time of 6 min. Ethanol solutions with known concentrations of Trolox were used for calibration. The results were expressed as the Trolox equivalent antioxidant capacity (TEAC) in g Trolox/100 g of the soluble solids of the original coffee.

2.2.1.2. FRAP methodology. The reduction power of the brew was evaluated following Vignoli et al. (2012). The samples were prepared at a concentration of 1.5 mg/mL. The filtrate resulting from this preparation had a concentration of 0.4 mg/mL. The FRAP reagent was prepared by mixing 2.5 mL of a 10 mM TPTZ solution with 40 mM HCl in 2.5 mL of a 20 mM FeCl<sub>3</sub> ·  $6H_2O$  solution and 25 mL of a 0.3 mM acetate buffer solution pH 3.6. This solution was incubated at 37 °C for 30 min. To evaluate the antioxidant capacity, 900 µL of the freshly FRAP reagent was mixed to 90 µL of distilled water and 10 µL of the test sample or standard. The readings were taken at 595 nm after 30 min at 37 °C. Solutions with known concentrations of Trolox were used for calibration. The results were expressed in g of Trolox/100 g of the soluble solids of the original coffee.

2.2.1.3. Folin–Ciocalteau methodology. Samples of coffee were prepared at 3 mg/mL. An aliquot of the filtrate (100  $\mu$ L) with a concentration of 0.83 mg/mL of soluble solids was added to 7.5 mL of distilled water and 300  $\mu$ L of 0.9 N Folin–Ciocalteau reagent. After stirring and mixing, 1 mL of 20% Na<sub>2</sub>CO<sub>3</sub> solution and 1.1 mL of distilled water were added. Solutions were maintained at room temperature for 60 min for reading at 765 nm (Vignoli et al., 2012). Gallic acid standard solutions were used for calibration. The results were expressed in g of gallic acid/100 g the soluble solids of the original coffee.

### 2.2.2. Determination of 5-CQA, caffeine, trigonelline, furfural and HMF

A high performance liquid chromatography (HPLC) methodology adapted from Alves, Dias, Benassi, and Scholz (2006) was used for the simultaneous determination of caffeine, 5-CQA, trigonelline, furfural and HMF. After the preparation of coffee brews, as previously described, the samples were filtered at 0.22 µm and directly injected into the chromatographic system. A  $4.6 \times 250$  mm 5  $\mu$ m particle Spherisorb ODS2 column (Waters, Taunton, USA) was used. Compounds were eluted with gradients containing 5% acetic acid (A) and acetonitrile (B), as follows: 0-5 min: 4% B; 5-10 min: 10% B; 10-30 min: 10% B; 30-40 min: 0% B; and 40-50 min: 4% B, at a flow rate of 0.7 mL/min. Trigonelline, caffeine, furfural and HMF were detected at 272 nm, while 5-CQA was detected at 320 nm. Quantification was carried out by external standardization using a 5-point calibration curve with triplicate measurements. 5-COA was evaluated over the range 5 to 30 µg/mL, caffeine from 10 to 50 µg/mL, trigonelline from 15 to 50 µg/mL, hydroxymethylfurfural from 0.5 to 8 µg/mL and furfural from 0.05 to 1 µg/mL. All results were expressed as g or mg of the bioactive compound/100 g of soluble solids in the original coffee.

#### 2.2.3. Determination of melanoidins

The dialysis membrane separation process described by Bekedam, Schols, Boekel, and Smit (2006) was used with some modifications. A total of 5 samples of arabica coffee and 5 samples of robusta coffee across the range of the study (25, 40, 55, 65 and 80 IR) were selected to determine the content of melanoidins. The analyses were conducted in duplicate. The selected samples (30 g) were added to 200 mL of boiling water and filtered with Mellita filter paper. The concentration of the filtered soluble solids was determined. The filtrate (30 mL) was transferred to a dialysis membrane with a cutoff of 12-14 kDa and placed in a beaker with 400 mL of distilled water under agitation. The water was changed every 8 h until it became colorless. The total volume of material retained by the membrane was determined and an aliquot was lyophilized. The amount of material with a molecular weight above 12-14 kDa, here considered to be melanoidins, was determined as a percentage of the original soluble solid mass. This fraction was expressed as g of melanoidins/100 g of soluble solids in the original coffee.

#### 2.2.4. Statistical analysis

Data of antioxidant activity and chemical composition related to bioactive compounds were subjected to principal component analysis by the "Multivariate Exploratory Techniques — Principal Components and Classification Analysis" procedure of the Statistics 7.1 package software (Statsoft, Inc., 2005). The composition parameters (furfural, HMF, trigonelline, 5-CQA, caffeine, and melanoidins) were the active variables used in the derivation of the principal components; the supplementary variables (antioxidant capacity methods) were projected onto the factor space.

#### 3. Results and discussion

# 3.1. The effect of the degree of roasting on the bioactive compounds of arabica and robusta coffees

Arabica and robusta coffees, roasted to a wide range of colors from light (80 IR, L\* from 31 to 33) to dark (25 IR, L\* from 12 to 14) (Table 1), were assayed. Fig. 1 shows the behavior of the bioactive compounds in the two species for different degrees of roasting. It is worth mentioning that the values correspond to mg or g/100 g soluble solids. All compounds were determined after obtaining the soluble solids originated from brewing. The mean value for caffeine was 4.70 g/100 g for arabica coffee and 7.20 g/100 g for robusta coffee (Fig. 1A). The literature reports that caffeine contents are highly dependent on species (robusta coffee has higher levels than arabica) and just slight losses are observed during the roasting process due to its thermal stability (Farah, 2012).

Trigonelline levels changed from about 3.3 to 1.4 g/100 g for arabica coffee and 2.2 to 0.2 g/100 g for robusta (Fig. 1B), with a mean decrease of 90% with the roasting process. The trigonelline content in roasted coffee depends on the species, roasting time and temperature since this compound is rapidly degraded during process, forming volatile compounds such as the pyridines, N-methylpyrrole and nicotinic acid (Murkovic & Bornik, 2007; Trugo & Macrae, 1984).

Content of furfural varied from 0.03 to 0.01 g/100 g for arabica coffee and from 0.014 to 0.010 g/100 g for robusta in the roasting degrees studied. HMF levels ranged from 0.23 to 0.00 g/100 g for arabica and 0.04 to 0.00 g/100 g for robusta (Fig. 1C and D). These compounds presented a marked decrease (67% for furfural and 100% for HMF) in a severe roasting process. It is interesting to notice that while in the light roasts compound contents were greater in arabica coffee, particularly for HMF, in the dark roast their contents were similar in the two species. These results agree with those from Murkovic and Bornik (2007) who observed a maximum formation of HMF at the beginning of the roasting process followed by rapid decomposition and similar levels in arabica and robusta coffees. HMF is formed by the dehydration of fructose or sucrose (via the generation of a highly reactive fructofuranosyl cation that can be quickly converted into HMF at high temperatures in dry systems) and from the heating of serine and threonine with sucrose (Gökmen, Açar, Köksoel, & Acar, 2007; Perez Locas & Yaylayan, 2008; Pulido, Hernández-García, & Saura-Calixto, 2003; Smith, 1963). The formation of HMF in parallel with the degradation of sucrose during the coffee roasting process begins at 170 °C and reaches its maximum at 230 °C. Rapid decomposition occurs at higher temperatures.

The 5-CQA contents decreased from 5.96 to 0.22 g/100 g for arabica coffee and from 6.19 to 0.13 g/100 g for robusta (Fig. 1E). The literature reports increasing degradation of chlorogenic acids during roasting, contributing to the formation of the final aroma and flavor of the roasted coffee. Up to 90% of the initial chlorogenic acids may be lost after a severe roasting process (Trugo & Macrae, 1986). Approximately half of the total chlorogenic acids degraded during roasting may be found in the pigment fraction, in the form of free quinic acid and as phenolic compounds of low molecular mass (Trugo, Maria, & Werneck, 1991). According to Perrone et al. (2012) chlorogenic acids are incorporated in melanoidins mainly at the beginning of the roasting process and degrade thereafter.

While the levels of 5-CQA, trigonelline, furfural and HMF decreased with the degree of roasting, the level of melanoidins increased from 14.40 to 23.60 g/100 g for arabica coffee and from 18.50 to 27.30 g/100 g for robusta (Fig. 1F). The behavior was similar in both species of coffee. During roasting, the low water activity and high temperature favored the development of the Maillard reaction. It is reported that the phenolic compounds also participate in this reaction, becoming part of the melanoidins (Bekedam, Schols, Boekel, & Smit, 2008; Nunes & Coimbra, 2001; Wang et al., 2011). Melanoidins are reported as one of the main components of roasted coffee, corresponding to 25% of the dry material (Daglia et al., 2004; Nicoli, Anese, Manzocco, & Lerici, 1997; Perrone et al., 2012) values very close to the results found in this study for dark roasted coffees (Fig. 1F).

Summarizing, arabica coffee had higher levels of trigonelline, furfural, HMF, and 5-CQA than robusta coffee at all degrees of roasting. Higher levels of caffeine were found for robusta coffee. The two species of coffee had similar levels of melanoidins for the same degree of roasting. With the exception of caffeine, which is thermostable, and melanoidins, which were formed during processing, the levels of all the other AA compounds studied decreased, as roasting degree increased from 80 IR to 25 IR (Fig. 1).

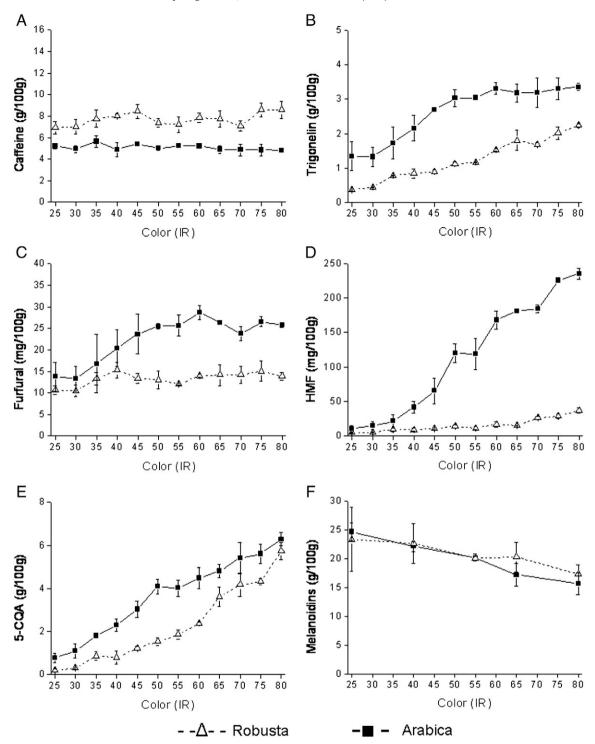


Fig. 1. Levels of caffeine (A), trigonelline (B), furfural (C), hydroxymethylfurfural (D), 5-CQA (E) and melanoidins (F) in arabica and robusta coffees over the roasting process.

#### 3.2. Evaluation of antioxidant activity

The AA of arabica and robusta coffees with different degrees of roasting was estimated by measuring the reducing capacity by Folin–Ciocalteau and FRAP method and considering the capacity to scavenging free radicals (ABTS cation) (Fig. 2).

The change in AA during roasting (Fig. 2) was much less pronounced than the variation in the bioactive compound contents (Fig. 1); in general, the AA remained stable or slightly decreased as roasting degree increased. In addition, different behaviors were observed depending on the method used for AA estimation. For robusta coffee, a decrease in

the AA values estimated by Folin–Ciocalteau and ABTS (28.2 for 18.6 g gallic acid/100 g and 48.2 to 36.4 g Trolox/100 g respectively) was observed, probably due to the loss of phenolic compounds during roasting. Similar behavior was observed for the arabica coffee. However, the AA estimated by FRAP methodology remained almost stable (from 16.6 to 15.9 g Trolox/100 g for robusta and 13.6 to 13.4 g Trolox/100 g for arabica). The differential behavior observed in FRAP results was probably due to the mechanism used in AA estimation, which is restricted to the measuring of compounds that promote electron transfer. Folin–Ciocalteau and ABTS measure the transfer of both electrons and H atoms (Prior et al., 2005).

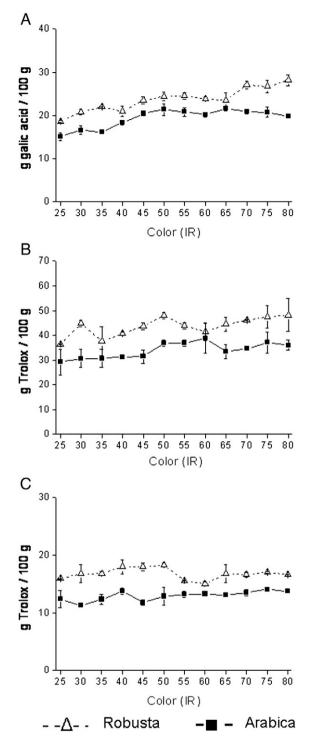


Fig. 2. AA in arabica and robusta coffees during roasting, evaluated by the Folin–Ciocalteau (A), ABTS (B) and FRAP (C) methods. Values are the mean of 3 repetitions  $\pm$  standard deviation.

Similar results were found by Sacchetti, Mattia, Pittia, and Mastrocola (2009) evaluating the effect of roasting degree on the ABTS radical scavenging activity of the brew from the roast. Medium roast brews showed an increase in radical scavenging activity compared with green coffee due to an increase in the AA of the non-phenolic fraction. However, when dark roasts were evaluated, AA decreased due to the loss of the phenolic fraction, since it was not balanced by the increase in the AA of the non-phenolic fraction (Perrone et al., 2012; Vignoli, Bassoli, & Benassi, 2011).

Principal component analysis was used to evaluate the relationship between the AA and the bioactive composition considering some degrees of roasting (25, 40, 55, 65 and 80 IR), samples for which the level of melanoidins had been determined. The first two principal components accounted for 93% of the total variance (Fig. 3A and B).

PC1 was mainly characterized by the levels of melanoidins, furfural, HMF, 5-CQA and trigonelline (Fig. 3A). PC2 correlated with AA measured using the Folin–Ciocalteau, ABTS and FRAP methods and caffeine content.

High correlations between Folin–Ciocalteau and ABTS (r = 0.91) and between Folin–Ciocalteau and FRAP (r = 0.79) were found. The Folin–Ciocalteau method determines the total polyphenol content, but has an oxidation/reduction reaction as its basic mechanism, which can be considered in the evaluation of AA (Prior et al., 2005). It is probable that the compounds measured by Folin–Ciocalteau were also involved in the ABTS radical scavenging and to a lesser extent with the product's reducing power, evaluated by the FRAP method. Amongst the chemical compounds, caffeine was the only one that showed high correlation with all methods: r of 0.87, 0.96 and 0.64 for ABTS, FRAP and Folin–Ciocalteau, respectively. The same behavior was reported by Pérez-Hernández et al. (2012).

In the scatterplot, the discrimination was observed by AA and/or by roasting degree (Fig. 3B). The dark color coffees (arabica and robusta), located in the lower part of the figure, were separated from the light colored samples, which had higher levels of 5-CQA and lower content of melanoidins. The arabica coffees were configured on the left side of the plot discriminated from the robusta coffees that were associated with higher caffeine levels and greater AA. Hence, with regard to the influence of the raw material on AA, in general, C. canephora coffees had greater AA than C. arabica ones (Figs. 2 and 3B). Similar results were report in literature (Daglia et al., 2004) but the behavior was usually attributed to the higher level of chlorogenic acids in robusta species. However, it can be observed in Fig. 1 that 5-CQA, which here represents the class of chlorogenic acids, was found either in similar or greater concentrations in arabica coffee than in robusta coffee. Higher contents of chlorogenic acids were usually observed in green beans of the robusta species (about 10% compared to 8% for arabica) (Leloup, 2006), but these compounds seem to be more degraded during roasting in the robusta matrix (Trugo & Macrae, 1986) (Fig. 1E). Hence, the greater antioxidant capacity of robusta coffee was mainly attributed to the higher caffeine content in this species, since it correlates positively with the AA. López-Galilea, De Peña, and Cid (2007) also reported a significant correlation between caffeine and the AA evaluated by DPPH (0.826) and redox potential (-0.844). Parras, Martinez-Tomé, Jiménez, and Murcia (2007) also described the higher TEAC values for caffeinated coffee brews than for the equivalent decaffeinated products. Vignoli et al. (2011), in a study with soluble coffees, found higher AA for robusta products, and associated this difference to its caffeine content.

Besides caffeine, only 5-CQA showed correlation with the AA estimated by the Folin–Ciocalteau method (r: 0.57) (Fig. 3A). No significant correlation was observed between AA estimated for different methodologies and the other compounds. It can therefore be inferred that in the roasted coffee matrix, it is difficult to observe a direct relation of AA with the content of specific potential bioactive compounds due to the degradation and simultaneous formation of different compounds during the roasting process. It could be clearly exemplified by the negative correlation between 5-CQA and melanoidins. As both of these compounds contribute to the AA of coffee, changes in AA values were less evident than the changes in the chemical composition with the roasting process. The presence of melanoidins in the final product partially compensates the loss of phenolic compounds with roasting. This behavior is especially interesting for arabica products, since the AA of robusta coffee is mainly dependent on the caffeine content.

Vignoli et al. (2011), in a similar study with soluble coffee, described that the influence of the roasting process (light, medium and dark roasting degrees) on the AA was even less pronounced, probably

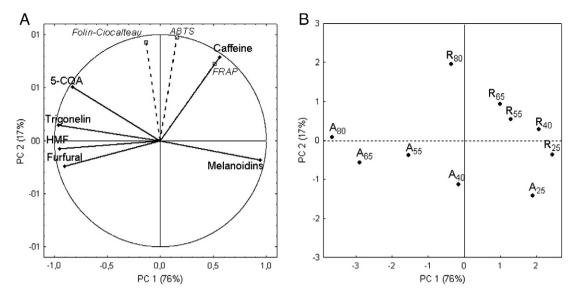


Fig. 3. Principal component analysis of AA and chemical compounds: variable projection (A) and sample plot (B). Species: arabica (A) and robusta (R); IR (index of reflectance); roasting degree from 80 IR (light) to 25 IR (dark). Variables: – active, --- supplementary.

because of the presence of a prior extraction step in the manufacturing process, as it favors.

There is little agreement in the literature about the influence of roasting on AA. Del Castillo, Ames, and Gordon (2002) found greater AA in the medium roast brew. Liu and Kitts (2011) and Perrone et al. (2012) found greater AA for light roast brews, while Nicoli et al. (1997) reported higher AA for medium and dark roast brews. In addition, the studies of the AA of coffee attribute this property principally to the level of phenolic compounds and melanoidins (Daglia et al., 2000; Borreli et al., 2002; Del Pino-García, Gonzáles-SanJosé, Rivero-Pérez, & Muñiz, 2012).

The use of different methods for estimating AA demonstrated that compounds such as 5-CQA, melanoidins and caffeine have different antioxidizing mechanisms. For example, the antioxidant properties of melanoidins have been ascribed to both the metal chelating capacity, as to the scavenging activity of free radical and oxygen species (Wang et al., 2011). Hence, the evaluation of AA by a single method cannot adequately represent the antioxidant capacity of a product.

#### 4. Conclusion

The coffee brew from different roasting degrees showed considerable antioxidant potential, which was influenced by the roasting conditions and the coffee species. The final AA of roasted coffee results from the contribution of different compounds. In addition to the phenolic compounds present in coffee, which are partially destroyed by the roasting process, other antioxidant compounds, such as melanoidins, may be formed and so it is possible to maintain or increase AA. However, as the intensity of roasting increases, the greater destruction of the phenolic compounds. Hence, coffees originating from light roasting show greater antioxidant capacity due to the greater polyphenol content. Robusta coffee shows greater AA than arabica coffees because of the AA of caffeine.

#### Acknowledgments

The authors would like to thank the National Council of Technological and Scientific Development, CNPq-Brazil, for their support.

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